205. *Cyanine Dyes containing the Pyrrocoline Nucleus. Part I.*

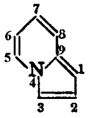
By F. G. Holliman and H. A. Schickerling.

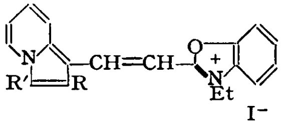
A series of azadimethincyanines containing the pyrrocoline nucleus has been synthesised by the condensation of 2-substituted-3-nitroso- and -3-acetyl-1-nitroso-pyrrocolines with heterocyclic compounds containing reactive methylene groups. Light absorptions of these dyes are given and discussed.

The fundamental feature of the majority of dyes is a conjugated chain of equal numbers of double and single bonds terminated at each end by an atom which can exist in lower and higher covalency states, the difference in charge being one unit: one of the terminal atoms is in the lower, whilst the other is in the higher covalency state (I, II, III). Such an arrangement permits of resonance between the two extreme electronic structures (*a* and *b*).

The cyanine dyes conform to the structure (I) and are characterised by having nitrogen for both terminal atoms, linked in heterocyclic systems in such a way that part of the periphery of each heterocyclic ring contributes to the conjugated system. For compounds of such a constitution, the lower, tercovalent state of the nitrogen atom demands that the heterocyclic nitrogen atoms, besides being linked in their respective ring systems, carry an additional group. The latter is present merely to provide for the bonding requirements, the bond to this group being the important feature and not the group itself; this group has, in fact, usually been methyl or ethyl. Bond requirements could, however, be satisfied in an alternative way : the additional valency to the nitrogen atom could be satisfied by a bond linking this atom to one of the atoms involved in the conjugated chain. In this way an additional ring system would be produced, the heterocyclic nitrogen atom thereby being a bridge atom between two fused ring systems. This paper records our initial experiments in preparing dyes of this type.

(IV.)





(V.)

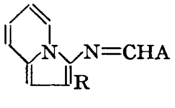
A suitable heterocyclic system for the synthesis of cyanine dyes with these characteristics is pyrrocoline (IV) (Scholtz, *Ber.*, 1912, **45**, 734). Dyes containing this nucleus have been reported only in a patent, *viz.*, cyanine dyes derived from pyrrocoline and benzoxazole (as V) (Brooker and Sprague, U.S.P. 2,409,612). Borrows, Holland, and Kenyon (*J.*, 1946, 1069 *et seq.*) recently reported that 2-substituted pyrrocolines (Tschitschibabin, *Ber.*, 1927, **60**, 1607) readily underwent nitrosation at position 3, and further that a nitroso-group could be introduced into position 1 if the more reactive 3-position was first substituted by an acetyl group. We have shown that the nitroso-group in these compounds, like that in nitrosoindoles (Mann and Haworth, *J.*, 1944, 670; Huang-Hsinmin and Mann, *J.*, 1949, 2911), can be condensed with reactive methylene groups in suitable heterocyclic systems with the production of dyes : since the five-membered ring of the pyrrocoline nucleus forms part of the conjugated system linking the two heterocyclic nitrogen atoms, the use of the 1- and the 3-nitroso-compounds provides dyes with conjugated chains of different lengths (compare VI, VIII, and X with VII, IX, and XI).

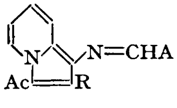
We have used the four nitroso-compounds synthesised by Borrows, Holland, and Kenyon (*loc. cit.*), *viz.* 2-methyl-3-nitroso-, 3-nitroso-2-phenyl-, 3-acetyl-2-methyl-1-nitroso-, and 3-acetyl-1-nitroso-2-phenyl-pyrrocoline, prepared essentially by the methods described by these workers, whose synthesis of 2-phenylpyrrocoline we have also adopted. For the 2-methyl compound, however, we have preferred to use the more readily prepared bromoacetone rather than chloroacetone (cf. Tschitschibabin and Stepanow, *Ber.*, 1929, **62**, 1068). In spite of the low yield (10%) recorded by Tschitschibabin (*Ber.*, 1927, **60**, 1607) for use of the bromo-compound, we have been able, by using only freshly prepared bromoacetone, by very careful temperature control during the reaction with α-picoline, and by using excess of sodium hydrogen carbonate in the cyclisation of the picolinium salt, to obtain 2-methylpyrrocoline in 61% yield.

The four nitroso-compounds have been condensed with α-picoline methiodide, quinaldine methiodide, and 2 : 3 : 3-trimethylindolenine methiodide, to give twelve azadimethincyanines (VI—XI; R = Me or Ph). A further range, with wider variation in the non-pyrrocolinyl nucleus, has been obtained by condensing 1- and 3-nitroso-2-phenylpyrrocoline with 6-ethoxy-2-methylquinoline ethiodide, 2-methyl-5 : 6-benzoquinoline methiodide, and 2-methylpyridino(2′ : 3′-5 : 6)quinoline methiodide.

Exploratory experiments on the condensation of 2-methyl-3-nitrosopyrrocoline and α-picoline methiodide in alcoholic solution showed that the use of piperidine as catalyst was inferior to the use of 0·1—0·2 molecular proportion of sodium hydroxide. This was so with regard to both the yield and the purity of the condensation product, which, when piperidine was used, appeared to

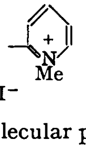
(VI, VIII, X.)





(VII, IX, XI.)

In (VI and VII)
A =



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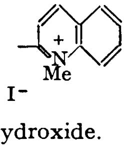

In (X and XI)
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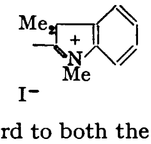


use of 0·1—0·2 molecular proportion of sodium hydroxide. This was so with regard to both the yield and the purity of the condensation product, which, when piperidine was used, appeared to separate in the smectic state on recrystallisation. Consequently we have used aqueous sodium hydroxide in this series of condensations and have found it to be satisfactory in all but a few cases: in the preparation of 2-[(1-methylpyridine)][3-(2-phenylpyrrocoline)]-α-azadimethincyanine iodide (VI; R = Ph) reversion to the use of piperidine, the proportion of which was critical, gave better yields, and in the condensations with 2 : 3 : 3-trimethylindolenine methiodide, satisfactory results were obtained only by using alcoholic sodium hydroxide.

The yields of the condensation products are obviously subject to variation from a number of factors: the reactivities of the nitroso- and the methyl groups in the reactants; the stability of the products; and, since the dyes were obtained by direct crystallisation and collection from the reaction mixture, their solubility in the solvent used (methyl or ethyl alcohol). Some indication of the reactivities could be obtained from the time taken for the initial green colour of the reaction mixture to begin to change as the colour of the dye became superimposed on that of the nitroso-compound. In some cases, this took place even in the absence of the catalyst, in others shortly after its addition in the cold, whilst some condensations required prolonged refluxing. From condensations with the same methylene compound, it was apparent that substitution of the 2-phenyl for the 2-methyl group had little effect on the reactivity of the nitroso-group in the pyrrocoline or 3-acetylpyrrocoline series. On the other hand, the change in colour took place far more rapidly with the 3-acetyl-1-nitroso- than with the 3-nitroso-derivatives, this being particularly noticeable with the 2-phenyl derivatives where higher yields of the condensation products from the acetyl compound were isolated without refluxing being necessary. Whether this increased reactivity of the nitroso-group should be attributed to its changed position, to an activating effect of the acetyl group, or to a combination of these factors is being investigated. The yield of dye obtained from the 3-acetyl-1-nitrosopyrrocolines was invariably greater than that from the corresponding 2-substituted compound; apart from the effect due to the nitroso-group, this appears to be connected with the lower solubility of the dyes containing the acetyl substituent.

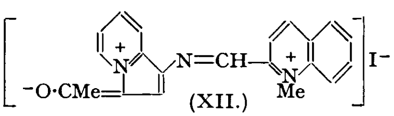
The absorption spectra, between 200 and 700 mμ., of our dyes were determined with a Beckman spectrophotometer (see table). The most outstanding feature of these is the change in the wave-length and intensity of the maxima on passing from the 2-substituted 3-pyrrocolinyl nucleus to the 2-substituted 3-acetyl-1-pyrrocolinyl nucleus: for all dyes except those derived from the indolenine, this change takes the form of a decrease in the intensity together with a hypsochromic shift of *ca.* 70—80 mμ., and doubtless arises from the fact that the conjugated chain linking the two heterocyclic nitrogen atoms is longer by one –CH=CH– group in the 3- than in the 1-pyrrocoline dyes. In the conventional type of cyanine dye, the increase in $\lambda_{max.}$ for an increase in conjugated chain length of two carbon atoms is about 100 mμ. (Brooker, Sprague, Smythe, and Lewis, *J. Amer. Chem. Soc.*, 1940, **62**, 1116), and the fact that, in our

Dye.					
Pyrrocoline nucleus.*	Other nucleus.†	Solvent.	$\lambda_{max.}$.	$10^{-4}\ \varepsilon_{max.}$.	$\lambda_3 - \lambda_1$.
M-3	P	Water	544	3·77	68
AM-1	,,	,,	478	1·81	
P-3	,,	,,	548	2·76	72
AP-1	,,	,,	476	2·04	
M-3	Q	,,	596	4·05	84
AM-1	,,	,,	512	3·07	
P-3	,,	,,	600	3·40	84
AP-1	,,	,,	516	2·51	
M-3	I	Alcohol	[560] 596	[1·15] 1·32	30
AM-1	,,	,,	566	3·42	
P-3	,,	,,	554	1·50	− 6
AP-1	,,	,,	560	2·68	
P-3	EQ	,,	606	6·08	74
AP-1	,,	,,	532	3·84	
P-3	BzQ	,,	608	5·72	76
AP-1	,,	,,	532	3·88	
P-3	PyQ	,,	610	6·10	72
AP-1	,,	,,	538	3·52	

* M-3 = 3-(2-Methylpyrrocoline).
AM-1 = 1-(3-Acetyl-2-methylpyrrocoline).
P-3 = 3-(2-Phenylpyrrocoline).
AP-1 = 1-(3-Acetyl-2-phenylpyrrocoline).

† P = 2-(1-Methylpyridine).
Q = 2-(1-Methylquinoline).
I = 2-(1 : 3 : 3-Trimethylindolenine).
EQ = 2-(6-Ethoxy-1-methylquinoline).
BzQ = 2-(1-Methyl-5 : 6-benzoquinoline).
PyQ = 2-[1-Methylpyridino(2′ : 3′-5 : 6)quinoline].

compounds, the shift in $\lambda_{max.}$ is some 20—30 mμ. less may be due to the fact that the dyes with the shorter chain have an acetyl group present in position 3. It is likely that the presence of this group allows such forms as (XII) to contribute to the resonance state, and, whereas the shortening of the conjugated chain leads to the observed hypsochromic shift, the additional resonance arising from the presence of the acetyl group might well lead to a partially neutralising bathochromic effect. With such resonance possibilities with the acetyl group, the 2-substituted 3-acetyl-1-pyrrocoline dyes bear a certain resemblance to the merocyanins (cf. Mees, " The Theory of the Photographic Process," New York, 1942, p. 1035).



(XII.)

The case of the indolenine compounds is anomalous : in both the 2-methyl- and the 2-phenylpyrrocoline pairs, the change from the 3-pyrrocoline to the 3-acetyl-1-pyrrocoline system produces an increase in absorption intensity. Furthermore, with the 2-methylpyrrocoline compounds the hypsochromic effect of shortening the conjugated chain is reduced to only 30 mμ., whilst with the 2-phenylpyrrocoline-indolenine dyes, the effect is reversed, shortening of the chain leading to a bathochromic effect of 6 mμ. In view of these anomalies, we have attempted, for comparison, to synthesise analogous dyes by condensation of the nitrosopyrrocolines with 2-methylbenzthiazole methiodide and 2-methylbenzoxazole ethiodide. Although both 2-methyl-3-nitroso- and 3-acetyl-2-methyl-1-nitroso-pyrrocoline thus gave intense colours with 2-methylbenzthiazole methiodide in boiling alcohol in the presence of sodium hydroxide, a dye was only obtained from the acyl pyrrocoline. With 2-methylbenzoxazole ethiodide and 3-nitroso-2-phenylpyrrocoline, no colour change could be induced; the more reactive 3-acetyl-1-nitroso-2-phenylpyrrocoline caused a slow colour change but no dye could be isolated. This failure to effect condensation between nitrosopyrrocolines and 2-methylbenzoxazole ethiodide is interesting in view of Mann and Haworth's failure (*J.*, 1944, 670) to condense their nitrosoindoles with the same reactive methylene compound.

EXPERIMENTAL.

(M. p.s are uncorrected.)

" Dry alcohol " refers to solvent which has been dried by refluxing with sodium and ethyl phthalate before fractionation.

2-*Methylpyrrocoline* (cf. Tschitschibabin, *Ber.*, 1927, **60**, 1614).—α-Picoline (20 g.), thoroughly chilled in ice-water, was treated with bromoacetone (*Org. Synth.*, **10**, 12) (30 g., 1 mol.) with swirling. The mixture was removed from the cooling bath, but was replaced therein immediately it showed signs of becoming warm. By such continued control, the reaction was allowed to proceed, without the temperature rising appreciably, until the mixture had become a thick, viscous syrup. This was set aside at room temperature during 3 hours, by which time it had crystallised. A solution of the picolinium salt in water (240 c.c.) was extracted with ether (80 c.c.) and, after treatment with sodium hydrogen carbonate (40 g.), was heated under reflux on a water-bath; the temperature of the bath was slowly raised to boiling and held there for 2 hours. Steam-distillation of the mixture then gave 2-methylpyrrocoline which was dried in air. 17·6 G. (61%) were obtained, of m. p. 59·5° unchanged on sublimation.

3-*Nitroso*-2-*phenylpyrrocoline.*—Some modification and amplification of the method of Borrows, Holland, and Kenyon (*J.*, 1946, 1076) is recorded. 2-Phenylpyrrocoline (*idem, ibid.*) (12·5 g.) was dissolved in concentrated hydrochloric acid (40 c.c.), and the solution diluted at 35° with water (80 c.c.). A solution of sodium nitrite (6·25 g., 1·5 mols.) in water (33 c.c.) was added dropwise, with stirring, the temperature being kept at 35°. The orange-red precipitate began to form when most of the nitrite had been added. After 1 hour at room temperature the thick magma was filtered off. The solid was dissolved in water (1 l.), the solution cooled to 40°, and solid sodium hydrogen carbonate carefully added with stirring, until some carbonate remained undissolved ; this excess was then brought into solution by careful heating (≯80°). On slow cooling with continual stirring, the green nitroso-compound gradually crystallised from the emulsion and was filtered off after 10 minutes at 0°. The original filtrate from the reaction mixture was worked up in the same way and the combined lots of 3-nitroso-2-phenylpyrrocoline were recrystallised from 50% aqueous alcohol, to give 10 g. (70%) of m. p. 98—99° (Borrows, Holland, and Kenyon report m. p. 97·5—98°).

[2-(1-*Methylpyridine*)][3-(2-*methylpyrrocoline*)]-α-*azadimethincyanine Iodide* (VI ; R = Me).—A solution of 2-methyl-3-nitrosopyrrocoline (*idem, ibid.*) (1 g.), α-picoline methiodide (1·47 g., 1 mol.), and 5% aqueous sodium hydroxide (0·5 c.c., 0·1 mol.) in alcohol (30 c.c.) was refluxed, a crystalline precipitate rapidly being produced. After 2 hours, the mixture was cooled and the solid collected. Recrystallisation from water gave fine black needles of the *azacyanine* (44·5%), m. p. 262—263° (decomp.) (Found : C, 50·4 ; H, 4·1. $C_{16}H_{16}N_3I$ requires C, 50·9 ; H, 4·2%).

[2-(1-*Methylpyridine*)][3-(2-*phenylpyrrocoline*)]-α-*azadimethincyanine Iodide* (VI ; R = Ph).—(*a*) 3-Nitroso-2-phenylpyrrocoline (1 g.) and α-picoline methiodide (1·06 g., 1 mol.) in alcohol (15 c.c.) were treated with 5% aqueous sodium hydroxide (0·8 c.c., 0·2 mol.), the colour of the solution immediately changing from green to scarlet. After 6 hours' boiling, the solution was cooled. The crystalline solid deposited was recrystallised from water, giving the greenish-brown *azacyanine* (11·5%), m. p. 212—213° (decomp.) (Found : C, 57·3 ; H, 4·2. $C_{21}H_{18}N_3I$ requires C, 57·4 ; H, 4·1%).

(*b*) The same weights of the nitroso-compound and the methiodide in alcohol (20 c.c.) were treated with piperidine (0·2 g., 0·5 mol.). The mixture was refluxed and after 5—10 minutes began to change colour. After 5·5 hours' boiling, cooling gave 0·16 g. (8·5%) of the *cyanine*. Addition of a further quantity of piperidine (0·2 g., 0·5 mol.) and further refluxing gave an additional quantity of the dye (0·18 g.), but further increase in the proportion of piperidine was unsuccessful. Recrystallisation from water gave brown crystals m. p. 212—213° (decomp.) unchanged on admixture with the product from (*a*) (Found : C, 57·2 ; H, 4·1%).

[2-(1-*Methylpyridine*)][1-(3-*acetyl*-2-*methylpyrrocoline*)]-α-*azadimethincyanine Iodide* (VII ; R = Me).—3-Acetyl-2-methyl-1-nitrosopyrrocoline (*idem, ibid.*) (0·5 g.), and α-picoline methiodide (0·58 g., 1 mol.) in alcohol (18 c.c.) treated with 5% aqueous sodium hydroxide (0·25 c.c., 0·1 mol.) gave an immediate dark red, crystalline precipitate. After 10 minutes, this *dye* was collected (0·62 g., 60%) and recrystallised from water, forming dark, brownish-red needles, m. p. 243—235° (decomp.) (Found : C, 51·0; H, 4·3. $C_{18}H_{18}ON_3I$ requires C, 51·6; H, 4·3%). Refluxing the filtrate from the reaction mixture failed to yield a further quantity of dye.

[2-(1-*Methylpyridine*)][1-(3-*acetyl*-2-*phenylpyrrocoline*)]-α-*azadimethincyanine Iodide* (VII ; R = Ph).—3-Acetyl-1-nitroso-2-phenylpyrrocoline (*idem, ibid.*) (1 g.) and α-picoline methiodide (0·82 g., 1 mol.), dissolved in alcohol (20 c.c.), were treated with 5% sodium hydroxide solution (0·3 c.c., 0·1 mol.) which caused an immediate change in colour from green to red. After 6 hours' boiling, cooling of the solution gave a crystalline precipitate (0·92 g., 50%), m. p. 211—212° (decomp.). Recrystallisation from water gave golden-brown needles of the *hydrate* of unchanged m. p. (Found : C, 55·2, 55·0 ; H, 4·5, 4·5 ; loss in wt. at 100°/15 mm. during 2 hours, 3·7%. $C_{23}H_{20}ON_3I,H_2O$ requires C, 55·3 ; H, 4·4% ; H_2O, 3·6%).

[3-(2-*Methylpyrrocoline*)][2-(1-*methylquinoline*)]-α-*azadimethincyanine Iodide* (VIII ; R = Me).—2-Methyl-3-nitrosopyrrocoline (1 g.) and quinaldine methiodide (1·78 g., 1 mol.) in methyl alcohol (30 c.c.) with 5% sodium hydroxide solution (0·5 c.c., 0·1 mol.) were refluxed. Solid separated and after 5·5 hours the solution was cooled and the solid *salt* collected (1·24 g., 46%). Two recrystallisations from water gave dark green needles, m. p. 252—253° (decomp.) (Found : C, 56·3 ; H, 4·4. $C_{20}H_{18}N_3I$ requires C, 56·2 ; H, 4·2%).

[3-(2-*Phenylpyrrocoline*)][2-(1-*methylquinoline*)]-α-*azadimethincyanine Iodide* (VIII ; R = Ph).—A solution of 3-nitroso-2-phenylpyrrocoline (1 g.) and quinaldine methiodide (1·28 g., 1 mol.) in alcohol (30 c.c.) was treated with 5% aqueous sodium hydroxide and refluxed for 8 hours. The solid *iodide* separating was removed after 3, 6, and 8 hours, giving a total of 1·13 g. (51%). Recrystallisation (10% aqueous alcohol) gave dark reddish-brown needles, m. p. 226—228° (decomp.) (Found : C, 61·4 ; H, 4·3. $C_{25}H_{20}N_3I$ requires C, 61·4 ; H, 4·1%).

[1-(3-*Acetyl*-2-*methylpyrrocoline*)][2-(1-*methylquinoline*)]-α-*azadimethincyanine Iodide* (IX ; R = Me).—3-Acetyl-2-methyl-1-nitrosopyrrocoline (0·5 g.) and quinaldine methiodide (0·71 g., 1 mol.) in alcohol (25 c.c.) treated with 5% aqueous sodium hydroxide (0·25 c.c., 0·1 mol.) gave an immediate colour change, accompanied by the deposition of crystals. After 2 minutes' boiling, the mixture was cooled and the solid collected (0·8 g., 68%). Recrystallisation (water) gave brownish-red needles of the *cyanine iodide dihydrate*, m. p. 222—223° (decomp.) (Found : C, 53·0, 52·8 ; H, 4·9, 4·6 ; loss in weight at 100°/15 mm. during 2 hours, 6·6. $C_{22}H_{20}ON_3I,2H_2O$ requires C, 52·3 ; H, 4·7 ; H_2O, 7·1%).

[1-(3-*Acetyl*-2-*phenylpyrrocoline*)][2-(1-*methylquinoline*)]-α-*azadimethincyanine Iodide* (IX ; R = Ph).—Refluxing a solution of 3-acetyl-1-nitroso-2-phenylpyrrocoline (1 g.) and quinaldine methiodide (1·08 g., 1 mol.) in alcohol (20 c.c.) caused a change in colour to greenish-red. Further change to reddish-violet was produced upon the addition of 5% sodium hydroxide solution (0·4 c.c., 0·13 mol.), and refluxing induced rapid precipitation of golden-brown crystals. The mixture was cooled after 2 hours' refluxing and the cyanine iodide collected (1·44 g., 79%). It recrystallised from water as the *monohydrate*, golden-brown platelets, m. p. 214—215° (decomp.) (Found : C, 59·6, 59·3 ; H, 4·3, 4·2 ; loss in weight at 100°/15 mm. during 2 hours, 3·07. $C_{27}H_{22}ON_3I,H_2O$ requires C, 59·0 ; H, 4·4 ; H_2O, 3·27%).

[3-(2-*Methylpyrrocoline*)][2-(1 : 3 : 3-*trimethylindolenine*)]-α-*azadimethincyanine Iodide* (X ; R = Me).—A solution of 2-methyl-3-nitrosopyrrocoline (0·30 g.) and 2 : 3 : 3-trimethylindolenine methiodide (0·57 g., 1 mol.) in dry alcohol (12 c.c.) was treated with 5% alcoholic sodium hydroxide (0·30 c.c., 0·2 mol.) and refluxed. The colour changed slowly to deep purple in the first 2 hours, but no solid separated. After 7 hours the mixture was chilled but yielded no solid. Concentration and storage at 0° finally gave 0·12 g. (14·3%) of deep purple crystals which, recrystallised from alcohol, had m. p. 186—189° (decomp.) (Found : C, 57·0 ; H, 4·9. $C_{21}H_{22}N_3I$ requires C, 56·9 ; H, 5·0%).

With aqueous sodium hydroxide in place of the alcoholic reagent the *cyanine* was obtained in somewhat lower yield (10·7%).

[3-(2-*Phenylpyrrocoline*)][2-(1 : 3 : 3-*trimethylindolenine*)]-α-*azadimethincyanine Iodide* (X ; R = Ph).—3-Nitroso-2-phenylpyrrocoline (0·4 g.) and 2 : 3 : 3-trimethylindolenine methiodide (0·54 g., 1 mol.) in solution in dry alcohol (12 c.c.) were treated with 5% alcoholic sodium hydroxide (0·29 c.c., 0·2 mol.). Change in colour to blue only took place slowly on refluxing which was continued for 6 hours. The cyanine iodide (0·34 g., 37·5%) separated at 0° during 3 days and was recrystallised from alcohol, to give the *trihydrate* as purple needles, m. p. 249—250° (Found : C, 55·6 ; H, 5·1 ; loss in weight at 100°/15 mm. during 2 hours, 9·4. $C_{26}H_{24}N_3I,3H_2O$ requires C, 55·8 ; H, 5·3 ; H_2O, 9·6%).

The use of aqueous alkali as the catalyst in this condensation led to the production of the desired dye, but in lower yield (33·1%). Piperidine, on the other hand, only succeeded in producing a slight colour change in the reaction mixture during some 7 hours' refluxing.

[1-(3-*Acetyl*-2-*methylpyrrocoline*)][2-(1 : 3 : 3-*trimethylindolenine*)]-α-*azadimethincyanine Iodide* (XI ; R = Me).—3-Acetyl-2-methyl-1-nitrosopyrrocoline (0·3 g.) and 2 : 3 : 3-trimethylindolenine methiodide (0·45 g., 1 mol.) in dry alcohol (10 c.c.) with 5% alcoholic sodium hydroxide (0·25 c.c., 0·2 mol.) was refluxed during 6 hours : a gradual change in colour to red took place in the first 2 hours. The solid (0·16 g., 22%) separating overnight was recrystallised from alcohol, to give golden-brown crystals of the *azacyanine*, m. p. 203—205° (decomp.) (Found : C, 54·2, 54·2; H, 4·9, 4·8. $C_{23}H_{24}ON_3I,H_2O$ requires C, 54·8; H, 5·2%).

Aqueous alkali was unsatisfactory, giving only a 3% yield.

[1-(3-*Acetyl-2-phenylpyrrocoline*)][2-(1 : 3 : 3-*trimethylindolenine*)]-*a-azadimethincyanine Iodide* (XI; R = Ph).—Heating 3-acetyl-1-nitroso-2-phenylpyrrocoline (0·40 g.) with the indolenine methiodide (0·46 g., 1 mol.) in dry alcohol (10 c.c.) caused the development of a purple colour in the initially green solution. The addition of 5% alcoholic sodium hydroxide (0·24 c.c., 0·2 mol.) increased the rate of colour change and the mixture was then refluxed for 7 hours. Solid soon began to separate and more crystallised on cooling. Next morning the dye was collected (0·25 g., 30%) and recrystallised from alcohol as golden-brown crystals of the *monohydrate*, m. p. 226—228° (Found : C, 59·0; H, 4·9; loss in weight at 100°/15 mm. for 2 hours, 3·7. $C_{28}H_{26}ON_3I,H_2O$ requires C, 59·4; H, 4·9; H_2O, 3·2%).

Both aqueous alkali and piperidine gave a marked colour change; with the former a low yield (16%) of dye was obtained whilst with the latter only unchanged pyrrocoline could be isolated.

[3-(2-*Phenylpyrrocoline*)][2-(6-*ethoxy*-1-*ethylquinoline*)]-*a-azadimethincyanine Iodide.*—3-Nitroso-2-phenylpyrrocoline (0·39 g.) and 6-ethoxy-2-methylquinoline ethiodide (0·60 g., 1 mol.) in alcohol (10 c.c.) were treated with 5% aqueous sodium hydroxide (0·27 c.c., 0·2 mol.). The colour of the boiling solution slowly changed to blue. After 7 hours the solution was cooled and set aside overnight, yielding 0·38 g. (40%) of dark green crystals which recrystallised from 50% aqueous alcohol, as prisms of the *hemihydrate*, m. p. 187° (decomp.) (Found : C, 59·9, 60·0; H, 4·6, 4·8; loss in weight at 100°/15 mm. during 2·5 hours, 1·8. $C_{28}H_{26}ON_3I,\frac{1}{2}H_2O$ requires C, 60·4; H, 4·8; H_2O, 1·6%).

[1-(3-*Acetyl-2-phenylpyrrocoline*)][2-(6-*ethoxy*-1-*ethylquinoline*)]-*a-azadimethincyanine Iodide.*—Addition of 5% aqueous sodium hydroxide (0·27 c.c., 0·2 mol.) to a solution of 3-acetyl-1-nitroso-2-phenylpyrrocoline (0·46 g.) and 6-ethoxy-2-methylquinoline ethiodide (0·60 g., 1 mol.) in alcohol (10 c.c.) produced an immediate change in colour to deep purple. Crystallisation of the condensation product took place during refluxing, which was continued during 6 hours. After 12 hours at room temperature, the golden-brown dye was collected (0·77 g., 74·7%) and recrystallised from 33% aqueous alcohol, giving fine needles of a *hydrate*, m. p. 211° (decomp.) (Found : C, 57·7, 58·3; H, 4·8, 5·0; loss in weight at 100°/15 mm. during 2·5 hours, 4·1. $C_{30}H_{28}O_2N_3I,1\frac{1}{2}H_2O$ requires C, 58·5; H, 5·0; H_2O, 4·1%).

[3-(2-*Phenylpyrrocoline*)][2-(1-*methyl*-5 : 6-*benzoquinoline*)]-*a-azadimethincyanine Iodide.*—3-Nitroso-2-phenylpyrrocoline (0·26 g.) and 2-methyl-5 : 6-benzoquinoline methiodide (0·40 g., 1 mol.), dissolved in methyl alcohol (23 c.c.), were treated with 5% sodium hydroxide solution (0·19 c.c., 0·2 mol.), and the mixture refluxed. A colour change to deep green soon took place, and after 3 hours solid began to separate. After 6·5 hours, the mixture was cooled and set aside overnight before the *iodide* (0·32 g., 50%) was collected and recrystallised (water, 10% aq. alcohol) to give dark green prisms, m. p. 205° (decomp.) (Found : C, 65·2; H, 4·2. $C_{29}H_{22}N_3I$ requires C, 64·7; H, 4·1%).

[1-(3-*Acetyl-2-phenylpyrrocoline*)][2-(1-*methyl*-5 : 6-*benzoquinoline*)]-*a-azadimethincyanine Iodide.*—A solution of 3-acetyl-1-nitroso-2-phenylpyrrocoline (0·24 g.) and 2-methyl-5 : 6-benzoquinoline methiodide in methyl alcohol (15 c.c.) was treated with 5% sodium hydroxide solution (0·14 c.c., 0·2 mol.), whereupon an immediate colour change to brownish-red and separation of solid took place. After 7 hours' boiling, the mixture was cooled and set aside overnight, to yield 0·30 g. (58%) of the *azacyanine iodide*, recrystallisation of which from 40% aqueous alcohol gave reddish-brown needles, m. p. 231° (decomp.) (Found : C, 63·8; H, 3·7. $C_{31}H_{24}ON_3I$ requires C, 64·0; H, 4·1%).

[3-(2-*Phenylpyrrocoline*)][2-(1-*methylpyridino*(2′ : 3′-5 : 6)*quinoline*)]-*a-azadimethincyanine Iodide.*—3-Nitroso-2-phenylpyrrocoline (0·33 g.) and 2-methylpyridino(2′ : 3′-5 : 6)quinoline methiodide (0·50 g., 1 mol.) in methyl alcohol (25 c.c.) with 5% sodium hydroxide solution (0·24 c.c., 0·2 mol.) rapidly deposited crystals on refluxing. After 5 hours, the mixture was cooled and set aside overnight, then yielding 0·28 g. (35%) of dark green crystals. Recrystallisation from 40% aqueous alcohol gave flat triangular crystals of the *azacyanine iodide*, m. p. 215° (decomp.) (Found : C, 62·0; H, 3·8. $C_{28}H_{21}N_4I$ requires C, 62·2; H, 3·9%).

[1-(3-*Acetyl*-2-*phenylpyrrocoline*)][2-(1-*methylpyridino*(2′ : 3′-5 : 6)*quinoline*)]-*a-azadimethincyanine Iodide.*—3-Acetyl-1-nitroso-2-phenylpyrrocoline (0·39 g.) and 2-methylpyridino(2′ : 3′-5 : 6)quinoline methiodide (0·50 g., 1 mol.) in methyl alcohol (25 c.c.), treated with 5% aqueous sodium hydroxide (0·24 c.c., 0·2 mol.), gave an immediate precipitate with a colour change to deep reddish-brown. After 5 hours' refluxing and then setting aside overnight, the *azacyanine iodide* was collected (0·70 g., 81%). Owing to its very slight solubility the dye could not be recrystallised (Found : C, 61·2; H, 3·9. $C_{30}H_{23}ON_4I$ requires C, 61·8; H, 3·9%).

[1-(3-*Acetyl-2-methylpyrrocoline*)][2-(3-*methylbenzthiazole*)]-*a-azadimethincyanine Iodide.*—3-Acetyl-2-methyl-1-nitrosopyrrocoline (0·42 g.) and 2-methylbenzthiazole methiodide (0·60 g., 1 mol.) in methyl alcohol (8 c.c.), on warming, gave a precipitate of a dark solid. Methyl alcohol (7 c.c.) and 5% alcoholic sodium hydroxide (0·33 c.c., 0·2 mol.) were adde dand the mixture was refluxed for 5·5 hours. Next morning the brown crystals (0·66 g., 67%) were collected and washed with alcohol and then ether. Recrystallisation was difficult and was accomplished from nitromethane to yield a *hydrate* as clusters of needles, m. p. 246·5—247·5° (Found : C, 49·3; H, 3·8; loss in weight at 100°/15 mm. during 30 minutes, 2·5. $C_{20}H_{18}ON_3IS,\frac{2}{3}H_2O$ requires C, 49·3; H, 4·0; H_2O, 2·5%).

Attempted Condensation of 2-Methyl-3-nitrosopyrrocoline and 2-Methylbenzthiazole Methiodide.—The nitroso-compound (0·33 g.) and the methiodide (0·60 g., 1 mol.) in methyl alcohol (8 c.c.) with 5% alcoholic sodium hydroxide solution (0·33 c.c., 0·2 mol.) were refluxed during 6 hours. Almost immediately, the colour of the mixture darkened, and dark crystals began to separate. The solid (0·16 g.) was collected after 12 hours at room temperature and washed with alcohol, then with ether. The product proved very difficult to recrystallise : alcohol-extraction gave a soluble fraction which proved not to be the desired dye (Found : C, 56·2 ; H, 4·6. Calc. for $C_{18}H_{16}N_3IS$: C, 49·9 ; H, 3·7%).

Attempted Condensation of 3-*Nitroso*-2-*phenylpyrrocoline with* 2-*Methylbenzoxazole Ethiodide*.—The nitroso-compound (0·38 g.) and the ethiodide (0·50 g., 1 mol.) in alcohol (12 c.c.) with 5% aqueous sodium hydroxide (0·27 c.c., 0·2 mol.) were refluxed for 7 hours during which a greenish-brown solid separated ; apart from this no colour change was noticed. The solid separating later was unchanged ethiodide.

Use of piperidine (1 mol.) in place of sodium hydroxide gave no colour change and no solid was isolated.

Attempted Condensation of 3-*Acetyl*-1-*nitroso*-2-*phenylpyrrocoline with* 2-*Methylbenzoxazole Ethiodide*.—Refluxing a solution of the nitroso-compound (0·12 g.) and the ethiodide (0·13 g., 1 mol.) in alcohol (5 c.c.) with 5% sodium hydroxide solution (0·07 c.c., 0·2 mol.) produced a very slow colour change to deep bluish-green during 6 hours. Only unchanged nitroso-compound was isolated.

Photographic Properties of the Dyes (VI—IX; R = Me or Ph).—These dyes have been tested for photographic properties in the laboratories of Messrs. Kodak, Ltd., who report that when the dyes were added to emulsions of various types desensitisation and loss of contrast were caused in all cases. Furthermore they were ineffective as backing dyes for photographic plates.

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