184. *The Condensation Products of the* 1 : 2-*Disubstituted* 3-*Nitrosoindoles A New Type of Cyanine Dye.*

By Frederick G. Mann and R. Colin Haworth.

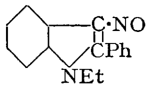
It is shown that 2-aryl-1-alkyl- and 1 : 2-diaryl-indoles react with nitrous acid to give green crystalline 3-nitroso-derivatives. 1-Alkyl-2-methyl- and 1-aryl-2-methyl-indoles give, however, green dinitroso-derivatives, the nitrous acid attacking the 2-methyl group as well as the 3-position in the indole ring. The 3-nitrosoindoles condense readily with the quaternary salts of many suitable heterocyclic compounds having reactive methyl groups: *e.g.*, 3-nitroso-2-phenyl-1-ethylindole (I) condenses with α-picoline methiodide, furnishing (2-*phenyl*-1-*ethyl*-3-*indole*)(1-*methyl*-2-*pyridine*)-α-*azadimethincyanine iodide* (IV). Many compounds of this type have been prepared; they represent a novel type of cyanine dye, and possess photo-desensitising properties. Variation of the quaternary salts employed and of the substituents in both reactants will thus provide a wide range of these cyanine dyes for photographic application.

The 3-nitrosoindoles also condense with other compounds containing a reactive methylene group, *e.g.*, ethyl cyanoacetate, dibenzoylmethane, to give simple anil-like condensation products. The nitrosoindoles oxidise other methylene compounds; *e.g.*, they convert thioindoxyls into the corresponding thioindigotins: the initial reaction here is doubtlessly also condensation to form an anil, which then reacts with unchanged thioindoxyl to give the thioindigotin and the aminoindole.

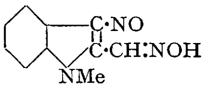
It has been shown by Campbell and Cooper (J., **1935**, 1208) and by Womack, Campbell, and Dodds (J., **1938**, 1402) that nitrous acid converts 2-phenyl-1-methylindole into the green crystalline 3-nitroso-2-phenyl-1-methylindole, the properties of which were studied. Crowther, Mann, and Purdie (J., **1943**, 58) showed that the formation of these green 3-nitroso-derivatives was a general reaction of 2-aryl-1-alkylindoles; many such derivatives were prepared as a ready method of characterising the parent indoles. They also obtained a green nitroso-derivative from 2-phenyl-5-methyl-1-ethylindole, and we have now obtained a similar derivative from 5-*ethoxy*-2-*phenyl*-1-*ethylindole*: these results, by excluding the 5-position for the nitroso-group, confirm the allocation of this group to the 3-position by Campbell and his co-workers.

We have now investigated in detail, first, the extent to which the formation of these green 3-nitrosoindoles is dependent on the nature of the substituents in the 1- and 2-positions, and secondly, certain condensation reactions which the 3-nitroso-group in these compounds undergoes.

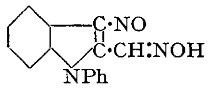
On the first point, three other classes of indoles had to be studied, namely, 1 : 2-diaryl-, 1 : 2-dialkyl-, and 1-aryl-2-alkyl-indoles. We have found that 1 : 2-*diphenylindole* readily gave the green 3-*nitroso*-1 : 2-*diphenylindole*, which has many of the chemical properties of, *e.g.*, 3-nitroso-2-phenyl-1-ethylindole (I) : it is clear, therefore, that 1 : 2-diarylindoles behave similarly to the original 2-aryl-1-alkylindoles. The examples we have taken of the remaining two classes of indoles were 1 : 2-dimethylindole and 1-*phenyl*-2-*methylindole* : these both behaved abnormally, however, for the only product in each case that we have been able to isolate by the action of nitrous acid was a crystalline green *dinitroso*-derivative. Since direct nitrosation of the benzene ring in substituted indoles has not been observed under these conditions, it is almost certain that these two products, formulated in their (probably more stable) tautomeric form, are 3-*nitroso*-1-*methyl*-2-*oximinomethylindole* (II) and 3-*nitroso*-1-*phenyl*-2-*oximinomethylindole* (III) respectively. It is probable that this abnormal formation of these dinitroso-derivatives is peculiar to those 1 : 2-dialkyl- and 1-aryl-2-alkyl-indoles which have a 2-methyl group, since the latter is probably more reactive towards nitrous acid than any other alkyl group. We intend later to prepare indoles of these two types having alkyl groups other than methyl in the 2-position, in order to determine this point.



(I.)

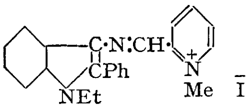


(II.)

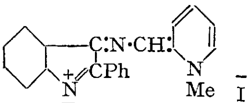


(III.)

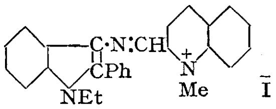
For investigating the condensation reactions of these 3-nitroso-derivatives, we have selected 3-nitroso-2-phenyl-1-ethylindole (I) for our main study. We have confirmed Campbell's observation that these nitroso-derivatives do not apparently condense with primary amines. When, however, this nitroso-compound was treated with α-picoline methiodide in alcoholic solution containing a trace of piperidine, ready condensation occurred, with the formation of the intensely coloured (2-*phenyl*-1-*ethyl*-3-*indole*)(1-*methyl*-2-*pyridine*)-α-*azadimethincyanine iodide* (IV). This compound represents an entirely novel type of cyanine dye : it has the conjugate linkage characteristic of this class of compound, and the cation also clearly exists as a resonance hybrid of the two forms (IV) and (IV*A*). Quinaldine methiodide similarly gave (2-*phenyl*-1-*ethyl*-3-*indole*)(1-*methyl*-2-*quinoline*)-α-*azadimethincyanine iodide* (V). Many similar compounds have been prepared, in view of the importance of these compounds in photographic chemistry. γ-Picoline methiodide also condensed with the nitrosoindole under the influence of piperidine to give the corresponding (1-*methyl*-4-*pyridine*) *iodide* (VI) and lepidine methiodide gave the (1-*methyl*-4-*quinoline*) *iodide* (VII). In view of these results, it might have been expected that either or both of the methyl groups in 2 : 4-dimethylpyridine methiodide would condense with the nitroso-indole : no condensation product could be isolated, however.



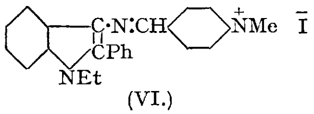
(IV.)



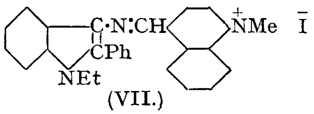
(IV*A*.)



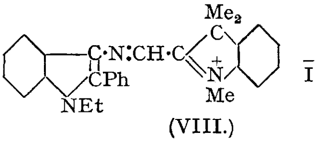
(V.)



(VI.)



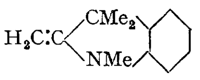
(VII.)

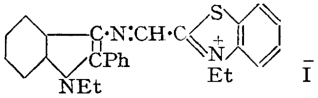


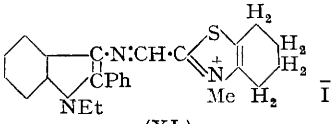
(VIII.)

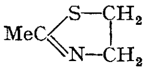
There is little doubt that in the above reactions the piperidine exercises its normal function in such condensations; *e.g.*, that it reacts with the α-picoline methiodide to give piperidine hydriodide and 1-methyl-2-methylenepyridine; the latter then condenses with the nitrosoindole, and the product at once reclaims hydrogen iodide from the piperidine salt to give the stable cyanine (IV). It is noteworthy that 2 : 3 : 3-trimethylindolenine methiodide readily condensed, without a catalyst, to give (2-*phenyl*-1-*ethyl*-3-*indole*)(1 : 3 : 3-*trimethyl*-2-*indolenine*)-α-*azadimethincyanine iodide* (VIII). This ready condensation was not unexpected, because the indolenine methodide is known to lose hydrogen iodide easily, giving 1 : 3 : 3-trimethyl-2-methylene-indoline (IX) : consequently a boiling alcoholic solution of the methiodide undoubtedly contains traces of hydrogen iodide and the reactive indoline (IX) and conditions for condensation, with subsequent recombination with the hydrogen iodide, must be ideal. The pure indoline (IX) in alcoholic solution would not condense with the nitroso-indole. This was also not unexpected, because the condensation product, had it been formed, would have been devoid of the stabilising effect of the resonance—and in effect of all the characteristic structural features—of cyanine compounds : its formation therefore would proceed only if an acid (*e.g.*, hydrogen iodide) were present for immediate union to give the stable cyanine (as VIII).

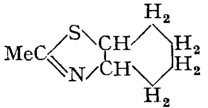
The reactivity of heterocyclic oxygen and sulphur compounds having apparently suitable methyl groups for condensation with the nitrosoindole is noteworthy. The methiodides of 2-methyloxazoline and of 2-methylbenzoxazole gave no condensation, in spite of a wide variety of conditions utilised. On the other hand, the ethiodide of 2-methylbenzthiazole and the methiodide of 2-methyltetrahydrobenzthiazole readily condensed, giving the (1-*ethyl*-2-*benzthiazole*) *iodide* (X) and the (1-*methyl*-2-*tetrahydrobenzthiazole*) *iodide* (XI) respectively: furthermore, 2-methylbenzselenazole methiodide similarly furnished the (1-*methyl*-2-*benzselenazole*) *iodide* (as X). In contradistinction to these results, however, no condensation could be effected with the quaternary salts of 2-methylthiazoline (XII), 2-methylhexahydrobenzthiazole (XIII) or 2-methyldihydro-1 : 3-thiazine (XIV). It would appear, therefore, that the 2-methyl group in this type of heterocyclic compound will react with the nitrosoindole only if the nitrogen and sulphur atoms are linked through two carbon atoms, and if the latter in turn are joined by a double bond. This lack of reactivity in the quaternary salts of (XIV) is, however, in marked contrast to the results of Hamer and Rathbone (J., 1943, 243), who showed that the methiodide of (XIV) condensed with ethyl orthoformate in pyridine solution to give bis-2-(3-methyldihydro-1 : 3-thiazine)trimethincyanine iodide.

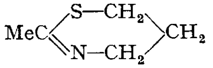

(IX.)


(X.)


(XI.)


(XII.)

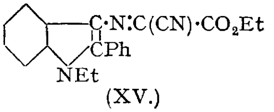

(XIII.)

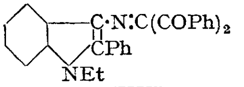

(XIV.)

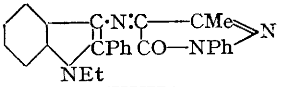
Many condensation products similar to those formulated above have been prepared from 3-nitroso-2-*p*-chlorophenyl-1-ethylindole, from 3-nitroso-1 : 2-diphenylindole, and from the 1-methyl-dinitroso-derivative (II), but only ill-defined derivatives have been obtained from the 1-phenyl-dinitroso-derivative (III).

It is known that, when in cyanine dyes the chain of atoms linking the two heterocyclic nuclei is composed solely of :CH· groups, *i.e.*, is a pure methin chain, the dyes almost always possess photo-sensitising properties, but when this chain contains nitrogen atoms as well as :CH· groups, the dyes may have either photo-sensitising or photo-desensitising properties on the normal photographic plate. Kendall (*J. Soc. Dyers and Col.*, 1936, **52**, 13) has suggested as an empirical rule that, when the nitrogen atom in the chain is separated from the nitrogen atoms of the heterocyclic nuclei by an odd number of carbon atoms, the compound will be a photo-sensitiser : when, however, this nitrogen atom is separated from either of the " heterocyclic " nitrogen atoms by an even number of carbon atoms, the compound will be a photo-desensitiser. In all the members of our new type of cyanine dyes (IV—XI) the nitrogen atom of the chain is separated from *both* heterocyclic nitrogen atoms by an even number of carbon atoms, and on Kendall's rule the compounds should be desensitisers. The action of these compounds on the photographic plate has been investigated by the staff of Imperial Chemical Industries Ltd. (Dyestuffs Division), who find that many of the dyes do in fact possess very powerful desensitising properties * (for details, see p. 676). These compounds, moreover, have other properties which, although varying within wide limits, frequently enhance the practical value of the dyes as desensitisers. At the low concentration at which they are applied, only slight staining of the emulsion is produced, and this staining is completely bleached subsequently by the acid fixing bath. The desensitising action of many of the dyes is not adversely affected by contact with neutral or alkaline developer solutions, and is in some cases actually enhanced. Furthermore, the application of certain of these compounds as desensitisers does not seriously impair the latent image in the exposed emulsion, nor does it cause undue fogging during the subsequent development. It is obvious that by varying the substituents in the 3-nitrosoindoles and also the heterocyclic methylene compounds with which they are condensed, a very large number of these new cyanine dyes can be prepared, and a wide choice of compound is thus available for photographic application.

Other types of compounds containing reactive methylene groups fall into two classes, according to their reaction with our nitrosoindoles. The members of the first class undergo normal condensation with loss of water; since no question of quaternary salt formation is involved, the mechanism of this reaction is almost certainly not identical with that previously described. Thus ethyl cyanoacetate condensed with 3-nitroso-2-phenyl-1-ethylindole (I), giving 3-*carbethoxycyanomethyleneamino*-2-*phenyl*-1-*ethylindole* (XV); dibenzoylmethane gave 3-*dibenzoylmethyleneamino*-2-*phenyl*-1-*ethylindole* (XVI); 1-phenyl-3-methylpyrazolone gave 3-1′-*phenyl*-3′-*methyl*-4′-*pyrazolylamino*-2-*phenyl*-1-*ethylindole* (XVII).


(XV.)

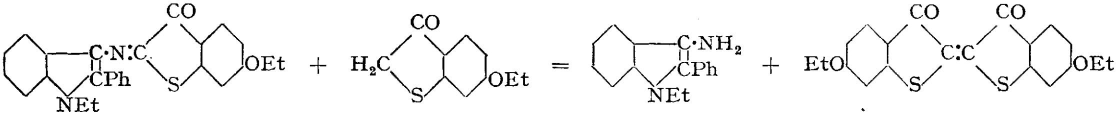

(XVI.)

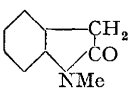

(XVII.)

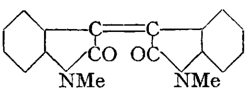
---

* Patent protection pending.

In the second class, however, 6-ethoxythioindoxyl * (XVIII) gave 6 : 6′-diethoxythioindigotin (XIX), and 6 : 7-benzthioindoxyl * similarly gave 6 : 7 : 6′ : 7′-dibenzthioindigotin; furthermore, 1-methyloxindole (XX) gave 1 : 1′-dimethyl*iso*indigotin (XXI). The members of this second class therefore undergo oxidation by the nitrosoindole. It is almost certain, however, that the initial reaction of members of this class is identical with that of the first class above; *e.g.*, that 6-ethoxythioindoxyl (XVIII) undergoes simple condensation to the aza-derivative (XXII). The latter, however, has the normal properties of an anil, and readily reacts with another molecule of the original methylene compound (XVIII) to give the 6 : 6′-diethoxythioindigotin (XIX). This mechanism must in each such case involve the formation of 3-*amino*-2-*phenyl*-1-*ethylindole* (XXIII). The nature of this amine renders its isolation from the above reaction mixtures very difficult; we have prepared it, however, by direct reduction of the nitrosoindole (I). Confirmation of the mechanism of this reaction is given by the work of Stollé *et al.* (*J. pr. Chem.*, 1930, **128**, 1), who showed that 1-methyloxindole (XX) also gave 1 : 1′-dimethyl*iso*indigotin (XXI) when boiled with *p*-nitrosodimethylaniline; clearly in this reaction the anil must have been the essential intermediate product.


(XXII.) (XVIII.) (XXIII.) (XIX.)

(XX.)



(XXI.)

EXPERIMENTAL.

The preparation of the indoles and their nitroso-derivatives is described first, and then the condensation derivatives of each nitrosoindole in turn. Solvents used for recrystallisation are given in parenthesis after the name of the compound concerned.

2-Phenyl-1-ethylindole and its 3-nitroso-derivative (I) were prepared as described by Crowther, Mann, and Purdie (*loc. cit.*) : the latter compound was further characterised as its *picrate*, reddish-orange needles (alcohol), m. p. 141—143° (Found : C, 55·4; H, 4·0. $C_{16}H_{14}ON_2,C_6H_3O_7N_3$ requires C, 55·1; H, 3·6%).

Reduction.—Zinc dust (8 g.) and concentrated hydrochloric acid (27 c.c.) were added in alternate small portions during 1 hour to a solution of the above nitrosoindole (5 g.) in boiling alcohol (100 c.c.). The deep green solution became red, and later pale yellow. The solution was then boiled for a further 30 minutes, cooled, and slowly diluted with water (200 c.c.). The pale brown precipitate, recrystallised from very dilute hydrochloric acid (charcoal), gave the *monohydrated hydrochloride* of 3-*amino*-2-*phenyl*-1-*ethylindole* (XXIII), m. p. 238—239° (Found : C, 66·6; H, 6·9; N, 9·8; Cl, 12·0. $C_{16}H_{16}N_2,HCl,H_2O$ requires C, 66·1; H, 6·5; N, 9·6; Cl, 12·2%) : 3·0 g., 52%. This salt crystallised from alcohol as the *mono-ethyl-alcoholate*, m. p. 238—239° (Found : C, 67·5; H, 7·1. $C_{16}H_{16}N_2,HCl,C_2H_6O$ requires C, 67·8; H, 7·2%).

5-*Ethoxy*-2-*phenyl*-1-*ethylindole.*—(*a*) A mixture of *p*-phenetidine (396 g.) and ethyl bromide (342 g.; 1·1 mols.), when set aside in a securely stoppered thick-walled bottle for 12 hours, became almost solid. The bottle was then heated at 60° for 4 hours. An aqueous solution of the product was basified and extracted with ether (500 c.c.). The solvent was removed from the dried extract, and the residue on distillation gave two fractions, (i) b. p. 129—132°/15 mm. (108 g.); (ii) b. p. 132—135°/15 mm. (305 g., 65%) : fraction (ii) was pure N-*ethyl*-p-*phenetidine* (Found : C, 72·7; H, 9·25. $C_{10}H_{15}ON$ requires C, 72·7; H, 9·1%), but fraction (i) was not quite pure.

(*b*) A solution of sodium nitrite (130 g.) in water (460 c.c.) was added during 20 minutes to a mixture of fraction (ii) above (305 g.; 1 mol.), concentrated hydrochloric acid (270 c.c.), and crushed ice (800 g.), the temperature being kept below 10°. After 2 hours' stirring, the dark brown, crystalline *N*-nitroso-*N*-ethyl-*p*-phenetidine (150 g., 42%) was collected; m. p. 23·5—24·5°. [Fraction (i) above, similarly treated, gave a second crop, 46 g.] This nitrosoamine could not be distilled even in a vacuum, and further purification was not attempted.

(*c*) The reduction of the above nitrosoamine to *as.*-*p*-phenetylethylhydrazine, $EtO{\cdot}C_6H_4{\cdot}NEt{\cdot}NH_2$, was attempted under various conditions, but the product was always contaminated with *N*-ethylphenetidine; these compounds have b. p.'s lying close together and cannot be separated satisfactorily by distillation. The following method, however, gives a sample of the hydrazine pure enough for indole formation by a Fischer synthesis. A solution of the nitrosoamine (196 g.) in acetic acid (285 c.c.) was added during 4·5 hours to a well-stirred mixture of zinc dust (285 g.) and water (430 c.c.), the temperature being kept between 10° and 20° : below this range, reduction ceased, whereas above it considerable reduction of the hydrazine occurred. The final mixture was stirred for 2 hours, then warmed to 60°, and filtered : the residue was washed with 5% hydrochloric acid (500 c.c.). The united filtrate and washings were cooled, basified, and extracted with ether. After drying and removal of the solvent, distillation in coal-gas gave two fractions : (i) b. p. 101—106°/0·7 mm., 23 g., (ii) b. p. 107—113°/0·7 mm., 98 g. Fraction (ii) on redistillation gave two fractions, (iii) b. p. 109—111°/0·7 mm., 56·6 g. (Found : C, 73·8; H, 9·8; N, 11·0. $C_{10}H_{16}ON_2$ requires C, 66·7; H, 8·9; N, 15·6%); (iv) b. p. 111—113°/0·7 mm., 22·8 g. (Found : C, 69·0; H, 9·2; N, 13·9%). Fraction (iii) clearly contained a high proportion of the amine, and fraction (iv) of the hydrazine.

(*d*) Fraction (iv) (11·6 g.), acetophenone (7·9 g.; 1 mol.), and acetic acid (0·3 g.) were heated together at 100° for 5 minutes, and powdered zinc chloride (50 g.) then added. A vigorous reaction occurred, and the temperature rose to 170°; it was then maintained at 150° for 10 minutes. The cold product was extracted with dilute hydrochloric acid, and the insoluble residue taken up in benzene. The dried benzene extract was distilled in coal-gas, 5-*ethoxy*-2-*phenyl*-1-*ethylindole* being obtained as a viscous oil, b. p. 200—210°/0·7 mm. : 5·2 g., 30%. The oil readily solidified, and gave colourless crystals (acetic acid, alcohol), m. p. 112—113° (Found : C, 84·6; H, 7·2. $C_{18}H_{19}ON$ requires C, 81·5; H, 7·2%. Satisfactory carbon values could not be obtained).

---

* These substituted thioindoxyls were chosen because their $>CH_2$ groups were known to have high reactivity (Harley-Mason and Mann, J., 1942, 404).

3-*Nitroso*-5-*ethoxy*-2-*phenyl*-1-*ethylindole*.—A solution of sodium nitrite (1·68 g.; 1·7 mols.) in water (3 c.c.) was slowly added to one of the indole (3·7 g.) in acetic acid (100 c.c.). After 2 hours the mixture was diluted with water, and the precipitated 3-*nitroso*-derivative collected: green crystals (alcohol), m. p. 136—137·5° (Found: C, 73·3; H, 6·6; N, 9·5. $C_{18}H_{18}O_2N_2$ requires C, 73·5; H, 6·1; N, 9·5%); 1·2 g., 29%.

1 : 2-*Diphenylindole*.—Acetic acid (0·5 c.c.) was added to a mixture of *as.*-diphenylhydrazine (55 g.) and acetophenone (36 g.; 1 mol.): a cloudiness developed as hydrazine formation proceeded. Powdered dry zinc chloride (160 g.) was added; the mixture, when cautiously heated, first became almost solid, then a vigorous reaction occurred, the temperature rising spontaneously from 130° to 200°. After 5 minutes at this temperature, the mixture was cooled and extracted with dilute hydrochloric acid, and the residual indole taken up in ether (600 c.c.). After removal of the ether from the dried extract, the residue was fractionally distilled, 1 : 2-*diphenylindole* being obtained first as a syrup, b. p. 198—200°/0·7 mm. (20 g., 25%), which however readily solidified, and gave colourless crystals (acetic acid, alcohol), m. p. 80—82° (Found: C, 89·3; H, 5·8; N, 5·5. $C_{20}H_{15}N$ requires C, 89·2; H, 5·6; N, 5·2%). Pfulf (*Annalen*, 1887, **239**, 223) claimed to have prepared this indole as a viscous oil.

Sodium nitrite (2·5 g.; 1·6 mols.) in water (5 c.c.) was added to a solution of the indole (6 g.) in acetic acid (200 c.c.). After 1 hour, the green crystals of 3-*nitroso*-1 : 2-*diphenylindole* which had separated were collected (4·3 g.), a further crop (0·8 g., 77% in all) being obtained by diluting the filtrate with water: m. p. 200—202° (alcohol) (Found: C, 80·5; H, 4·4; N, 9·55. $C_{20}H_{14}ON_2$ requires C, 80·5; H, 4·7; N, 9·4%).

1 : 2-Dimethylindole was prepared by the following modification of Degen's method (*Annalen*, 1886, **236**, 152). Glacial acetic acid (0·3 c.c.) was added to a mixture of phenylmethylhydrazine (27 g.) and acetone (19·4 c.c.; 1 mol.): heat was immediately generated, and water separated as hydrazone formation proceeded. The mixture was set aside overnight and then refluxed on a water-bath for 3 hours. The product was dried (sodium sulphate) and distilled, the hydrazone being obtained as a pale yellow oil, b. p. 112—117°/20 mm.: 32·8 g. (92%). A mixture of the hydrazone (32·8 g.) and powdered anhydrous zinc chloride (160 g.) was then heated at 130° for 3 hours. The dark warm product was vigorously agitated with dilute sulphuric acid, and the residue then dissolved in benzene, dried (sodium sulphate), and distilled, 1 : 2-dimethylindole being obtained as a pale yellow oil, b. p. 145—149°/16 mm. (7·2 g., 24%); it readily solidified, giving colourless crystals (petrol), m. p. 52—54°. Degen (*loc. cit.*) gives m. p. 56°.

The *dinitroso*-derivative (II) was best prepared as follows. A solution of 1 : 2-dimethylindole (1 g.) in acetic acid (60 c.c.) was cooled until the acid began to crystallise. Finely powdered sodium nitrite (0·5 g.; 1 mol.) was slowly added with stirring, the mixture becoming dark green and then greenish-brown, and a green solid separating. The mixture was set aside until it reached room temperature, and then filtered. The green 3-*nitroso*-1-*methyl*-2-*oximinomethylindole* (II) thus collected (0·4 g., 27%) was washed with water, dried, and recrystallised from alcohol: m. p. 173° (decomp., effer.) (Found: C, 59·4; H, 4·7; N, 20·7. $C_{10}H_9O_2N_3$ requires C, 59·1; H, 4·4; N, 20·7%). The use of larger proportions of sodium nitrite in the above preparation caused the compound (II) to be contaminated with other products.

1-*Phenyl*-2-*methylindole*.—Acetic acid (0·3 c.c.) was added to a mixture of diphenylhydrazine (110 g.) and acetone (66 c.c.; 1·2 mols.), water rapidly separating. The mixture was refluxed for 6 hours, acetic acid (200 c.c.) and powdered zinc chloride (50 g.) then added, and the refluxing continued for another 8 hours. The dark solution was vigorously stirred with much dilute hydrochloric acid, and the residue dissolved in ether, dried (sodium sulphate), and distilled: the crude *indole* was obtained as a pale yellow oil. b. p. 132—170°/0·4 mm. (44 g., 35%), no definite fraction occurring within this range. The addition of a small quantity of alcohol to the distillate, however, caused the indole to solidify: colourless crystals (alcohol), m. p. 58—58·5° (Found: C, 86·6; H, 6·5; N, 6·3. $C_{15}H_{13}N$ requires C, 86·9; H, 6·3; N, 6·8%).

A solution of this indole (2·0 g.) in acetic acid (50 c.c.) was chilled until almost solid. It was vigorously stirred whilst a solution of sodium nitrite (1·48 g.; 2·2 mols.) in water (2 c.c.) was rapidly added: the acetic acid melted and a precipitate appeared. After 1 hour at room temperature, the greenish-brown solid was collected, and washed with water and then cold alcohol, the brown impurity being thus removed. The residual 3-*nitroso*-1-*phenyl*-2-*oximinomethylindole* (III) thus obtained (1·8 g., 70%) was recrystallised from alcohol and then benzene: pale green crystals, m. p. 186° (decomp.) (Found: C, 67·9; H, 4·5; N, 15·7. $C_{15}H_{12}O_2N_3$ requires C, 67·9; H, 4·15; N, 15·8%). The use of smaller proportions of sodium nitrite in the above preparation gave either a mixture of (III) with unchanged indole, or ill-defined brown amorphous products from which no definite compound could be isolated.

The derivatives (or other products) obtained from each of the above nitrosoindoles are given in turn below.

For the preparation of the cyanine dyes, sodium hydroxide could be used as a catalyst only for those condensations involving α- or γ-picoline methiodides: its use in other condensations gave impure products. Piperidine could be advantageously used, however, for all condensations requiring a catalyst. The colour of the crystalline cyanine dyes, being largely determined by surface reflexion, usually differed from that of their solutions in organic solvents. The colours of the solutions varied from dark reddish-brown to deep permanganate or reddish-violet: the colours of the crystalline dyes are specifically stated below.

Derivatives from 3-*Nitroso*-2-*phenyl*-1-*ethylindole* (I).—(1) (2-*Phenyl*-1-*ethyl*-3-*indole*)(1-*methyl*-2-*pyridine*)-α-*azadimethincyanine iodide* (IV). A solution of the nitrosoindole (2 g.), α-picoline methiodide (1·88 g.; 1 mol.), and piperidine (0·3 c.c.) in alcohol (50 c.c.) was refluxed for 5 hours, the colour becoming deep reddish-brown. The precipitated *cyanine iodide* (1·7 g., 46%) was collected from the cold solution; when washed and recrystallised from alcohol, it was obtained as reddish-brown crystals, m. p. 214—216° (Found: C, 59·1; H, 5·0; N, 9·2; I, 26·9. $C_{23}H_{22}N_3I$ requires C, 59·1; H, 4·7; N, 9·0; I, 27·2%). The piperidine could be replaced by 5% aqueous sodium hydroxide (0·3 c.c.).

(2) The corresponding (1-*methyl*-2-*quinoline*) *cyanine iodide* (V) was similarly prepared by using quinaldine methiodide (2·3 g.; 1 mol.). The permanganate-coloured solution was cooled, and the crude iodide collected (2·1 g., 51%); greenish-brown crystals (methyl alcohol), m. p. 218—219° (Found: C, 63·1; H, 4·8; N, 8·5; I, 24·6. $C_{27}H_{24}N_3I$ requires C, 62·7; H, 4·6; N, 8·1; I, 24·6%).

(3) Repetition of Experiment (1), quinaldine ethiodide (2·4 g.; 1 mol.) being used, gave a rapid reaction; the solution became permanganate-coloured immediately on boiling. After 7 hours' refluxing, cooling gave brownish-green crystals (1·5 g., 35%) of (2-*phenyl*-1-*ethyl*-3-*indole*) (1-*ethyl*-2-*quinoline*)-α-*azadimethincyanine iodide* (alcohol), m. p. 209—210° (Found: C, 63·6; H, 5·2; N, 7·75; I, 24·0. $C_{28}H_{26}N_3I$ requires C, 63·3; H, 4·9; N, 7·9; I, 23·9%). A small second crop was obtained by concentrating the mother-liquor.

(4) Experiment (1) was repeated, using however γ-picoline methiodide (1·88 g.) in methyl alcohol (30 c.c.) with 5% aqueous caustic soda (0·5 c.c.) as a catalyst and 12 hours' refluxing. The (1-*methyl*-4-*pyridine*) *cyanine iodide* (VI) (1·1 g., 30%) separated as reddish-brown crystals (methyl alcohol), m. p. 204—205° (Found: C, 59·3; H, 5·0; N, 9·25; I, 27·2. $C_{23}H_{22}N_3I$ requires C, 59·1; H, 4·7; N, 9·0; I, 27·2%).

γ-Picoline methiodide was readily prepared without a solvent: colourless crystals (acetone containing some methyl alcohol), m. p. 148—150° (Found: N, 6·0. Calc. for $C_7H_{10}NI$: N, 6·0%). Clemo and Gourlay (J., 1938, 478) give m. p. 149—150°.

(5) A solution of the nitrosoindole (2 g.), lepidine methiodide (2·3 g.; 1 mol.), and piperidine (0·1 c.c.) in alcohol

(50 c.c.) was refluxed for 3 hours, a violet coloration rapidly developing and solid dye separating. Filtration of the cold mixture furnished brownish-green crystals (2·8 g., 75%) of the (1-*methyl*-4-*quinoline*) *cyanine iodide* (VII) : recrystallisation from alcohol furnished the *mono-alcoholate*, m. p. 233—234° (Found : C, 61·9; H, 5·2; N, 7·6; I, 22·6. $C_{27}H_{24}N_3I,C_2H_6O$ requires C, 61·8; H, 5·4; N, 7·5; I, 22·5%). Long exposure in a vacuum over phosphoric oxide gave the solvent-free *iodide*, of unchanged m. p. (Found : C, 62·5; H, 4·6; N, 8·05; I, 24·7. $C_{27}H_{24}N_3I$ requires C, 62·7; H, 4·6; N, 8·1; I, 24·6%).

(6) The use of lepidine ethiodide (2·4 g.; 1 mol.) in Expt. (5) gave brownish-green crystals (3·2 g., 75%) of the (1-*ethyl*-4-*quinoline*)*cyanine iodide* (as VII), iridescent green crystals from alcohol, m. p. 230—231° (Found : C, 63·1; H, 5·1; N, 7·8; I, 24·0. $C_{28}H_{26}N_3I$ requires C, 63·3; H, 4·9; N, 7·9; I, 23·9%).

(7) When a solution of the nitrosoindole (1 g.), 1 : 3 : 3-trimethyl-2-methyleneindoline (IX) (0·71 g.; 1 mol.), and piperidine (0·1 c.c.) in alcohol (50 c.c.) was boiled for 7 hours, the colour of the solution darkened, but on cooling, the unchanged nitrosoindole crystallised. When, however, 2 : 3 : 3-trimethylindolenine methiodide (1·2 g.; 1 mol.) was used, the solution rapidly developed a deep red colour on boiling without a catalyst. After 8 hours' refluxing, the solution was cooled: reddish-brown needles (1 g., 47%) of the (1 : 3 : 3-*trimethyl*-2-*indolenine*) *cyanine iodide* (VIII) separated : m. p. 220—221° after recrystallisation from alcohol (Found : C, 62·6; H, 5·3; N, 8·0; I, 23·8. $C_{28}H_{28}N_3I$ requires C, 63·0; H, 5·25; N, 7·9; I, 23·8%).

Piggott (U.S.P. 2,016,836) has described the nitration of 2 : 3 : 3-trimethylindolenine metho-hydrogen sulphate, whereby two isomeric mononitro-1 : 3 : 3-trimethyl-2-methyleneindolines, m. p. 100° and 140—143°, were obtained; the former gave a mononitro-2 : 3 : 3-trimethylindolenine methobromide, m. p. 256°. The position of the nitro-groups in these compounds was not determined. To ascertain whether cyanine formation was affected by substituents, the above methobromide (1·2 g.) was refluxed in alcohol (40 c.c.) with the nitrosoindole (1 g.; 1 mol.) for 6 hours. The deep red solution was cooled and poured into ether (400 c.c.). The precipitated reddish-brown crystals (0·7 g., 33%) of the (*nitro*-1 : 3 : 3-*trimethyl*-2-*indolenine*) *cyanine bromide*, recrystallised from amyl alcohol, separated as a *monohydrate*, m. p. 224—225° (Found : C, 60·7; H, 5·2; N, 10·2; Br, 15·0. $C_{28}H_{27}O_2N_4Br,H_2O$ requires C, 61·2; H, 5·3; N, 10·2; Br, 14·6%).

(8) When a mixture of the nitrosoindole (2 g.) and 2-methylbenzthiazole ethiodide (2·44 g.; 1 mol.) in alcohol (40 c.c.) was boiled, reaction readily occurred without a catalyst, the solution becoming permanganate-coloured. After 2 hours' refluxing and subsequent cooling, the iridescent red crystals (3·4 g., 79%) of the (1-*ethyl*-2-*benzthiazole*) *cyanine iodide* (X) were collected : after crystallisation from alcohol, m. p. 212—213° (Found : C, 58·3; H, 4·9; N, 7·7; I, 23·3. $C_{26}H_{24}N_3IS$ requires C, 58·1; H, 4·5; N, 7·8; I, 23·6%).

(9) Smith and Sapiro (*Trans. Roy. Soc. S. Africa*, 1929, **18**, 229) describe 2-methyltetrahydrobenzthiazole methiodide as an extremely deliquescent solid, exceedingly soluble in water and alcohol : they give an analysis but no m. p. We find that the methiodide, recrystallised from absolute alcohol, has m. p. 114—116° with slight preliminary softening, if great care is taken to ensure that the specimen is dry. The use of this methiodide (2·4 g.) in the previous experiment, with piperidine as a catalyst, gave scarlet crystals (2·0 g., 47%) of the (1-*methyl*-2-*tetrahydrobenzthiazole*) *cyanine iodide* (XI), m. p. 224° after recrystallisation from alcohol (Found : C, 57·1; H, 5·1; N, 7·6; I, 25·3. $C_{25}H_{26}N_3IS$ requires C, 56·9 H, 4·9; N, 8·0; I, 24·1%). Consistent values for iodine could not be obtained.

(10) Repetition of Expt. (8), 2-methylbenzselenazole methiodide (2·7 g.; 1 mol.) in alcohol (60 c.c.) being used, rapidly gave a deep-red solution from which crystals separated after 30 minutes' boiling. After 5 hours' refluxing, the solution was cooled, and the greenish-brown iridescent needles (2·2 g., 48%) of the (1-*methyl*-2-*benzselenazole*) *cyanine iodide* (as X) collected, washed with water, methyl alcohol and ether, and recrystallised from methyl alcohol : m. p. 223° (decomp.) (Found : C, 50·7; H, 3·7; N, 7·4; I, 22·4. $C_{25}H_{22}N_3ISe$ requires C, 52·6; H, 3·9; N, 7·4; I, 22·3%. Low and inconsistent carbon values were always obtained).

(11) A mixture of the nitrosoindole (2·65 g.), ethyl cyanoacetate (1·20 g.; 1 mol.), and zinc chloride (0·1 g.) was heated in a dry atmosphere at 135—140° for 3 hours. The viscous dark-red cold product solidified when mixed with alcohol : recrystallisation from alcohol gave orange crystals (1·5 g., 41%) of 3-*carbethoxycyanomethyleneamino*-2-*phenyl*-1-*ethylindole* (XV), m. p. 143—144° (Found : C, 72·9; H, 5·4; N, 12·2. $C_{21}H_{19}O_2N_3$ requires C, 73·0; H, 5·5; N, 12·2%).

(12) A mixture of the nitrosoindole (1 g.), dibenzoylmethane (0·9 g.; 1 mol.), and zinc chloride (0·1 g.) was heated in coal-gas at 140° for 30 minutes. The cold red solid residue, crushed, washed with water, and recrystallised from alcohol, gave brown needles (0·7 g., 38%) of 3-*dibenzoylmethyleneamino*-2-*phenyl*-1-*ethylindole* (XVI), m. p. 161—163° (Found : C, 81·4; H, 5·45; N, 6·2. $C_{31}H_{24}O_2N_2$ requires C, 81·6; H, 5·3; N, 6·1%).

A similar condensation was attempted with acetylacetone, but no satisfactory product could be isolated.

(13) Expt. (12) was repeated, 1-phenyl-3-methylpyrazolone (0·70 g.; 1 mol.) being used, with heating at 135—140° for 2 hours. The cold solid product, similarly treated, gave brown iridescent crystals (0·4 g., 25%) of 3-1′-*phenyl*-3′-*methyl*-4′-*pyrazolylamino*-2-*phenyl*-1-*ethylindole* (XVII), m. p. 207—208° (Found : C, 76·8; H, 5·7; N, 14·3. $C_{26}H_{22}ON_4$ requires C, 76·8; H, 5·4; N, 13·8%).

(14) A mixture of the nitrosoindole (1 g.), 6-ethoxythioindoxyl (XVIII) (0·79 g.; 1 mol.), zinc chloride (0·1 g.), and acetic acid (10 c.c.) was refluxed at 130—135° for 30 minutes and then cooled, in a coal-gas atmosphere throughout. The red residue was triturated with alcohol and collected : one half, recrystallised from nitrobenzene, gave red crystals of 6 : 6′-diethoxythioindigotin (XIX), m. p. above 260° (Found : C, 62·3; H, 4·35. Calc. for $C_{20}H_{16}O_4S_2$: C, 62·5; H, 4·2%); the second half, subjected to reductive acetylation by the method of Harley-Mason and Mann (*loc. cit.*), gave diacetyldihydro-6 : 6′-diethoxythioindigotin (acetic acid), m. p. 224—225°, alone and when mixed with an authentic specimen.

(15) Repetition of Expt. (14), 6 : 7-benzthioindoxyl (0·80 g.; 1 mol.) being used, and heating at 125° for 10 minutes, gave ultimately red crystals of 6 : 7 : 6′ : 7′-dibenzthioindigotin (nitrobenzene), m. p. above 290° (Found : C, 72·6; H, 3·4. Calc. for $C_{24}H_{12}O_2S_2$: C, 72·7; H, 3·0%).

(16) A mixture of the nitrosoindole (2 g.), 1-methyloxindole (XX) (1·2 g.; 1 mol.), and zinc chloride (0·1 g.) was heated in coal-gas. It melted at 110°, and a vigorous reaction occurred at 140°, a red solid forming : the temperature was then kept at 135—140° for 2 hours. The cold product, crushed, washed with water and recrystallised from acetone, gave crimson needles (0·3 g., 25%) of 1 : 1′-dimethyl*iso*indigotin (XXI), m. p. 263—264° (Found : C, 74·0; H, 5·0; N, 9·6. Calc. for $C_{18}H_{14}O_2N_2$: C, 74·5; H, 4·8; N, 9·6%). Stollé (*loc. cit.*) gives m. p. 265°.

The nitrosoindole could not be condensed with rhodanine, in spite of a variety of conditions employed.

Derivatives from 3-*Nitroso*-2-p-*chlorophenyl*-1-*ethylindole*.—For the preparation of this nitrosoindole, see Crowther, Mann, and Purdie (*loc. cit.*).

(1) The nitrosoindole (2 g.), α-picoline methiodide (1·65 g.; 1 mol.), and 5% aqueous sodium hydroxide (0·5 c.c.) in methyl alcohol (30 c.c.) were refluxed for 12 hours : hydriodic acid of constant b. p. (0·2 c.c.) was then added, and the mixture cooled. Brown needles (0·8 g., 18%) of (2-p-*chlorophenyl*-1-*ethyl*-3-*indole*)(1-*methyl*-2-*pyridine*)-α-*azadimethincyanine iodide* (as IV) separated; m. p. 212—214°, after recrystallisation from methyl alcohol (Found : C, 54·7; H, 4·2; N, 8·8; Cl + I, 32·6. $C_{23}H_{21}N_3ClI$ requires C, 55·0; H, 4·2; N, 8·4; Cl + I, 32·4%).

(2) Repetition of Expt. (1), γ-picoline methiodide (1·65 g.) being used and 6 hours' refluxing, furnished reddish-

brown crystals (becoming green when crushed) (0·8 g., 18%) of the (1-*methyl*-4-*pyridine*) *cyanine iodide* (as VI) (methyl alcohol), m. p. 253—254° (Found : C, 54·9; H, 4·3; N, 8·1; Cl + I, 32·5%).

(3) Refluxing the nitrosoindole (1 g.), lepidine methiodide (1 g.; 1 mol.), and piperidine (0·3 c.c.) in methyl alcohol (40 c.c.) for 4 hours gave brown crystals having a green reflexion (1·6 g., 78%) of the (1-*methyl*-4-*quinoline*) *cyanine iodide* (as VII), which crystallised from methyl alcohol as a *mono-alcoholate*, m. p. 245—247° (Found : C, 57·7; H, 4·7; N, 7·1; Cl + I, 27·5. $C_{27}H_{23}N_3ClI,CH_4O$ requires C, 57·6; H, 4·6; N, 7·2; Cl + I, 27·8%).

(4) Repetition of Expt. (3), 2-methylbenzthiazole ethiodide (1·07 g.; 1 mol.) in ethyl alcohol (40 c.c.) being used, gave iridescent brownish-green crystals (1·3 g., 65%) of the (1-*ethyl*-2-*benzthiazole*) *cyanine iodide* (as X) (alcohol), m. p. 240—241° (Found : C, 55·0; H, 4·4; N, 7·3; Cl + I, 27·5. $C_{26}H_{23}N_3ClIS$ requires C, 54·6; H, 4·0; N, 7·35; Cl + I, 28·4%).

Derivative from 3-*Nitroso*-5-*ethoxy*-2-*phenyl*-1-*ethylindole*.—(1) The nitrosoindole (1 g.), lepidine methiodide (0·97 g.; 1 mol.), and piperidine (0·2 c.c.) in methyl alcohol (20 c.c.), refluxed together for 4 hours, furnished greenish-violet crystals (1·55 g., 80%) of (5-*ethoxy*-2-*phenyl*-1-*ethyl*-3-*indole*) (1-*methyl*-4-*quinoline*)-α-*azadimethincyanine iodide* (as VII), which crystallised from much methyl alcohol with 0·5 mol. of solvent; m. p. 244—245° (Found: C, 61·2; H, 5·3; N, 7·5; I, 22·3. $C_{29}H_{28}ON_3I,\frac{1}{2}CH_4O$ requires C, 61·3; H, 5·2; N, 7·3; I, 22·0%). Long exposure in a vacuum over sulphuric acid gave the solvent-free *iodide*, m. p. unchanged (Found : C, 61·9; H, 5·2. $C_{29}H_{28}ON_3I$ requires C, 62·0; H, 5·0%).

Derivatives from 3-*Nitroso*-1 : 2-*diphenylindole*.—(1) The nitrosoindole (2 g.), α-picoline methiodide (1·58 g.; 1 mol.), 5% aqueous sodium hydroxide (0·5 c.c.), and methyl alcohol (40 c.c.) were refluxed together for 12 hours. Hydriodic acid of constant b. p. (0·2 c.c.) was added, and cooling gave brown crystals (0·95 g., 27%) of (1 : 2-*diphenyl*-3-*indole*)(1-*methyl*-2-*pyridine*)-α-*azadimethincyanine iodide* (as IV), which crystallised from methyl alcohol as a *monohydrate*, which melted at *ca.* 125°, resolidified, and melted at 215—216° (Found : C, 60·3; H, 4·4; N, 7·8; I, 24·1. $C_{27}H_{22}N_3I,H_2O$ requires C, 60·8; H, 4·5; N, 7·9; I, 23·8%).

(2) Repetition of Expt. (1), γ-picoline methiodide (1·58 g.) being used, furnished reddish-brown crystals having an iridescent green surface reflexion (0·8 g., 23%) of the (1-*methyl*-4-*pyridine*) *cyanine iodide* (as VI), m. p. 276° (Found : C, 63·0; H, 4·9; N, 8·3; I, 25·3. $C_{27}H_{22}N_3I$ requires C, 62·9; H, 4·3; N, 8·15; I, 24·7%).

(3) The nitrosoindole (1 g.), lepidine methiodide (0·95 g.; 1 mol.), and piperidine (0·3 c.c.) in methyl alcohol (30 c.c.) were refluxed for 4 hours and then cooled. Reddish-brown crystals (1·8 g., 86%) of the (1-*methyl*-4-*quinoline*) *cyanine iodide* (as VII) separated: recrystallisation from methyl alcohol furnished a *mono-methyl alcoholate*, m. p. 180—183° with preliminary softening (Found : C, 63·9; H, 4·7; N, 6·8; I, 21·3. $C_{31}H_{24}N_3I,CH_4O$ requires C, 64·3; H, 4·7; N, 7·0; I, 21·3%).

(4) Refluxing a solution of the nitrosoindole (1 g.) and 2 : 3 : 3-trimethylindolenine methiodide (1 g.; 1 mol.) in alcohol (30 c.c.) gave ready condensation without a catalyst. After 4 hours' boiling, cooling gave crimson crystals (0·85 g., 44%) of the (1 : 3 : 3-*trimethyl*-2-*indolenine*) *cyanine iodide* (as VIII) (ethyl alcohol), m. p. 232—233° (Found : C, 65·8; H, 5·2; N, 7·2; I, 21·6. $C_{32}H_{28}N_3I$ requires C, 66·1; H 4·8; N, 7·2; I, 21·9%).

(5) Repetition of Experiment (4), 2-methylbenzthiazole ethiodide (1·02 g.; 1 mol.) being used, gave crimson crystals (1·3 g., 66%) of the (1-*ethyl*-2-*benzthiazole*) *cyanine iodide* (as X), m. p. 204—205° after crystallisation from alcohol, in which it was only slightly soluble (Found : C, 61·2; H, 4·8; N, 7·1; I, 21·5. $C_{30}H_{24}N_3IS$ requires C, 61·5; H, 4·1; N, 7·2; I 21·7%).

Derivatives from 3-*Nitroso*-1-*methyl*-2-*oximinomethylindole* (II).—A solution of the dinitrosoindole (II) (1 g.) and 2-methylbenzthiazole ethiodide (1·4 g.; 1 mol.) in alcohol (60 c.c.), when refluxed for 5 hours, rapidly developed a deep red colour and deposited reddish-brown crystals of (1-*methyl*-2-*oximinomethyl*-3-*indole*)(1-*ethyl*-2-*benzthiazole*)-α-*azadimethincyanine iodide*. The latter (0·9 g., 40%) were collected from the cold product, and recrystallised from alcohol; m. p. 209° (decomp.) (Found : C, 49·5; H, 4·2; N, 11·1; I, 26·5. $C_{20}H_{19}ON_4IS$ requires C, 49·0; H, 3·9; N, 11·4; I, 25·9%). The assumption that it is the 3-nitroso-group which has undergone condensation in the above reaction is based on analogy with the previous condensations.

We are indebted to the staff of Imperial Chemical Industries Ltd. (Dyestuffs Division) for the following report on the desensitising properties of the cyanine dyes :

"The results tabulated below refer to the determination of the comparative useful desensitising effect of the dyes compared with that of Pinakryptol Yellow. The figures represent an accurate comparison between the dyes only when employed under the particular conditions defined. Alteration in these conditions (*e.g.*, concentration), the use of a different test emulsion, or alteration in the properties of the dye (*e.g.*, change of an anion leading to a change in solubility) would lead to different and largely unpredictable results.

"The method of evaluation is based on a conventional method of employing desensitisers in processing optically sensitised emulsions. The value of the dye solution for this purpose compared with a similar solution of Pinakryptol

Compound.	A.	B.	C.	Remarks.
Pinakryptol yellow	0 : 200	0	100	U.D.
3-*Nitroso*-2-*phenyl*-1-*ethylindole condensed with :*				
α-Picoline methiodide	40 : 160	0·19	9	U.D. Stain, nil.
Quinaldine methiodide	30 : 170	0·80	2060	N-U.D. Stain, nil.
Quinaldine ethiodide	30 : 170	0·47	1750	Stain, trace.
γ-Picoline methiodide	20 : 180	0·10	13	U.D. Stain, nil.
Lepidine methiodide	40 : 160	0·16	374	Slightly Unv.D. Stain, trace.
Lepidine ethiodide	40 : 160	0·24	558	U.D. Stain, nil.
2 : 3 : 3-Trimethylindolenine methiodide	30 : 170	0·02	79	U.D. Stain, trace.
Nitro-2 : 3 : 3-trimethylindolenine methobromide	100 : 100	0·11	26	U.D. Stain, nil.
2-Methylbenzthiazole ethiodide	100 : 100	0·40	664	U.D. Stain, nil.
3-*Nitroso*-2-p-*chlorophenyl*-1-*ethylindole condensed with :*				
α-Picoline methiodide	30 : 170	0·10	12	U.D. Stain, nil.
γ-Picoline methiodide	60 : 140	0·00	112	U.D. Stain, nil.
Lepidine methiodide	60 : 140	0·44	835	Stain, trace.
2-Methylbenzthiazole ethiodide	30 : 170	0·22	380	Slightly N-U.D. Stain, slight.
3-*Nitroso*-1 : 2-*diphenylindole condensed with :*				
α-Picoline methiodide	30 : 170	0·04	21	U.D. Stain, nil.
γ-Picoline methiodide	30 : 170	0·30	58	U.D. Stain, nil.
Lepidine methiodide	100 : 100	0·36	400	U.D. Stain, trace.
2 : 3 : 3-Trimethylindolenine methiodide	100 : 100	0·03	31	U.D. Stain, nil.
2-Methylbenzthiazole ethiodide	100 : 100	0·92	391	Unv.D. Stain, nil.

Yellow is deduced from a joint consideration of two factors, namely, the fog density, and the exposure required to give a density of 0·2 above the fog level. Values less than 0·2 for the former and greater than 25 for the latter (Pinakryptol Yellow having values of 0·0 and 100 respectively) approximately define the limiting properties of dye solutions of practical value. The dyes (VIII), the 2-*p*-chlorophenyl analogue of (VI), and perhaps (VII) are examples of desensitisers of probable practical value.

"*Method of evaluation.* The dye is dissolved in water containing a minimum proportion of ethyl alcohol to give a 0·02% solution stable at 20°. The photographic plate (Ilford S.R. Panchromatic) is bathed in the dye solution in total darkness with moderate agitation for 2 minutes. After removal of the surface liquid, the emulsion is exposed under a step wedge to a standard (tungsten) light source for a suitable time (predetermined by separate test exposures) such that an approximately negative reproduction of the wedge image is obtained on subsequent development in a fresh bath of the standard developer for 4 minutes. The plate is fixed (15 minutes), washed and dried.

"The standard developer and fixing bath have the following composition and were used at 21° ± 0·5°:

"*Developer.* Metol, 1·31 g., quinol, 3·83 g., anhydrous sodium carbonate, 15·4 g., anhydrous sodium sulphite, 22·2 g., potassium bromide, 0·55 g., water to make solution to 1 l.

"*Fixing bath.* Sodium thiosulphate, 340 g., potassium metabisulphite, 39 g., water to make solution to 1 l.

"From density measurements on the dry plates, the fog density and the relative exposures required to give a density of 0·2 above the fog level are determined in the usual way.

"In the Table opposite, Column A gives the alcohol–water ratio of the dye solution, Column B the relative overall fog density, and Column C the relative exposure to give density of 0·2 above fog. In the last column, the abbreviation 'U.D.' means uniform desensitisation, 'N.-U.D.' non-uniform desensitisation, and 'Unv.D.' uneven desensitisation."

We are greatly indebted to Imperial Chemical Industries, Ltd. (Dyestuffs Division), for facilities provided in support of this work.

THE UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, August* 30*th*, 1944.]