614. 1 : 2-*Disubstituted* 3-*Aminoindoles. Part I. Preparation and Reactions.*

By Huang-Hsinmin and Frederick G. Mann.

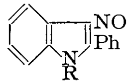
The 3-nitroso-derivatives of 2-phenyl-1-ethyl- and of 1 : 2-diphenyl-indole undergo smooth catalytic reduction to the corresponding 3-amino-derivatives, which are very readily oxidised in air but give stable crystalline acyl derivatives and also condense readily with various aldehydes. The condensation products with quinoline-2-aldehyde, when subsequently combined with methyl iodide, afford cyanine dyes identical in type with those previously prepared by condensing the 3-nitroso-indole with quinaldine methiodide.

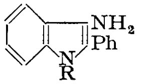
A by-product of the catalytic reduction is the corresponding azo-3-(1 : 2-disubstituted)-indole; in the 1 : 2-diphenyl series, a second form of this azo-compound can be obtained by oxidising the 3-amino-indole with nitrosodiphenylamine. *p*-Nitrosodimethylaniline reacts, however, with the 3-amino-indole to give an azoxy-derivative.

A number of the products obtained by atmospheric oxidation of the 3-amino-indoles have been isolated and investigated.

The bright green crystalline 1 : 2-disubstituted 3-nitrosoindoles of type (I), first prepared by Campbell and Cooper (*J.*, 1935, 1208) by the nitrosation of the corresponding 1 : 2-disubstituted indoles, were later used extensively by Mann and Haworth (*J.*, 1944, 670) for the preparation of a novel type of cyanine dye ; they were also prepared in number by Crowther, Mann, and Purdie (*J.*, 1943, 58) and by Brown and Mann (*J.*, 1948, 847, 858) for characterising the 1 : 2-disubstituted indoles which arose in their study of the cyclisation of phenylacylanilines. We have now investigated in detail the reduction of these 3-nitroso-indoles to the corresponding 3-amino-indoles, using for this purpose 3-nitroso-2-phenyl-1-ethylindole (I; R = Et) and 3-nitroso-1 : 2-diphenylindole (I; R = Ph). The first of these indoles had already been reduced by Mann and Haworth (*loc. cit.*) using zinc and hydrochloric acid, but only the hydrochloride of the 3-amino-indole was isolated. We find that both these nitroso-indoles in ethanolic solution undergo smooth reduction by hydrogen in the presence of a platinum catalyst, and 3-*amino*-2-*phenyl*-1-*ethylindole* (II; R = Et) and 3-*amino*-1 : 2-*diphenylindole* (II; R = Ph) are thus obtained. Other reducing agents, such as zinc and acetic acid, ammonium sulphide, and sodium dithionite (hydrosulphite), similarly produce the amines but far less satisfactorily. Both these amines can be distilled without apparent decomposition in a high vacuum, but the distillate in each case forms a gum which (in the 1 : 2-diphenyl series) later sets to a brittle glass. All attempts to crystallise these amorphous products have so far failed, partly because of the very ready atmospheric oxidation of these amines which necessitates their handling and storage in a vacuum or under nitrogen. The crystalline hydrochlorides of the amines are also readily oxidised and have to be similarly stored. The nature of the oxidation products is discussed later. The amines behave normally towards acylating agents, however, and the crystalline 3-*acetamido*-, 3-*benzamido*-, and 3-*benzenesulphonamido*-derivatives of 1-phenyl-2-ethyl- and of 1 : 2-diphenyl-indole have thus been prepared. It is noteworthy, however, that the 3-acetamido-derivatives which we have used extensively in further synthetic work (see following paper) are readily prepared in one operation by the catalytic reduction of the corresponding 3-nitroso-indoles in acetic anhydride suspension.

(I.)

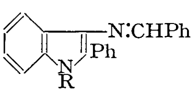




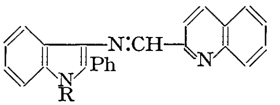
(II.)

The various classes of derivatives obtained from these 3-amino-indoles will be discussed under separate headings.

Schiff's Bases (*Azadimethin Derivatives*).—The 3-amino-indoles condense readily with many aldehydes, and, for example, the *benzylidene* derivatives (III) and the p-*dimethylamino-benzylidene* derivatives of 1-phenyl-2-ethylindole and of 1 : 2-diphenylindole are thus obtained.



(III.)



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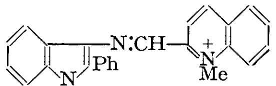
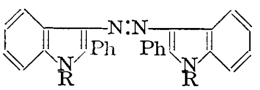


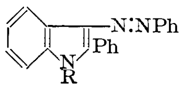
(V.)

Of greater interest, however, is the fact that quinoline-2-aldehyde undergoes a similar condensation, giving α-*azadimethin*[2-*phenyl*-1-*ethyl*-3-*indole*][2-*quinoline*] (IV; R = Et) and the 1 : 2-*diphenyl*-3-*indole* analogue (IV; R = Ph). These compounds readily form quaternary salts such as [2-phenyl-1-ethyl-3-indole][1-methyl-2-quinoline]-α-azadimethincyanine iodide (V; R = Et). These cyanine dyes are of the same type as those prepared by Mann and Haworth (*loc. cit.*) by the condensation of, *e.g.*, quinaldine methiodide with the corresponding 3-nitroso-indole in the presence of a trace of piperidine. Our new preparation thus affords an alternative, although less convenient, synthesis of this class of cyanine dye.

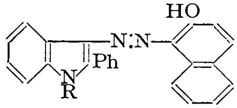
Azo-derivatives.—When 3-nitroso-2-phenyl-1-ethylindole (I; R = Et) was catalytically reduced, either in ethanol to give the 3-amino-compound, or in acetic anhydride to give the 3-acetamido-derivative, a small residue was always obtained which on purification afforded bright yellow crystals, m. p. 252°, the composition and molecular weight of which showed they were *azo*-3-(2-*phenyl*-1-*ethylindole*) (VI; R = Et). In later experiments, attempts were made to condense the 3-amino-compound with nitrosodiphenylamine, $Ph_2N\cdot NO$, but oxidation of the amine then occurred, and the same azo-derivative was isolated. The fact that this reaction was essentially caused by the nitrosoamine group and was independent of the particular aryl radicals, was proved in the 1 : 2-diphenyl series by repeating the experiment using nitrosodi-*p*-tolylamine, whereupon the azo-compound was again obtained.



(VI.)



(VII.)



(VIII.)

The catalytic reduction of 3-nitroso-1 : 2-diphenylindole (I; R = Ph) to the 3-amino-indole similarly gave a residue which on purification furnished *azo*-3-(1 : 2-*diphenylindole*) (VI; R = Ph) as yellow crystals, m. p. 185°. These will be referred to as the α-form. When, however, the 3-amino-indole was treated with either nitrosodiphenylamine or nitrosodi-*p*-tolylamine, an isomeric β-form (having the same molecular weight) was isolated as orange crystals, m. p. 336°. This β-form also occurred in another reaction, for, when the ethanolic mother-liquor from the recrystallisation of the crude 3-nitroso-1 : 2-diphenylindole was set aside for many weeks, a small deposit of the β-form collected, and when purified had m. p. 336°, alone and when mixed with that obtained by the nitrosodiphenylamine reaction. It is noteworthy that catalytic reduction of 3-nitroso-1 : 2-diphenylindole in acetic anhydride to give the 3-benzamido-derivative did not give the azo-compound as a by-product : in this respect the 1 : 2-diphenyl series differed from the analogous 2-phenyl-1-ethyl series.

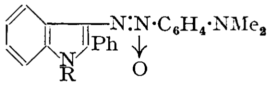
Since no method of converting either form into the other could be found, these forms represent apparently a very rare example of stable *syn*- and *anti*-azo-compounds. It will be noted that in previous examples of such geometric isomerism (Hartley, *J.*, 1938, 633; Cook, *J.*, 1938, 876; 1939, 1309, 1315), one form (presumably always the *cis*) has undergone conversion into the second (*trans*) form. In view of the remarkable nature of this isomerism, decisive evidence for the constitution of both forms was clearly desirable. They could not be synthesised unambiguously by the condensation of equimolecular quantities of the 3-nitroso- and the 3-amino-indole, because Campbell and Cooper (*loc. cit.*) and Mann and Haworth (*loc. cit.*) have shown that these 3-nitroso-indoles do not condense with primary amines. (It follows that the azo-compounds could not have thus arisen during reduction by the 3-amino-indole condensing with unreduced 3-nitroso-indole. It is probable that reduction of the latter proceeds through the 3-hydroxylamino-compound, R·NH·OH, which can then either undergo further reduction to the amino-compound or condense with itself with loss of water to give the stable azo-derivative.) The reverse process, namely reduction of the azo-compounds to give solely the 3-amino-indoles, could not be effected owing to the great stability of these azo-compounds, and it became clear that a reductive process sufficiently violet to break the –N:N– link, even if it could be found, might also reduce the indole to the indoline, and a mixture of racemates could then result. It is noteworthy that no decisive evidence for such geometric isomerism was detected with azo-3-(2-phenyl-1-ethylindole) (VI; R = Et), and it would appear that the occurrence of such isomerism is dependent on the size (or shape) of the disubstituted indole nucleus, and that the isomeric stability of the two forms may also be closely associated with their chemical stability.

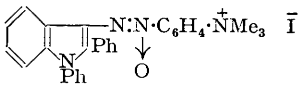
Other azo-derivatives could be obtained by standard reactions. Thus 3-*benzeneazo*-2-*phenyl*-1-*ethylindole* (VII; R = Et) could be obtained either by the condensation of nitrosobenzene with 3-amino-2-phenyl-1-ethylindole, or by that of benzenediazonium chloride with 2-phenyl-1-ethylindole. A further method was available by diazotising 3-amino-2-phenyl-1-

ethylindole and condensing the product with, for example, β-naphthol in alkaline solution: by these means the red crystalline 3-(2-*hydroxynaphthalene*-1-*azo*)-2-*phenyl*-1-*ethylindole* (VIII; R = Et) was obtained. It is noteworthy, however, that this diazotised 3-amino-indole would not condense with dimethylaniline. None of the various azo-compounds obtained by these reactions showed any indication of geometric isomerism.

Azoxy-derivatives.—3-Amino-2-phenyl-1-ethylindole reacted readily with *p*-nitrosodimethylaniline to give p-*dimethylaminobenzene*-N′-*azoxy*-3-(2-*phenyl*-1-*ethyl*)*indole* (IX; R = Et), and the corresponding *azoxy*-3-(1 : 2-*diphenylindole*) (IX; R = Ph) was similarly obtained; the latter product was further characterised as its *methiodide* (X). It is clear that this reaction with *p*-nitrosodimethylaniline, like that with nitrosodiphenylamine, involves oxidation of the 3-amino-group. Other examples are known, however, of the similar formation of azoxy-compounds: thus Ruggli and Petitjean (*Helv. Chim. Acta*, 1938, **21**, 716) have shown that aniline reacts with *p*-dinitrosobenzene to give an azoxy-derivative, and other types of compound will also give such derivatives by reaction with *p*-nitrosodimethylaniline (cf. Dalgliesh and Mann, *J.*, 1947, 559).

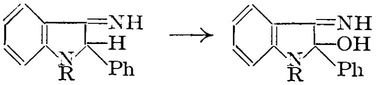
(IX.)



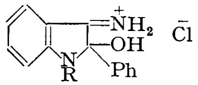


(X.)

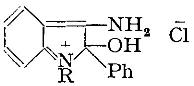
Oxidation Derivatives.—The extremely ready oxidation of the above two 3-amino-indoles undoubtedly gives rise to a number of derivatives, the complete separation and structural elucidation of which would require a considerable investigation. It appears clear, however, that these 1 : 2-disubstituted 3-aminoindoles can react in the tautomeric 3-iminoindoline form (II-A), because the 1-ethylindole (II; R = Et) in, for instance, ethereal solution is readily oxidised to a yellow compound, m. p. 132°, the composition of which indicates that it is 3-*imino*-2-*hydroxy*-2-*phenyl*-1-*ethylindoline* (XI; R = Et), and the 1-phenylindole (II; R = Ph) similarly gives the yellow 1-*phenylindoline* analogue (XI; R = Ph), m. p. 142°. It is noteworthy that these compounds give an orange-red and a red hydrochloride respectively; this marked change in colour on salt formation is not unexpected, because the cation produced from each base would exist as a resonance hybrid of the two canonical forms shown in (XII-A) and (XII-B).



(II-A.) (XI.)

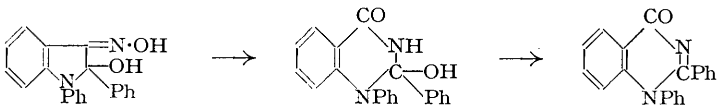


(XII-A.)



(XII-B.)

We have investigated more fully the behaviour of 3-amino-1 : 2-diphenylindole, because this compound on atmospheric oxidation produces also a well-defined colourless oxidation product, in which the oxidation has apparently proceeded one stage further, for its composition indicates that it is 3-*oximino*-2-*hydroxy*-1 : 2-*diphenylindoline* (XIII). This compound, on heating, melts at 209·5—210°, resolidifies, and melts again at 280—281°. The compound, m. p. 281°, obtained by this heat treatment can thus be readily produced; it is also a well-defined crystalline compound but has the molecular formula $C_{20}H_{14}ON_2$, *i.e.*, it has been formed by loss of water from the compound (XIII) and is isomeric with the original green 3-nitroso-indole (I; R = Ph). Further investigation showed that it could also be obtained from the 3-oximino-compound (XIII) by boiling the latter with ethanolic hydrogen chloride or with aqueous sodium hydroxide, although boiling ethanolic potassium hydroxide ruptured the heterocyclic ring with the production of *N*-phenylanthranilic acid. Furthermore the new compound of m. p. 281° readily gave a yellow *methiodide*, m. p. 260—263°.



(XIII.) (XIV.) (XV.)

The constitution of this compound remains uncertain. It is suggested however that the oximino-compound (XIII) may be highly susceptible to the Beckmann rearrangement, and under the influence of heat or the above reagents gives the unstable quinazolone derivative

(XIV), which immediately loses water to give 4-*keto*-1 : 2-*diphenyl*-1 : 4-*dihydroquinazoline* (XV). Parallel Beckmann rearrangements in indole derivatives are well known : for example, 3-oximino-2-phenylindole (XVI) when treated with ethereal phosphorus trichloride at room temperature is converted into 4-keto-2-phenyl-3 : 4-dihydroquinazoline (XVII) (Alessandri, *Atti R. Accad. Lincei*, 1913, **22**, ii, 152, 229), whilst isatin-2 oxime (XVIII) under the influence of alkali gives the diketoquinazolidine (XIX) tautomeric with 2 : 4-dihydroxyquinazoline. Compounds of type (XV) appear to be unknown, however, and their reactivity towards methyl iodide (which one would expect to be low) is necessarily also unknown.

(XVI.) (XVII.) (XVIII.) (XIX.)

We have not ignored a further possibility, namely that in the compounds (XI) and (XIII) the heterocyclic ring has opened at the N–C link, and that these compounds are consequently the monoimide and mono-oxime respectively of, for example, *o*-anilinobenzil. However, no reliable evidence for such a change in structure could be obtained.

EXPERIMENTAL.

2-Phenyl-1-ethylindole and its 3-nitroso-derivative were prepared as Crowther, Mann, and Purdie (*loc. cit.*) direct.

1 : 2-*Diphenylindole and its* 3-*Nitroso-derivative*.—The following modifications of the method of Mann and Haworth (*loc. cit.*) have improved the yields of these compounds.

A mixture of *as*-diphenylhydrazine (44 g.), acetophenone (32 g., 1·1 mols.), and acetic acid (0·5 c.c.) was heated on a water-bath for 1·5 hours. The crude yellow hydrazone thus obtained was thoroughly mixed with finely powdered zinc chloride (132 g.) and then heated with stirring in a bath at 180°. Reaction occurred when the mixture reached *ca.* 130°; the vessel was then immediately removed from the bath, and the rise in temperature checked as much as possible by vigorous stirring and gentle cooling in water. When the temperature (which should not have exceeded 200°) began to fall, the vessel was returned to the bath at 180° for 10 minutes. The black tar was then poured into 5% hydrochloric acid (150 c.c.), and the indole extracted 4 times with ether (250 c.c. × 4) and then with benzene (100 c.c.). The united dried extracts were concentrated, and the residue was first heated at 16 mm. to remove readily volatile impurities and then distilled at a lower pressure. The indole had b. p. 188—190°/0·2 mm., 196—198°/0·6 mm., and readily solidified; after crystallisation from ethanol or acetic acid it had m. p. 82·5° (21·5 g., 43% yield).

A solution of the indole (32 g.) in acetic acid (640 c.c.) was cooled and vigorously stirred while a solution of sodium nitrite (10 g., 1·2 mols.) in water (14 c.c.) was added dropwise so that the temperature was maintained at 17—19°. Green crystals of the 3-nitroso-derivative separated almost immediately; the final mixture was stirred for a further 30 minutes and filtered. The crude nitroso-compound, when washed on the filter with ether (100 c.c.) changed from yellowish-green to bluish-green : it then had m. p. 204—206° (28·8 g.). The united mother-liquor and ethereal washings were vigorously stirred while being slowly diluted with water (2 l.); a second crop of m. p. 198—200° (6·5 g.) was thus precipitated. The total yield was almost theoretical. Recrystallisation of the united crops from ethanol gave the pure 3-nitroso-indole, m. p. 206—207° (34 g., 96%). It was this ethanolic mother-liquor which when set aside for a considerable period deposited a small quantity of the azo-derivative (see p. 2909).

3-*Amino*-2-*phenyl*-1-*ethylindole* (II; R = Et).—A suspension of the finely powdered 3-nitroso-compound (I; R = Et) (15 g.) in ethanol (50 c.c.) containing reduced Adams's catalyst (from 0·1 g. of dioxide) was hydrogenated in the usual way at room temperature and just above 760 mm. pressure. Hydrogen (1900 c.c., 1·42 mols.) was absorbed during 4 hours, the green suspension being converted into a sticky yellow solution. This solution was then filtered under nitrogen, and the ethanol distilled under reduced pressure. The residue, when distilled in nitrogen at 0·9 mm., gave the 3-*amino*-compound as a golden-yellow syrup, b. p. 194—196° (Found : C, 78·8; H, 6·5; N, 11·5. $C_{16}H_{16}N_2$ requires C, 81·3; H, 6·8; N, 11·9%. Consistent values for carbon could not be obtained, partly owing to the ready oxidation in air) (8·7 g., 61% yield). Other b. p.s observed were 192°/0·8 mm. and 170°/0·1 mm. The residue in the distilling flask provided azo-3(-2-phenyl-1-ethylindole) (VI; R = Et) and is described later.

The reduction, when performed at 70° with hydrogen at 50 atmospheres pressure, gave the same product, and no reduction to the indoline was detected.

The 3-amino-compound was characterised by conversion into the following derivatives.

Hydrochloride. Dry hydrogen chloride was passed into a dry ethereal solution of the base which was maintained at 0° under nitrogen. An orange-coloured precipitate was obtained which when exposed to damp air rapidly formed a sticky dark violet mass. It was therefore rapidly recrystallised from anhydrous ethanol with exclusion of air, and the *hydrochloride* obtained as colourless crystals, m. p. 242—244° (decomp.), which rapidly became pink on exposure to air (Found : C, 69·9; H, 6·3; N, 9·95; Cl, 13·5. $C_{16}H_{16}N_2$,HCl requires C, 70·4; H, 6·3; N, 10·3; Cl, 13·0%). The ethanolic mother-liquor when boiled in air deposited a green substance. This hydrochloride in the form of a monohydrate was obtained by Mann and Howarth (*loc. cit.*) by the reduction of the 3-nitrosoindole with zinc and hydrochloric acid.

Picrate. When ethanolic solutions of the 3-amino-indole and of picric acid were mixed in a nitrogen atmosphere, the mixture immediately became red and then gradually darkened, while green crystals separated. These crystals, when recrystallised from ethanol, gave the dark green crystalline picrate, m. p. 172—174° (Found : C, 57·2; H, 4·5; N, 15·0. Calc. for $C_{16}H_{16}N_2,C_6H_3O_7N_3$: C, 56·7; H, 4·1; N, 15·0%). This picrate is presumably identical with that prepared by Castellana and d'Angelo (*Gazzetta*, 1906, **36**, ii, 60) by the reduction of 3-nitroso-2-phenyl-1-ethylindole, for which they record m. p. 173°.

3-*Acetyl derivative.* A solution of the 3-amino-indole in acetic anhydride was boiled for a few minutes, cooled, mixed with water, heated under reflux to hydrolyse the excess of anhydride, and cooled. The aqueous layer was decanted, and the yellowish-brown sticky residue stirred with acetone to induce crystallisation. The crystalline product when recrystallised from acetone gave the 3-*acetamido*-compound as colourless crystals, m. p. 180° (Found : C, 77·9; H, 6·7; N, 10·3. $C_{18}H_{18}ON_2$ requires C, 77·7; H, 6·5; N, 10·1%). This compound was also obtained when a solution of the 3-nitroso-indole (3 g.) in acetic anhydride (15 c.c.) containing Adams's catalyst (0·02 g.) was shaken with hydrogen at room temperature for 30 minutes, after which absorption of hydrogen (457 c.c., 1·7 mols.) was complete. The mixture was decomposed with water, cooled, and filtered. The solid product so obtained was boiled with acetone (100 c.c.), filtered to remove an insoluble product, and then cooled, whereupon the yellowish-orange azo-indole (VI; R = Et) crystallised (see below). The filtered mother-liquor, when concentrated and cooled, deposited the 3-acetamido-compound, which after recrystallisation from acetone had m. p. 180°, mixed and unmixed. This method of preparation is obviously superior to that involving the free amino-indole.

3-*Benzoyl derivative.* Obtained in the usual way by shaking the 3-amino-indole in suspension in aqueous sodium hydroxide with benzoyl chloride, this *derivative* after recrystallisation from ethanol formed colourless crystals, m. p. 209·5° (Found : C, 80·8; H, 6·2; N, 8·1. $C_{23}H_{20}ON_2$ requires C, 81·2; H, 5·9; N, 8·2%). When assessing the comparative value of other reducing agents for the preparation of the 3-amino-indole (see below), it was found most convenient to isolate and determine the latter as this derivative.

3-*Benzenesulphonyl derivative.* A solution of the 3-amino-indole in dry pyridine was treated with benzenesulphonyl chloride under nitrogen and then heated under reflux for 2 hours, cooled, and poured into water. The precipitated gum readily solidified and when recrystallised from ethanol gave the 3-*benzenesulphonamido*-compound as colourless crystals, m. p. 165° (Found : C, 70·1; H, 5·5; N, 7·4. $C_{22}H_{20}O_2N_2S$ requires C, 70·2; H, 5·35; N, 7·45%).

We have investigated the action of a number of reducing agents on 3-nitroso-2-phenyl-1-ethylindole, and have confirmed that it can be reduced to the 3-amino-compound by zinc and hydrochloric acid as Mann and Haworth (*loc. cit.*) claimed, and also by zinc and acetic acid and by ammonium sulphide. The yields obtained by these methods are low and (probably owing to the unstable nature of the product) are markedly affected by apparently slight changes in the experimental conditions; catalytic reduction is therefore by far the most satisfactory method.

It is noteworthy, however, that none of these methods apparently carried the reduction one stage further to the indoline, for no indication of the presence of this compound in the crude reaction mixture was obtained. This is the more surprising because 1 : 2-disubstituted indoles can be reduced to the corresponding indoline by zinc and hydrochloric acid. This fact is illustrated by the following preparation.

2-*Phenyl*-1-*ethylindoline.*—A mixture of 2-phenyl-1-ethylindole (5 g.), zinc dust (8 g.), and ethanol (100 c.c.) was stirred on a boiling water-bath while concentrated hydrochloric acid (27 c.c.) was added dropwise during 1 hour. The solution was then heated under reflux for a further 30 minutes, cooled, filtered, and evaporated under reduced pressure. The residue was thoroughly stirred with water and then repeatedly extracted with ether. The dried filtered extract, on removal of the ether, gave a yellow oil (3·3 g., 65%) and a brown tar; the oil, when decanted and distilled, gave the *indoline* as a colourless oil, b. p. 174—176°/14 mm., 155—157°/1·8 mm. (Found : C, 87·1; H, 7·8; N, 6·1. $C_{16}H_{17}N$ requires C, 86·1; H, 7·6; N, 6·3%). It gave a *picrate*, yellow crystals from ethanol, m. p. 113° (Found : C, 59·0; H, 4·6; N, 12·4. $C_{16}H_{17}N,C_6H_3O_7N_3$ requires C, 58·5; H, 4·4; N, 12·4%), and a *methiodide*, colourless needles from ethanol, m. p. 173·5—174° (Found : C, 56·4; H, 5·6; N, 3·7. $C_{17}H_{20}NI$ requires C, 55·9; H, 5·5; N, 3·8%).

3-*Amino*-1 : 2-*diphenylindole* (II; R = Ph).—An ethanolic suspension of the 3-nitroso-indole (I; R = Ph) was catalytically reduced at room temperature precisely as was the previous 1-ethyl-analogue, and distillation of the final product gave the 3-*amino-indole* as an orange syrup, b. p. 199—210°/0·003 mm., which solidified to a brittle transparent glass, m. p. 50—53° (Found : C, 83·2; H, 5·2; N, 9·6. $C_{20}H_{16}N_2$ requires C, 84·5; H, 5·7; N, 9·85%. Consistent values for carbon again could not be obtained) (yield, 67%). Other preparations gave the following b. p.s : 228°/0·015 mm. and 239—242°/0·025 mm. The undistilled residue yielded the α-form of azo-3-(1 : 2-diphenylindole) (see below). This 3-amino-indole was characterised by the preparation, as above, of the following derivatives.

The unstable *hydrochloride*, when recrystallised from ethanolic ether, gave colourless crystals, m. p. 223—225°, which became pink immediately if powdered in the open air; the unsatisfactory analysis was apparently due to this instability, which precluded effective recrystallisation (Found : C, 72·6; H, 6·3; N, 8·3. $C_{20}H_{16}N_2$,HCl requires C, 74·9; H, 5·3; N, 8·7%). When recrystallised from acetone, the crystals had m. p. 177—182° but gave inconsistent analyses.

The very soluble picrate was prepared from an ethereal solution of the amine and an acetone solution of picric acid. The yellow crystals were washed with the latter solution and then had m. p. 184—187°, but analyses indicated a product rendered impure by dissociation. The use of other solvents, and recrystallisation, gave similar impure samples.

The 3-*acetyl* derivative formed large colourless crystals, m. p. 230°, from acetone (Found : C, 80·6;

H, 5·9; N, 8·9. $C_{22}H_{18}ON_2$ requires C, 81·0; H, 5·6; N, 8·6%). Catalytic reduction of the 3-nitroso-indole in acetic anhydride, performed as for the 1-ethyl analogue, gave this compound in 87% yield.

The 3-*benzoyl* derivative formed colourless crystals, m. p. 175°, from ethanol (Found: C, 83·9; H, 5·8; N, 7·6. $C_{27}H_{20}ON_2$ requires C, 83·5; H, 5·2; N, 7·2%).

The 3-*benzenesulphonyl* derivative, after recrystallisation from ethanol and then from benzene, formed colourless crystals, m. p. 218° (Found: C, 73·8; H, 4·45; N, 6·6. $C_{26}H_{20}O_2N_2S$ requires C, 73·6; H, 4·8; N, 6·6%).

The conversion of the 3-nitro-indole into the 3-amino-indole was also carried out with zinc and hydrochloric acid, ammonium sulphide and sodium dithionite (hydrosulphite), but these were all inferior to catalytic hydrogenation. When a xylene solution of 1 : 2-diphenylindole was heated under reflux for 6 hours with sodamide, the unchanged indole was subsequently recovered in 85% yield.

Schiff's Bases (*Azadimethin Derivatives*).—(*a*) A mixture of the 3-amino-indole (II; R = Et) (1 g.) and benzaldehyde (2·4 c.c.) was heated at 190—200° for 4 hours under nitrogen. The dark brown liquid when cold readily crystallised when rubbed, particularly when acetic acid was added. The solid product when crystallised first from light petroleum (b. p. 60—80°) and then from ethanol gave 3-*benzylideneamino*-2-*phenyl*-1-*ethylindole* (III; R = Et) as pale yellow crystals, m. p. 126° (Found: C, 85·0; H, 6·1; N, 8·8. $C_{23}H_{20}N_2$ requires C, 85·2; H, 6·2; N, 8·65%).

The 1 : 2-*diphenyl* analogue (III; R = Ph), similarly prepared and recrystallised from ethanol, formed yellow crystals, m. p. 163° (Found: C, 86·8; H, 5·7; N, 7·6. $C_{27}H_{20}N_2$ requires C, 87·2; H, 5·4; N, 7·5%).

(*b*) A mixture of the 3-amino-indole (II; R = Et) (0·86 g.) and *p*-dimethylaminobenzaldehyde (0·6 g., 1·1 mols.) was similarly heated at 150—160° for 8 hours. The cold orange-red viscous product, when stirred with ethanol, gave the solid 3-p-*dimethylaminobenzylideneamino*-2-*phenyl*-1-*ethylindole* (as III; R = Et), which after crystallisation from ethanol afforded yellow needles, m. p. 164° (Found: C, 81·4; H, 7·0; N, 11·5. $C_{25}H_{25}N_3$ requires C, 81·6; H, 6·9; N, 11·4%).

The 1 : 2-*diphenyl* analogue (as III; R = Ph), after crystallisation from acetone, formed yellow crystals, m. p. 197° (Found: C, 83·7; H, 6·4; N, 10·2. $C_{29}H_{25}N_3$ requires C, 83·85; H, 6·1; N, 10·1%).

(*c*) A mixture of the 3-amino-indole (II; R = Et) (1·16 g.) and quinoline-2-aldehyde (0·78 g., 1 mol.) was heated under nitrogen at 150—160° for 2 hours. The resulting black syrup was then heated under reflux with ethanol (4 c.c.). The cold solution deposited yellow crystals, which after crystallisation from ethanol afforded α-*azadimethin*[2-*phenyl*-1-*ethyl*-3-*indole*][2-*quinoline*] (IV; R = Et) as fluorescent greenish-yellow plates, m. p. 160° (Found: C, 83·3; H, 6·0; N, 11·7. $C_{26}H_{21}N_3$ requires C, 83·2; H, 5·6; N, 11·2%).

The 1 : 2-*diphenyl* analogue (IV; R = Ph), similarly prepared, crystallised when the crude melt was heated under reflux with xylene and then cooled; crystallisation from acetone then gave bright yellow needles, m. p. 247—247·5° (Found: C, 85·4; H, 5·2; N, 10·0. $C_{30}H_{21}N_3$ requires C, 85·1; H, 5·0; N, 9·9%). In an evacuated desiccator containing sulphuric acid, the crystals developed a red surface film.

It is noteworthy that no well-defined product could be obtained from the attempted condensation of 3-amino-1 : 2-diphenylindole with *m*-hydroxybenzaldehyde, benzoquinone, or 1-methyloxindole.

Cyanine Dyes.—(a) [2-*Phenyl*-1-*ethyl*-3-*indole*][1-*methyl*-2-*quinoline*]-α-*azadimethincyanine iodide*. A mixture of the compound (IV; R = Et) and an excess of methyl iodide was heated in a sealed tube at 100° for 23 hours, during which period the original yellow solution became red and deposited a voluminous red precipitate. The latter, when recrystallised from methanol, gave the above cyanine iodide as bright red crystals, m. p. 221—222° (Found: C, 62·7; H, 4·9; N, 8·25. Calc. for $C_{27}H_{24}N_3I$: C, 62·7; H, 4·7; N, 8·1%). Mann and Haworth (*loc. cit.*) prepared this compound by their shorter method, and described it as greenish-brown crystals, m. p. 218—219°. A sample of their product had the same m. p., both alone and mixed with that now described, when the m. p.s were determined under identical conditions of heating. Their product, moreover, when freshly recrystallised from methanol, now gave bright red crystals of unchanged m. p. The significance of this change in colour is uncertain: it may be due to crystal size, to dimorphism, or to a faint trace of impurity in Mann and Haworth's original specimen.

(b) [1 : 2-*Diphenyl*-3-*indole*][1-*methyl*-2-*quinoline*)-α-*azadimethincyanine iodide* (V; R = Ph). A mixture of the compound (IV; R = Ph) and methyl iodide was heated under reflux for 76 hours. The dark crystals which had separated were filtered from the cold product and thoroughly washed with xylene. A portion of these crystals when recrystallised from methanol gave the pure *cyanine iodide* as long red needles; another portion, recrystallised from ethanol containing 10% of water, gave the pure iodide as compact dense permanganate-coloured crystals. This difference was determined entirely by the solvent, since each form could be converted into the other by crystallisation from the appropriate solvent. Each form, and a mixture of both, on heating began to soften at *ca.* 180° and to decompose at *ca.* 200° with separation of a yellow solid at 230° which ultimately melted at 242—244°, while a violet coloration appeared in the upper and cooler portion of the tube; this behaviour undoubtedly indicated that the methiodide was partly dissociating into the original azadimethin (IV; R = Ph) under the influence of heat (Found: C, 65·5; H, 4·4; N, 7·6. $C_{31}H_{24}N_3I$ requires C, 65·7; H, 4·3; N, 7·4%). The time of heating in the preparation could be reduced to 38 hours if the original mixture was diluted with nitromethane and maintained at 48—52°.

When the compound (IV; R = Ph) with an excess of pure methyl toluene-*p*-sulphonate was heated under reflux in xylene solution for 4·5 hours, the corresponding *cyanine toluene*-p-*sulphonate* separated as dark red crystals, which on recrystallisation from methanol formed violet leaflets of the *mono-methanolate*, m. p. 258—261° (Found: C, 72·75; H, 5·65; N, 6·85; S, 4·6. $C_{38}H_{31}O_3N_3S,CH_4O$ requires C, 73·0; H, 5·5; N, 6·55; S, 5·0%). A hot ethanolic solution of this salt, when treated with an excess of ethanolic sodium iodide, gave dark red crystals of the above cyanine iodide (V; R = Ph), which after recrystallisation from ethanol, behaved identically on heating (alone or mixed).

The cyanine iodide was also prepared by Mann and Haworth's method, a solution of 3-nitroso-1 : 2-diphenylindole (1 g.) and quinaldine methiodide (0·85 g., 1 mol.) in ethanol (25 c.c.) containing a trace of piperidine being heated under reflux for 6 hours. The cold solution deposited permanganate-coloured crystals which, after recrystallisation from methanol, behaved on heating similarly to the previous preparation (Found : C, 65·8; H, 4·7; N, 7·6; I, 22·4%).

Azo-derivatives.—*Azo*-3-(2-*phenyl*-1-*ethylindole*) (VI; R = Et). (i) The residue from the distillation of 3-amino-2-phenyl-1-ethylindole (II; R = Et) (p. 2906), obtained by the catalytic reduction of the 3-nitroso-indole (15 g.), when stirred with acetone (25 c.c.) deposited the above *azo*-compound (0·93 g.) in two distinct crystalline forms, large reddish-brown compact crystals (0·51 g.) and minute yellow crystals (0·42 g.), each of m. p. 184—186°. Recrystallisation of either form from benzene and then from benzene–ethanol gave yellow leaflets, m. p. 251—252° (Found : C, 82·2; H, 6·3; N, 11·8. $C_{32}H_{28}N$ requires C, 81·9; H, 6·1; N, 12·0%).

(ii) The hot acetone extract of the crude 3-acetamido-indole, obtained by reductive acetylation of the 3-nitroso-indole, on cooling deposited the above azo-compound (p. 2907). This sample when recrystallised as above had m. p. 251—252°, unchanged by admixture with the above sample.

(iii) A mixture of the 3-amino-indole (0·21 g.), nitrosodiphenylamine (0·18 g., 1 mol.) and acetic acid (2·5 c.c.) was shaken under nitrogen for 1 hour, during which the solution became red, then violet, and finally green. The product was set aside overnight, and a crop of the above crude azo-compound (0·1 g.) then collected. The filtrate was evaporated to a syrup, which solidified when rubbed with light petroleum (b. p. 40—60°). This solid on crystallisation from ethanol afforded a second crop of the azo-compound (0·15 g.). The united crops when recrystallised from ethanol gave the pure azo-compound as yellowish-orange leaflets, m. p. 251—252°, unchanged by admixture with that obtained as in (i) (Found : C, 82·2; H, 5·9; N, 12·2%).

Azo-3-(1 : 2-*diphenylindole*) (VI; R = Ph).—(i) *a-Form.* The residue from the distillation of 3-amino-1 : 2-diphenylindole (II; R = Ph) (p. 2907) was heated under reflux with acetone (15 c.c.). The cold mixture deposited the above azo-compound as yellow crystals (4·4 g., 31%), m. p. 181—182°, increased to 185° by further recrystallisation from acetone [Found : C, 84·8; H, 5·3; N, 10·0%; *M* (ebullioscopic in 1·7% benzene solution) 560, (in 2·9% solution) 590, (in 2·1% *p*-xylene solution) 580. $C_{40}H_{28}N_4$ requires C, 85·0; H, 5·0; N, 9·9%; *M*, 565].

(ii) *β-Form* (*a*). When a mixture of the 3-amino-indole (0·4 g.), nitrosodiphenylamine (0·28 g.), and acetic acid (3 c.c.) was prepared under nitrogen, the nitrosoamine dissolved readily, but gentle warming was necessary to dissolve the indole. The solution was shaken for 2 hours, whereupon it became deep-green, and was then set aside overnight. The yellow crystalline deposit of the azo-compound (0·1 g., 26%) was collected, washed with acetic acid, and recrystallised from benzene (5 c.c.). Two forms of crystal separated, pale yellow needles and compact yellow crystals, each of m. p. 318—322°. Recrystallisation of the mixture from benzene gave a uniform orange needles, m. p. 336° (Found : C, 85·4; H, 5·0; N, 9·8%; *M* (ebullioscopic in 0·58% benzene solution) 600, (in 0·86% *p*-xylene solution) 510. The low solubility in these boiling solvents prevented accurate molecular-weight determinations). This preparation was repeated many times : the highest yield (31%) of the azo-compound was obtained when the mixture was set aside for 46 hours.

(*b*) Repetition of experiment (*a*) using nitrosodi-*p*-tolylamine (1 mol.) gave a more rapid deposition of the azo-compound in 42% yield; recrystallisation from xylene or acetic acid gave orange needles, m. p. 336° (mixed and unmixed with previous sample) (Found : N, 9·7%).

(*c*) The ethanolic mother-liquor from the crystallisation of crude 3-nitroso-1 : 2-diphenylindole (I; R = Ph), when set aside for several weeks, deposited a small quantity of the orange *β*-form of the azo-compound. (It was undoubtedly this compound which was present in the two crops of the crude nitroso-indole and whose removal by ether-washing changed the colour of these crops : direct evaporation of the ether washings always afforded the azo-compound.) This material, when recrystallised from benzene, gave orange crystals containing 1 mole of benzene of crystallisation (Found : C, 85·9; H, 5·3; N, 9·1. $C_{40}H_{28}N_4,C_6H_6$ requires C, 86·0; H, 5·3; N, 8·7%); heating at 150°/0·4 mm. readily gave the solvent-free compound (Found : C, 85·1; H, 5·1; N, 10·1%). These crystals, both before and after removal of the benzene, had m. p. 336°, mixed and unmixed with sample obtained in (*a*).

Attempts to synthesise either of these forms by the condensation of the 3-amino-indole with the 3-nitroso-indole, or by the coupling of the diazotised 3-amino-indole with 1 : 2-diphenylindole failed.

Properties of the a- and β-forms of the azo-compound (VI; R = Ph). Both forms had a low solubility in the usual boiling organic solvents, but that of the *a*-form was uniformly slightly higher than that of the *β*-form. An approximate determination showed that 0·1 g. of the *β*-form would dissolve in 100 c.c. of glacial acetic acid at 18°, and 0·15 g. at the b. p. of the solvent. Prolonged boiling of each form in acetic acid, acetone, ethanol, or xylene gave the unchanged material on cooling. No indication of interconversion was detected when solutions of each form in xylene were exposed to ultra-violet light for 142 hours. Each form could be sublimed unchanged when suitably heated at 0·1 mm. pressure.

The *a*-form was unaffected by attempted catalytic reduction in ethanol or in acetic anhydride, and by the action of sodium dithionite (hydrosulphite) in aqueous ethanol or in dioxan. Stannous chloride in hydrochloric acid, or zinc and hydrochloric acid in dioxan, gave only indefinite products which could not be purified. Zinc and hydrochloric acid in aqueous ethanol did, however, give a very small yield of the 3-amino-indole, identified as the 3-benzamido-indole, m. p. 168—172° (alone and mixed).

3-*Benzeneazo*-2-*phenyl*-1-*ethylindole* (VII; R = Et).—(*a*) A solution of equimolecular quantities of the 3-amino-indole (II; R = Et) and nitrosobenzene in acetic acid was shaken under nitrogen for 1 hour and then set aside overnight. The reddish-brown crystals which had separated from the green solution, when collected and recrystallised from ethanol, gave orange crystals of the azo-compound, m. p. 140°, unchanged by admixture with the following specimen.

(*b*) A solution of pure aniline (0·47 c.c.) in concentrated hydrochloric acid (1·5 c.c.) diluted with water (10 c.c.) was diazotised with a solution of sodium nitrite (0·35 g.) in water (3 c.c.) and then mixed with a solution of hydrated sodium acetate (2 g.) in water (5 c.c.). This mixture was then added dropwise to a solution of 2-phenyl-1-ethylindole (1·1 g.) in 90% ethanol (170 c.c.) at 0—5° over 1 hour. Orange crystals of the above *azo*-compound (74% yield) were thus obtained and when recrystallised from ethanol had m. p. 140° (Found : C, 81·1; H, 5·75; N, 13·5. $C_{22}H_{19}N_3$ requires C, 81·2; H, 5·9; N, 12·9%).

No similar compound could be obtained either by condensing the 3-amino-indole with *p*-nitrosodimethylaniline or by coupling the diazotised 3-amino-indole with *p*-dimethylaniline.

3-*Benzeneazo*-1 : 2-*diphenylindole* (VII; R = Ph).—This azo-compound was similarly prepared by the condensation of the 3-amino-indole with nitrosobenzene in acetic acid solution. It separated from light petroleum (b. p. 100—120°) in large orange-red crystals, m. p. 197·5—199°, and from ethanol–chloroform in long orange needles, m. p. 198—199° (Found : C, 83·2; H, 5·3; N, 11·4. $C_{26}H_{19}N_3$ requires C, 83·6; H, 5·1; N, 11·3%).

3-(2-*Hydroxynaphthalene*-1-*azo*)-2-*phenyl*-1-*ethylindole* (VIII; R = Et). The freshly distilled 3-amino-indole (0·52 g.) was dissolved in warm 5% hydrochloric acid (10 c.c.) under nitrogen. When the mixture was cooled to 0°, a dark green gum separated. A cold solution of sodium nitrite (0·16 g.) in water (2 c.c.) was then added dropwise with shaking, and the resulting mixture filtered directly into an alkaline solution of an excess of β-naphthol. The precipitated azo-compound (1·7 g.) when recrystallised from ethanol gave long deep-red needles, m. p. 183° (Found : C, 79·2; H, 5·4; N, 10·9. $C_{26}H_{21}ON_3$ requires C, 79·8; H, 5·4; N, 10·7%).

The analogous *azo*-3-(1 : 2-*diphenylindole*) (VIII; R = Ph), similarly prepared and recrystallised, gave deep-red crystals, m. p. 241° (Found : C, 81·4; H, 5·2; N, 9·9. $C_{30}H_{21}ON_3$ requires C, 82·0; H, 4·8; N, 9·6%).

Azoxy-compounds.—p-*Dimethylaminobenzene*-N′-*azoxy*-3-(*phenyl*-1-*ethylindole*) (IX; R = Et). *p*-Nitrosodimethylaniline (0·45 g.) was added to a solution of the 3-amino-indole (II; R = Et) (0·71 g., 1 mol.) in acetic acid (7 c.c.) under nitrogen, and the mixture shaken for 1 hour and set aside overnight. The yellow solid product, when collected from the dark green mother-liquor, washed with acetic acid and ethanol, and then recrystallised from ethanol gave the *azoxy*-compound as large orange-coloured needles, m. p. 154° (Found : C, 75·2, 75·0; H, 6·4, 6·1; N, 15·1, 15·0. $C_{24}H_{24}ON_4$ requires C, 75·1; H, 6·3; N, 14·6%).

The analogous N′-*azoxy*-3-(1 : 2-*diphenylindole*) (IX; R = Ph), similarly prepared, formed yellow crystals, m. p. 239° (Found : C, 77·6; H, 6·05; N, 12·9. $C_{28}H_{24}ON_4$ requires C, 77·7; H, 5·6; N, 12·9%). A solution of this compound in methyl iodide when set aside at room temperature deposited the *methiodide* (X) as yellow crystals, m. p. 210—211°, unchanged in m. p. by recrystallisation from methanol from which however it separated as a *monomethanolate* (Found : C, 59·8; H, 5·0; N, 9·4. $C_{29}H_{27}ON_4I,CH_4O$ requires C, 59·4; H, 5·15; N, 9·2%).

Oxidation Products.—(1) *Imino-derivatives.* (*a*) 3-*Imino*-2-*hydroxy*-2-*phenyl*-1-*ethylindoline* (XI; R = Et). A solution of the pure freshly distilled 3-amino-indole (II; R = Et) in ether was exposed to the air with occasional stirring. The solution became green, and yellow crystals of the above 3-*imino*-compound separated; these, when collected and twice recrystallised from ether, had m. p. 132° (Found : C, 76·6; H, 6·8; N, 11·6. $C_{16}H_{16}ON_2$ requires C, 76·2; H, 6·4; N, 11·1%).

This oxidation proceeds so readily in ethereal solution that this solvent cannot be effectively used for extraction of the 3-amino-indole. For example, a solution of the hydrochloride (3 g.) of the 3-amino-indole was dissolved in ice-water, made alkaline with aqueous sodium hydroxide, and immediately extracted with ether. The solution was dried (Na_2SO_4), filtered, evaporated to *ca.* 3 c.c., and cooled. The yellow 3-imino-compound (XI; R = Et) (0·7 g.) readily crystallised from the green ethereal solution and when recrystallised as above had m. p. 131·5—132° (mixed and unmixed).

When dry hydrogen chloride was passed into a chilled ethereal solution of the 3-imino-compound, the orange-red *hydrochloride* (XII-A—B; R = Et) separated, and when recrystallised from ethanol–ether had m. p. 160° (Found : C, 66·7; H, 6·0; N, 9·5. $C_{16}H_{16}ON_2,HCl$ requires C, 66·8; H, 5·9; N, 9·7%).

(*b*) 3-*Imino*-2-*hydroxy*-1 : 2-*diphenylindole* (XI; R = Ph). An ethereal solution of the 3-amino-indole (II; R = Ph) when exposed to air at room temperature with stirring also became green, and deposited yellow crystals of the 3-*imino*-compound (XI; R = Ph), m. p. 142—142·5° after 3 recrystallisations from light petroleum (b. p. 100—120°) (Found : C, 80·4; H, 5·8; N, 9·6. $C_{20}H_{16}ON_2$ requires C, 80·0; H, 5·4; N, 9·3%). This compound also arose in other oxidations (see below), but the above conditions ensured freedom from the white 3-oximino-product.

The hydrochloride (XII-A—B; R = Ph), prepared similarly to that above, separated as a red precipitate which after crystallisation from ethanol–ether formed a *monohydrate*, m. p. 139—140° (Found : C, 67·8; H, 5·5; N, 8·1. $C_{20}H_{16}ON_2,HCl,H_2O$ requires C, 67·7; H, 5·4; N, 7·9%).

(2) 3-*Oximino*-2-*hydroxy*-1 : 2-*diphenylindole* (XIII). This compound could be obtained under various conditions : it is probable that a varying mixture of the 3-imino- and the 3-oximino-compounds was always obtained, and the product isolated depended on the method employed. (*a*) A solution of the freshly distilled 3-amino-indole (0·8 g.) in acetone (16 c.c.) was heated under reflux for 4 hours. The yellow solution slowly became green. It was then considerably concentrated by evaporation, and cooled, whereupon white crystals of the 3-*oximino*-compound (XIII) separated; these when recrystallised from acetone had m. p. 209·5—210°, resolidifying at a higher temperature and then melting again at 280—281° [Found : C, 76·1; H, 5·3; N, 8·8%; *M*, (ebullioscopic in 0·72% acetone solution) 340, (in 0·725% ethanol solution) 280. Low solubility precluded accurate results. $C_{20}H_{16}O_2N_2$ requires C, 75·9; H, 5·1; N, 8·9%; *M*, 316]. When this preparation was repeated using diethyl ketone as a solvent, the same product in smaller yield was obtained. This compound is less soluble in most solvents than the yellow 3-imino-compound, and the latter is therefore difficult to purify if heavily contaminated by the former.

(*b*) A solution of the 3-amino-indole (1·16 g.) in moist ether (30 c.c.) was heated under reflux for 24 hours, during which a fine stream of air was sucked by means of a capillary through the solution, more ether being occasionally added to maintain the volume. Yellow crystals began to separate from the deep-green solution after 5 hours. The crystals collected from the cold product were a mixture of the 3-imino- and the 3-oximino-compounds. Extraction with boiling light petroleum (b. p. 100—120°) left a residue of the 3-oximino-compound which after 2 recrystallisations from ethanol had m. p. as above (Found : C, 75·6; H, 5·3; N, 8·8%). The light petroleum extract gave the yellow 3-imino-compound, which, purified as above, had m. p. 142° (Found : N, 9·2%). A similar experiment in benzene solution also gave these two products.

Conversion of the 3-*Oximino-compound* (XIII) *into the Compound* $C_{20}H_{14}ON_2$.—(*a*) The pure oximino-compound was heated in a metal-bath at 250—290° for 10 minutes. It rapidly solidified on cooling, and after recrystallisation from acetone gave colourless crystals, m. p. 280—281° [Found : C, 80·5; H, 5·1; N, 9·2%; *M*, (ebullioscopic in 0·53% acetone solution) 280, (in 1·33% solution) 310, (in 1·10% acetonitrile solution) 250. $C_{20}H_{14}ON_2$ requires C, 80·5; H, 4·7; N, 9·4%; *M*, 298].

(*b*) When a solution of the oximino-compound in ethanolic hydrogen chloride was heated under reflux for 4 hours, cooled, poured into water, and neutralised, the same compound was isolated, with m. p. 281° after recrystallisation.

(*c*) When a suspension of the oximino-compound in 15% aqueous sodium hydroxide was similarly treated, the same compound, m. p. 280—281°, was ultimately obtained.

(*d*) When a solution of the oximino-compound in ethanolic potassium hydroxide was heated under reflux for 5 hours, cooled, poured into water, and acidified, *N*-phenylanthranilic acid was precipitated; after recrystallisation this had m. p. 180—182°, alone and when mixed with an authentic specimen.

The compound $C_{20}H_{14}ON_2$, *i.e.*, the presumed *quinazolone* (XV), can be recrystallised from methanol, ethanol and acetone; it is slightly soluble in dilute hydrochloric or sulphuric acid, forming pale yellow solutions, from which it is reprecipitated unchanged on neutralisation. A solution in cold methyl iodide when set aside became steadily more yellow : one minute's warming under reflux caused the solution to become turbid. The pale yellow crystals (m. p. 255—259°) of the *methiodide* which separated, when recrystallised from methanol, were unchanged in appearance, but when recrystallised from ethanol formed orange crystals of the *monoethanolate*, which after heating at 60°/0·4 mm. for 6 hours had m. p. 260—263° after softening at 255° (Found : C, 56·6, 56·6; H, 5·1, 4·8; N, 6·0, 6·1. $C_{21}H_{17}ON_2I,C_2H_6O$ requires C, 56·8; H, 4·8; N, 5·8%).

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