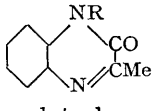
104. *Quinoxaline Cyanines. Part II.*

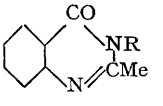
By A. H. Cook and C. A. Perry.

3-Keto-2-methyl-3 : 4-dihydroquinoxaline and its 4-*N*-methyl and -phenyl compounds give quaternary salts by addition to the basic nitrogen atom in the 1-position. In these salts the 2-methyl group is reactive and has been condensed with a variety of formic acid derivatives and aldehydes or equivalent compounds to give symmetrical and unsymmetrical oxygenated cyanines.

Except for diminished solubility these dyes resemble those derived from true quinoxalines, particularly in their deep blue colour.

Earlier workers have prepared cyanines from a variety of heterocyclic compounds containing reactive methyl groups. The cyanines now described differ, however, from previous examples in that the parent compounds contain an oxygenated ring system of type (I).

(I.) 

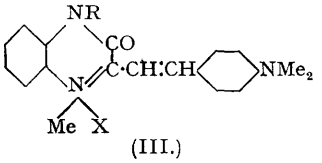
 (II.)

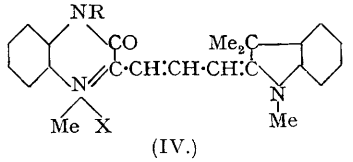
The closest previous approach to dyes of this class is the attempt of Bogert and Clark (*J. Amer. Chem. Soc.*, **1924, 46, 1294**) to utilise the quinazolone ring system (II) as the basis of cyanine dyes. These workers obtained coloured condensation products, but no true cyanines, from the methiodide of (II, R = H) and dimethylaminobenzaldehyde. The dyes now described are derived from dihydroketoquinoxalines and thus bear the same relation to those described in Part I (J., **1942**, 710) as Bogert and Clark's suggested compounds would bear to the quinazoline cyanines of Heilbron and his co-workers (J., 1932, 251). Incidentally preliminary experiments showed that the quaternary salts of (II, R = H) give brilliant colours with 1 : 3 : 3-trimethyl-2-methyleneindoline-ω-aldehyde, so the quinazolone cyanines can probably be obtained with the aid of more recent intermediates.

(I, R = H) is available in almost theoretical yield from *o*-phenylenediamine and cold aqueous pyruvic acid (Hinsberg, *Annalen*, 1896, **292**, 245). The *N*-methyl compound (I, R = Me) has been obtained by methylation with diazomethane (Ohle, Gross, and Wolter, *Ber.*, 1937, **70**, 2148); in our experience it is obtainable more conveniently by methylating the parent compound with methyl sulphate in alkaline solution. *N*-Ethylation was less satisfactory and *N*-benzylation could not be effected under moderate conditions. Unlike true quinoxalines (I) contains two dissimilar nitrogen atoms; one bears an acidic hydrogen atom and the other permits the formation of quaternary salts. When (I, R = H) was heated with methyl iodide at 100°, formation of methiodide was too slow to be useful; moreover, on prolonged heating, the crude product reacted with diphenylformamidine to give a dye under conditions which were successful with (I, R = Me) but not with the unmethylated compound quaternised in other ways, so *N*-methylation was also taking place. The *N*-methyl compound gave a well-defined ***monomethiodide*** and a similar quaternary salt was prepared from (I, R = Ph). Pure methiodides were, however, unnecessary for subsequent condensations; these were

successfully carried out by converting the parent bases into metho- or etho-sulphates, which were used without further purification. It was concluded that no appreciable *N*-alkylation of (I, R = H) occurred under the conditions employed, for it was shown that the products did not show the same behaviour as salts from *N*-substituted derivatives of (I, R = H).

In these quaternary salts the 2-methyl group is reactive, as it is in quinaldine quaternary salts and similar compounds. The crude methosulphate (I, R = H) condensed at once in a mixture of pyridine and acetic anhydride with *p*-dimethylaminobenzaldehyde or with 1 : 3 : 3-trimethyl-2-methyleneindoline-ω-aldehyde to give the dyes (III) and (IV) (R = H). Both the methosulphate and the ethosulphate of (I, R = H) condensed


(III.)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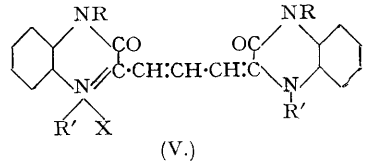
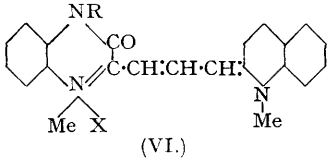

(V.)

rapidly with diphenylformamidine in the same medium to give the symmetrical compounds (V; R = H, R′ = Me or Et).

To extend the series to further unsymmetrical cyanines it was decided to utilise anilinovinyl derivatives of the second heterocyclic nucleus. Attempts to prepare anilinovinyl derivatives from quaternary salts of the dihydroquinoxalones (I; R = H, Me, or Ph) were fruitless, as were also attempts to obtain 2-ω-methylene aldehydes from the same quaternary salts, phosphorus oxychloride, and methylformanilide; approaches through this type of intermediate were therefore abandoned.

When anilinovinyl compounds such as those derived from quaternary salts of quinaldine, 2-methylbenzoxazole, or 2-methylbenzthiazole and crude dihydroquinoxalone quaternary salts were used, difficulties similar to those encountered in Part I were experienced. However, on boiling the appropriate reactants with excess of anhydrous sodium acetate in acetic anhydride, relatively good yields of the dyes (VI—VIII; R = H) were obtained :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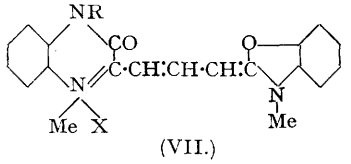
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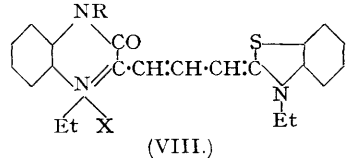
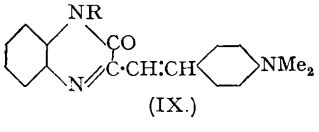
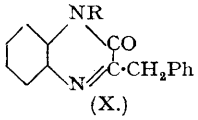

(VIII.)

Turning to (I, R = Me), both its pure methiodide and crude metho- and etho-sulphate preparations condensed very readily with *p*-dimethylaminobenzaldehyde or with 1 : 3 : 3-trimethyl-2-methyleneindoline-ω-aldehyde to give *N*-methyl analogues of (III) and (IV). On prolonged heating in acetic anhydride (less satisfactorily in absence of solvent but with the aid of zinc chloride) (I, R = Me) condensed with *p*-dimethylaminobenzaldehyde to the brick-red cyanine base (IX, R = Me). This combined at once with methyl sulphate in neutral solvents to give an intensely coloured solution spectroscopically identical with the cyanine prepared directly from the methosulphate. It gave also intensely coloured solutions with mineral acids (cf. Hamer, J., 1940, 799). A base (IX, R = Ph) showing similar behaviour was obtained from the phenyl analogue. Though it was later found that quaternary salts of (I, R = Me) condense surprisingly well with diphenylformamidine to give the *N*-methyl analogue of (V), the condensation could not be satisfactorily effected under the ordinary conditions nor was the preparation of the symmetrical dye successful when ethyl orthoformate or sodium formate was used in the usual media. The *N*-methyl analogue of (V) was, however, obtained remarkably cleanly by boiling the methosulphate of (I, R = Me) in alcoholic solution with ethyl orthoformate, preferably in presence of a little concentrated sulphuric acid. The yields were maximal after only 5 minutes' boiling. Some colour was produced in absence of quaternising agent, but the yield of dye under these conditions was very small. When the quaternary salts of (I, R = Me) were heated with 2-anilinovinyl- or 2-methylanilinovinyl-benzthiazole meth- or eth-iodide in acetic anhydride containing excess of anhydrous sodium acetate, the *N*-methyl analogue of (VIII) was obtained; the formation of colours, probably due to (VI) and VII (R = Me), was also observed.


(IX.)

(I, R = Ph) was quaternised with methyl or ethyl sulphate, and the crude salts condensed with other intermediates as in the case of the *N*-methyl compound. In this way *N*-phenyl analogues of the dyes (III—VIII) were prepared, usually in excellent yield.

2-*Keto*-3-*benzyl*-1 : 2-*dihydroquinoxaline* (X, R = H) was obtained from phenylpyruvic acid and *o*-phenylenediamine. Methylation with methyl sulphate in alkaline solution afforded (X, R = Me); this constitution rather than an *O*-methyl structure is probable from the similar reaction described earlier. Lastly, condensations of phenylpyruvic acid with *o*-aminodiphenylamine gave (X, R = Ph). These quinoxalines gave colours after quaternisation and condensation with *p*-dimethylaminobenzaldehyde or 1 : 3 : 3-trimethyl-2-methyleneindolinealdehyde. The dyes were, however, less stable than those with an unsubstituted polymethin chain and they were not closely examined.


(X.)

Some attempts were made to condense suitable quinoxaline quaternary salts with glutacondialdehyde dianil. Intensely coloured solutions were invariably obtained, but the instability of the dyes, presumably quinoxaline tricarbocyanines, defeated attempts to isolate them.

All the dyes described here bear a general resemblance to the true quinoxaline cyanines of Part I. The colours tend to fade in dilute solution and are reversibly discharged by alkali. The dyes were uniformly less soluble than their non-oxygenated analogues. More remarkable, however, is the fact that in most of them the marked bathochromic influence of the quinoxaline system can be traced as it can in the non-oxygenated compounds. Thus solutions are generally blue or blue-green, showing strong absorption in the red region of the spectrum.

Experimental.

[2-(3-*Hydroxy*-1-*methylquinoxaline*)][(4-*dimethylaminophenyl*)]*dimethincyanine Iodide* (III; R = H, X = I).—3-Hydroxy-2-methylquinoxaline (1 g.) was heated at 140° with methyl sulphate (0·6 c.c.) for 5—10 minutes, cooled, and the excess of methyl sulphate removed by washing with ether. The residue was treated with *p*-dimethylaminobenzaldehyde (1 g.) and acetic anhydride (10 c.c.), and the whole boiled for 15 minutes. The green solution was treated with water (50 c.c.) and excess of potassium iodide. The *iodide* of the dye was collected after some hours, washed with much water, and extracted with ether. The residue (1·45 g.) crystallised from alcohol and a little water in small feathery needles, m. p. 225—227° (Found: N, 9·5. $C_{19}H_{20}ON_3I$ requires N, 9·4%). Light absorption (alcohol): max., 6070 A.

[2-(3-*Keto*-1-*methyl*-3 : 4-*dihydroquinoxaline*)][2-(1 : 3 : 3-*trimethylindoline*)]*trimethincyanine Iodide* (IV; R = H, X = I).—The ketodihydroquinoxaline (1 g.) was quaternised with methyl sulphate (0·6 c.c.) at 140° for 15 minutes, and the product treated with trimethylmethyleneindoline-ω-aldehyde (1·25 g.) in acetic anhydride (8 c.c.) and pyridine (5 c.c.). After 2 hours at room temperature water (20 c.c.) and potassium iodide were added; the *dye* was washed with ether and crystallised from 50% alcohol. The yield was poor (Found: I, 25·8. $C_{23}H_{24}ON_3I$ requires I, 26·2%). Light absorption (alcohol): max., 6290, 5860, 5460 A.; II, III > I.

[*Bis*-2-(3-*hydroxy*-1-*methylquinoxaline*)]*trimethincyanine Acetate* (V; R = H, R′ = Me, X = O·CO·CH_3).—3-Hydroxy-2-methylquinoxaline (2 g.) was quaternised as in earlier experiments. The crude methosulphate was treated with acetic anhydride (10 c.c.), diphenylformamidine (1·25 g.), and lastly with pyridine (10 c.c.); heat was evolved. The solution was allowed to cool slowly; on dilution with water the dye was precipitated as a green deposit (2 g.). It was the *acetate* and crystallised from acetic acid in well-defined needles, m. p. 280° (decomp.) (Found: N, 13·4. $C_{23}H_{22}O_4N_4$ requires N, 13·4%). Light absorption (alcohol): max., 6390, 5880 A.; I > II.

[2-(3-*Keto*-1-*methyl*-3 : 4-*dihydroquinoxaline*)][2-(1-*methylquinoline*)]*trimethincyanine Iodide* (VI; R = H, X = I).—3-Hydroxy-2-methylquinoxaline (5 g.) was quaternised as usual with methyl sulphate (3·4 c.c.) and then boiled with 2-anilinovinylquinoline methiodide (6 g.), anhydrous sodium acetate (12 g.), and acetic anhydride (25 c.c.) for 15 minutes. The solution was decomposed with water, and the practically insoluble *iodide* (9 g.) crystallised from acetic acid, in which it gave a violet solution; m. p. 246° (Found: N, 8·8. $C_{22}H_{20}ON_3I$ requires N, 8·9%). Light absorption (alcohol): max., 5930, 5520 A.; I > II.

[2-(3-*Hydroxy*-1-*methylquinoxaline*)][2-(1-*methylbenzoxazole*)]*trimethincyanine Iodide* (VII; R = H, X = I).—2-Methylbenzoxazole methiodide (2 g.), diphenylformamidine (1·45 g.), and acetic anhydride (10 c.c.) were boiled for 20 minutes, and the solution then added with anhydrous sodium acetate (3 g.) to 3-hydroxy-2-methylquinoxaline (1·2 g.) quaternised in the usual manner with methyl sulphate (2 c.c.). The whole was boiled for 10 minutes, and the deep red dye (1·7 g.) precipitated with water. The *iodide*, crystallised from acetic acid, had m. p. 244° (Found: N, 9·1. $C_{20}H_{18}O_2N_3I$ requires N, 9·1%). Light absorption (alcohol): max., 6350, 5560, 5220 A.; II, III > I.

[2-(3-*Hydroxy*-1-*ethylquinoxaline*)][2-(1-*ethylbenzthiazole*)]*trimethincyanine Iodide* (VIII; R = H, X = I).—2-Methylbenzthiazole ethiodide (2 g.) was boiled for 20 minutes with acetic anhydride (10 c.c.) and diphenylformamidine (1·25 g.). To the solution were added 3-hydroxy-2-methylquinoxaline (1·2 g.), previously quaternised with ethyl sulphate (2 c.c.) in the usual manner, acetic anhydride (5 c.c.), and anhydrous sodium acetate (5 g.) and the whole was boiled for 10 minutes. The *iodide* (3·1 g.) was centrifuged after precipitation with water and potassium iodide. It separated from alcohol, in which it gave a magenta solution, as a powder, m. p. 260°. The recovery on crystallisation was poor (Found: I, 24·5. $C_{22}H_{22}ON_3IS$ requires I, 24·7%). Light absorption (alcohol): max., 5940, 5550 A.; II > I.

2-*Keto*-1 : 3-*dimethyl*-1 : 2-*dihydroquinoxaline* (I, R = Me).—3-Hydroxy-2-methylquinoxaline (50 g.), dissolved in 5% aqueous potassium hydroxide (600 c.c.), was treated with methyl sulphate (32 c.c.) with shaking in the cold. The clear solution on standing deposited the *N*-methyl compound (50 g.) in the pure state, identical with the product obtained by using diazomethane (Ohle, Gross, and Wolter, *loc. cit.*) or *via* *N*-methyl-*o*-phenylenediamine and pyruvic acid (Kehrmann and Messinger, *Ber.*, 1892, **25**, 1627). It was distilled at atm. pressure, b. p. 306°. The *methiodide* was obtained by heating the quinoxaline (2 g.) with methyl iodide (10 c.c.) at 100° for 48 hours. The crystalline mass was extracted thoroughly with ether and the residual, pale brown crystals were recrystallised from alcohol (charcoal); the methiodide separated in needles, m. p. 178° (decomp.) (Found: I, 39·9. $C_{11}H_{13}ON_2I$ requires I, 40·3%).

[2-(3-*Keto*-1 : 4-*dimethyldihydroquinoxaline*)][(4-*dimethylaminophenyl*)]*dimethincyanine Sulphate* (III; R = Me, X = SO_4).—2-Keto-1 : 3-dimethyl-1 : 2-dihydroquinoxaline (1 g.) was quaternised with methyl sulphate at 180° for 4 minutes, and *p*-dimethylaminobenzaldehyde (0·8 g.) in acetic anhydride (4 c.c.) added to the cooled product, followed by pyridine (1 c.c.). The reaction mixture soon became semi-solid and after a few minutes the dye was collected and washed with ether (2 g.). The *methosulphate* crystallised in green needles from methyl alcohol (Found: N, 9·8. $C_{21}H_{25}O_5N_3S$ requires N, 9·7%). Light absorption (alcohol): max., 6350, 6270 A.; II > I.

The cyanine *base* (IX, R = Me) was obtained by refluxing 2-keto-1 : 3-dimethyl-1 : 2-dihydroquinoxaline (1 g.) with *p*-dimethylaminobenzaldehyde (0·85 g.) in acetic anhydride (16 c.c.) for 8 hours. After cooling, the mixture was decomposed with water and basified. The light brown base (1·5 g.) crystallised from alcohol in brick-red needles, m. p. 186° (Found: N, 13·4. $C_{19}H_{19}ON_3$ requires N, 13·8%).

[2-(3-*Keto*-1 : 4-*dimethyldihydroquinoxaline*)][2-(1 : 3 : 3-*trimethylindoline*)]*trimethincyanine Chloride* (IV; R = Me, X = Cl).—The quinoxaline (1 g.) was heated at 180° for 50 minutes with methyl sulphate (2 c.c.), the mixture cooled, and acetic anhydride (4 c.c.) added, followed by 1 : 3 : 3-trimethyl-2-methyleneindoline-ω-aldehyde (1·2 g.) in pyridine (2 c.c.). The mixture was heated just to boiling and allowed to cool overnight. Water (250 c.c.) and sodium chloride were added, and the whole warmed on the steam for some hours. The *chloride* (1·1 g.) separated on cooling. After recrystallising from dilute acetic acid, it had m. p. 135° (Found: N, 10·0; Cl, 8·5. $C_{24}H_{26}ON_3Cl$ requires N, 10·3; Cl, 8·7%). Light absorption (alcohol): max., 6350, 5920, 5500 A.; II, III > I.

[2-*Bis*-(3-*keto*-1 : 4-*dimethyldihydroquinoxaline*)]*trimethincyanine Sulphate* (V; R = R′ = Me, X = SO_4).—(*a*) 2 Keto-1 : 3-dimethyl-1 : 2-dihydroquinoxaline (5 g.) was quaternised with methyl sulphate at 180° for 4 minutes, and the product boiled with methyl alcohol (20 c.c.), ethyl orthoformate (6 c.c.), and concentrated sulphuric acid (2 drops) for 5 minutes. The *methosulphate* (1·5 g.) was precipitated with water and crystallised from methyl alcohol containing a little sulphuric

acid; m. p. 227° (Found: N, 11·1. $C_{24}H_{26}O_6N_4S$ requires N, 11·2%). Light absorption (alcohol): max., 6520, 5980 A.; I > II. (*b*) The quinoxaline (17·4 g.) was quaternised with methyl sulphate (12·6 g.), and acetic anhydride (54 c.c.) added to the crude product, followed by diphenylformamidine (9·8 g.) and pyridine (10 c.c.), with cooling. When the reaction had subsided, the product was diluted with ether and the dye (12·8 g.) collected. It formed a lustrous green powder, from which a little tarry material could be extracted with warm benzene. On crystallisation from methanol a product identical with that prepared previously was obtained.

[2-(3-*Keto*-4-*methyl*-1-*ethyldihydroquinoxaline*)][2-(1-*ethylbenzthiazole*)]*trimethincyanine Iodide*.—2-Keto-1 : 3-dimethyldihydroquinoxaline (2·6 g.) was quaternised with ethyl sulphate (3 c.c.) at 180° for 4 minutes and then added to a solution prepared by boiling diphenylformamidine (1·47 g.) and 2-methylbenzthiazole ethiodide (4·6 g.) with acetic anhydride (20 c.c.) for 20 minutes. The whole was boiled for a few minutes, water added, and the oily dye caused to solidify by warming with aqueous potassium iodide (yield, 3 g.). The *iodide* was crystallised from alcohol acidified with a little hydrogen iodide; m. p. 180° (Found: N, 7·9. $C_{23}H_{24}ON_3IS$ requires N, 8·1%). Light absorption (alcohol): max., 5560, 5150 A.; I > II.

2-*Keto*-1-*phenyl*-3-*methyl*-1 : 2-*dihydroquinoxaline* (I, R = Ph).—This was best prepared by adding pyruvic acid to an equivalent amount of *o*-aminodiphenylamine dissolved in ether; slight heat was evolved. After evaporation of the solvent the residual orange solid crystallised from alcohol in pale yellow needles, m. p. 195° (cf. Kehrmann and Messinger, *Ber.*, 1892, **25**, 1628).

[2-(3-*Keto*-4-*phenyl*-1-*methyldihydroquinoxaline*)][(4-*dimethylaminophenyl*)]*dimethincyanine Chloride* (III; R = Ph, X = Cl).—2-Keto-1-phenyl-3-methyldihydroquinoxaline (5 g.) was heated with methyl sulphate (10 c.c.) at 180° for 4 minutes. The liquid was cooled, and acetic anhydride (20 c.c.) added, followed by *p*-dimethylaminobenzaldehyde (3·25 g.). The mixture was just heated to boiling, and water (250 c.c.) and excess of sodium chloride added. The green-bronze *chloride* was crystallised repeatedly from alcohol containing a little hydrochloric acid; m. p. 198—199° (Found: N, 9·9. $C_{25}H_{24}ON_3Cl$ requires N, 10·1%). Light absorption (alcohol): max., 6370 A.

The cyanine *base* (IX, R = Ph), prepared in the same way as the *N*-methyl analogue described above, separated as a brick-red crystalline powder, m. p. 210°, from alcohol (Found: N, 11·3. $C_{24}H_{21}ON_3$ requires N, 11·4%).

The corresponding 3-keto-4-phenyl-1-ethyldihydroquinoxaline dye was obtained in exactly similar manner from ethyl sulphate. 5 G. of the keto-compound afforded 8 g. of crude *chloride*, which was crystallised from alcohol containing hydrochloric acid; m. p. 281° (Found: N, 9·9. $C_{26}H_{26}ON_3Cl$ requires N, 9·8%). Light absorption (alcohol): max., 6500 A.

[2-(3-*Keto*-4-*phenyl*-1-*methyl*-3 : 4-*dihydroquinoxaline*)][2-(1 : 3 : 3-*trimethylindoline*)]*trimethincyanine Chloride* (IV; R = Ph, X = Cl).—The ketodihydroquinoxaline (1 g.) was quaternised at 180° for 30 minutes with methyl sulphate (2 c.c.) and then treated successively with acetic anhydride (4 c.c.), trimethylmethyleneindoline aldehyde (1 g.), and pyridine (3 c.c.). The whole was refluxed for 30 minutes, and hot water and excess of sodium chloride added. The *chloride* separated (1·6 g.) and was crystallised from dilute acetic acid; it had m. p. 252° (Found: Cl, 7·4. $C_{29}H_{28}ON_3Cl$ requires Cl, 7·6%). Light absorption (alcohol): max., 6530, 5950, 5540 A.; II > I > III.

[*Bis*-2-(3-*keto*-4-*phenyl*-1-*methyldihydroquinoxaline*)]*trimethincyanine Sulphate* (V; R = Ph, R′ = Me, X = SO_4).—3-Keto-4-phenyl-2-methyldihydroquinoxaline (5 g.) was quaternised as before with methyl sulphate. The product was dissolved in methyl alcohol (20 c.c.), 2 drops of concentrated sulphuric acid added, and the whole refluxed with ethyl orthoformate (6 c.c.) for 5 minutes. The *sulphate* was precipitated by water and crystallised from methyl alcohol containing sulphuric acid; m. p. 287° (Found: N, 8·8. $C_{34}H_{30}O_6N_4S$ requires N, 9·0%). Light absorption (alcohol): max., 6560, 6020 A.; I > II. The dye was red in alcohol but became blue on addition of acid.

[2-(3-*Keto*-4-*phenyl*-1-*methyl*-3 : 4-*dihydroquinoxaline*)][2-(1-*methylquinoline*)]*trimethincyanine Sulphate* (VI; R = Ph, X = SO_4).—2-Methylanilinovinylquinoline methiodide (3·8 g.) was shaken with aqueous sodium carbonate and benzene until all solid had disappeared. The benzene solution was filtered, dried, and evaporated. The residue, dissolved in pyridine (4 c.c.), was added to 3-keto-4-phenyl-2-methyldihydroquinoxaline methosulphate (prepared from 2·4 g. of quinoxaline) in acetic anhydride (6 c.c.); much heat was evolved. After cooling, the *sulphate* (1·8 g.) was collected, washed with ether, and crystallised from glacial acetic acid, forming small green needles, m. p. 244° (decomp.) (Found: S, 6·4. $C_{29}H_{27}O_5N_3S$ requires S, 6·5%). It gave purple solutions in the common solvents. Light absorption (alcohol): max., 6560 A.

[2-(3-*Keto*-4-*phenyl*-1-*methyl*-3 : 4-*dihydroquinoxaline*)][2-(1-*methylbenzthiazole*)]*trimethincyanine Chloride* (as VIII; R = Ph, X = Cl).—2-Methylanilinovinylbenzthiazole methiodide (2 g.) was treated with sodium carbonate and benzene as in the preceding preparation. The residue from the benzene extract was dissolved in pyridine (3 c.c.) and added to 3-keto-4-phenyl-2-methyldihydroquinoxaline (1·2 g.) which had been quaternised with methyl sulphate and dissolved in acetic anhydride (4 c.c.). Heat was evolved; after cooling, the mixture was decomposed with water and salted out with sodium chloride. The *chloride* was obtained as a dark red powder (0·8 g.) crystallising from dilute acetic acid; it had m. p. 235° (decomp.) (Found: Cl, 7·2. $C_{26}H_{22}ON_3ClS$ requires Cl, 7·2%). Light absorption (alcohol): diffuse band, max., *ca.* 5500 A.

2-*Keto*-3-*benzyl*-1 : 2-*dihydroquinoxaline* (X, R = H).—Phenylpyruvic acid (Erlenmeyer and Arbenz, *Annalen*, 1904, **333**, 228) (8·2 g.) in concentrated alcoholic solution was added to *o*-phenylenediamine (5 g.) also in alcoholic solution. The *quinoxaline* separated as a dense precipitate within a few seconds. It crystallised from alcohol in small needles, m. p. 196° (Found: N, 12·1. $C_{15}H_{12}ON_2$ requires N, 11·9%).

2-*Keto*-1-*phenyl*-3-*benzyl*-1 : 2-*dihydroquinoxaline* (X, R = Ph).—*N*-Phenyl-*o*-phenylenediamine (9·2 g.) and phenylpyruvic acid (8·2 g.) were condensed by mixing ethereal solutions of the reactants. The crude product (15 g.) obtained on evaporating the solvent crystallised from glacial acetic acid in needles, m. p. 166° (Found: N, 8·9, 9·1. $C_{21}H_{16}ON_2$ requires N, 9·0%). This and the preceding compound behaved qualitatively like other quinoxalines but the cyanine dyes rapidly disappeared and so were not isolated.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S.W. 7. [*Received, April 13th*, 1943.]