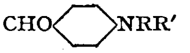
134. *Quinoxaline Cyanines. Part IV. Some Halogenated Styryl Derivatives.*

By R. M. ANKER and A. H. COOK.

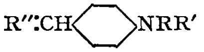
Three halogenated analogues of *p*-dimethylaminobenzaldehyde have been prepared and converted into styryl dyes by condensation with quaternary salts and other systems containing reactive methyl or methylene groups. Quinoxaline and hydroxyquinoxaline representatives recall the derivatives of dimethylaminobenzaldehyde in their intense blue colour.

IN Parts I and II (J., 1942, 710; 1943, 394) of this series there is described the condensation of quinoxalines and hydroxyquinoxalines with *p*-dimethylaminobenzaldehyde. B.P. 456,534 describes the preparation of some *p*-chloroalkylaminobenzaldehydes, and their condensation with reactive methyl or methylene groups is mentioned in B.P. 458,405. The halogen atoms in the resulting condensation products were stated to improve the shade and dyeing properties, and in view of the potential interest of quinoxaline dyes previously described for application to textiles, the preparation of p-*methyl*-β-*chloroethyl*- (I*a*), p-*ethyl*-β-*chloroethyl*- (I*b*), and p-di-β-*chloroethyl-aminobenzaldehyde* (I*c*) was undertaken, and their condensation with typical quinoxaline quaternary salts studied. The opportunity was also taken to prepare for comparative purposes condensation products between these aldehydes and other typical cyanine components.

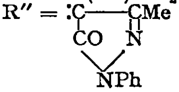
The aldehydes were obtained from methyl- or ethyl-aniline or aniline itself by introducing one or two *N*-hydroxyethyl groups; by using ethylene chlorohydrin in presence of magnesium oxide, formation of phenylmorpholine and other by-products was largely avoided. Chloroethylanilines resulted on treating the hydroxyethyl derivatives with thionyl chloride, and the aldehyde groups were introduced with formomethylanilide and phosphorus oxychloride.



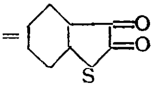
(I.) (*a*) R = Me, R′ = $CH_2{\cdot}CH_2Cl$
(*b*) R = Et, R′ = $CH_2{\cdot}CH_2Cl$
(*c*) R = R′ = $CH_2{\cdot}CH_2Cl$



(II.) (*a*) R″ = :C(CN)·CO_2H or :C(CN)·CO_2Et
(*b*) R″ =



(*c*) R″ =



These aldehydes behaved like dimethylaminobenzaldehyde but were generally less reactive. For instance, condensation with cyanoacetic acid or ester in alcoholic solution with a basic catalyst gave yellow-orange dyes (II*a*), and red dyes (II*b*) were obtained by condensation with 1-phenyl-3-methyl-5-pyrazolone. Further, red-brown dyes (II*c*) were formed by reaction with thioindoxyls in boiling acetic anhydride solution. Condensation with quaternary salts of α-picoline, quinaldine, 2-methylbenzthiazole, 2 : 3 : 3-trimethylindolenine, and 2-methyl-3 : 4-dihydroquinazolone in acetic anhydride, or ethanol containing piperidine afforded the corresponding styryl dyes in good yields. With quaternary salts of 2 : 3-dimethylquinoxaline, however, reaction was often effected cleanly in chloroform or tetrachloroethane containing molecular quantities of pyridine and acetic anhydride; the use of mixtures of pyridine and acetic anhydride alone was disappointing, although it was very effective with dimethylaminobenzaldehyde (cf. Part I); it appeared that the present dyes were still less stable or less readily formed in such media than those described earlier. Finally, condensation with 2-methyl-3-keto-3 : 4-dihydroquinoxaline and its derivatives * after previous quaternisation with methyl sulphate was effected in acetic anhydride containing a little pyridine; more of the basic catalyst gave obviously different products which were only coloured in solution in mineral acid.

Most of the dyes so prepared were markedly less soluble in the common solvents than the similar dyes derived from *p*-dimethylaminobenzaldehyde; in particular, the methiodides of some of the phenyl-substituted quinoxaline derivatives had only a slight solubility in water. The strong bathochromic influence of the quinoxaline system was again well marked, but spectrometric comparison of representative quinoxaline dyes revealed no significant differences in the shape of the absorption curves or in the positions of the absorption maxima. There were irregular differences in the intensity of absorption but these were probably solvent effects and were insufficient to produce any considerable change of shade. It seems therefore that the strong bathochromic influence of the quinoxaline system masks the effect of the halogen atoms which appears in other dyes.

EXPERIMENTAL.

p-*Methyl-β-chloroethylaminobenzaldehyde.*—Methyl-β-hydroxyethylaniline (Laun, *Ber.*, 1884, **17**, 676) (200 g.) in benzene (200 c.c.) was treated gradually with phosphorus oxychloride (60 c.c.), reaction being completed on the steam-bath for 1 hour. The cold product was poured into water (500 c.c.), treated with a slight excess of sodium hydroxide, and the oil extracted with benzene. Distillation, eventually in a vacuum, gave methyl-β-chloroethylaniline as an oil, b. p. 130°/14 mm. (yield, 190 g.) (Found : Cl, 20·9. Calc. for $C_9H_{12}NCl$: Cl, 20·9%) (cf. Clemo and Perkin, J., 1922, **121**, 642). Phosphorus oxychloride (220 c.c.) was added to a mixture of formomethylanilide (320 g.) and benzene (100 c.c.); after being stirred for 1 hr., the mixture was kept at 0° during addition of methyl-β-chloroethylaniline (190 g.) diluted with an equal volume of benzene. Finally, after being heated at 30—35° for 4 hrs., the mixture was poured on ice, and the solution neutralised with sodium hydroxide. From the extract, benzene and methylaniline were removed in a rapid current of steam, and the remaining *aldehyde* (70 g.) recrystallised from methanol; it had m. p. 70° (Found : C, 60·9; H, 6·0; N, 7·1. $C_{10}H_{12}ONCl$ requires C, 60·7; H, 6·1; N, 7·1%).

p-*Ethyl-β-chloroethylaminobenzaldehyde.*—Ethyl-β-hydroxyethylaniline (180 g.; b. p. 151°/14 mm.) was treated as its homologue in the preceding preparation .Ethyl-β-chloroethylaniline (170 g.) was obtained as an oil, b. p. 133°/14 mm. The *aldehyde* (80 g.) was a very viscous liquid which did not solidify; it had b. p. 162°/0·02 mm., or 95° in a high vacuum, and could only be distilled without decomposition at low pressure (Found : N, 6·9. $C_{11}H_{14}ONCl$ requires N, 6·6%). The *semicarbazone* recrystallised from pyridine; m. p. 201° (Found : Cl, 13·0. $C_{12}H_{17}ON_4Cl$ requires Cl, 13·2%).

p-*Di-β-chloroethylaminobenzaldehyde.*—Aniline (1 g.-mol.) aud ethylene chlorohydrin (1 g.-mol.), treated as in previous preparations (Knorr, *Ber.*, 1889, **22**, 2092), gave β-hydroxyethylaniline (0·9 g.-mol.), b. p. 185°/14 mm., which on further treatment with a molecular quantity of ethylene chlorohydrin gave di-β-hydroxyethylaniline (0·8 g.-mol.). The reaction could be carried out in one stage if its difficultly controllable nature and formation of "diethylene dianiline," m. p. 164°, were mitigated by stirring with 1 equiv. of magnesium oxide. Di-β-hydroxyethylaniline crystallised from benzene and had m. p. 59° (Found : C, 66·4; H, 8·3. Calc. for $C_{10}H_{15}O_2N$: C, 66·6; H, 8·4%). Di-β-chloroethylaniline was obtained in the usual way in almost theoretical yield; it distilled at 181°/14 mm. and, recrystallised from methanol, had m. p. 49°; Robinson and Watt (J., 1934, 1536) give m. p. 45° (Found : Cl, 32·6. Calc. for $C_{10}H_{13}NCl_2$: Cl, 32·6%). p-*Di-β-chloroethylaminobenzaldehyde* was prepared (yield, 70%) from the aniline in the usual manner. It crystallised from ethanol and had m. p. 88·5° (Found : N, 5·55; Cl, 28·2. $C_{11}H_{23}ONCl_2$ requires N, 5·7; Cl, 28·8%).

Condensations with Ethyl Cyanoacetate.—*p*-Methyl-β-chloroethylaminobenzaldehyde (7·7 g.) was boiled for 4 hrs. with ethanol (50 c.c.), ethyl cyanoacetate (5·0 g.), and piperidine (3 drops), and then cooled to 0°. *Ethyl* p-*methyl-β-chloroethylaminobenzylidenecyanoacetate* (11 g.) was filtered off, and recrystallised from ethanol, forming yellow microscopic needles, m. p. 105° (Found : N, 9·4. $C_{15}H_{17}O_2N_2Cl$ requires N, 9·5%). *Ethyl* p-*ethyl-β-chloroethylaminobenzylidenecyanoacetate* was prepared in the same way; it formed a yellow microcrystalline deposit, m. p. 124°, from ethanol (Found : N, 8·9. $C_{16}H_{19}O_2N_2Cl$ requires N, 9·1%).

Condensations with 1-*Phenyl*-3-*methyl*-5-*pyrazolone.*—The pyrazolone (5 g.) was refluxed with *p*-methyl-β-chloroethylaminobenzaldehyde (5·7 g.), ethanol (50 c.c.), and 3 drops of piperidine for 4 hrs. 1-*Phenyl*-3-*methyl*-4-p-*methyl-β-chloroethylaminobenzylidene*-5-*pyrazolone* separated on cooling; it crystallised from acetic acid in red needles, m. p. 154° (Found : N, 12·0. $C_{20}H_{20}ON_3Cl$ requires N, 11·9%). The 4-p-*ethyl* compound, prepared in the same way, formed

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* Patent application pending.

red needles, m. p. 117°, from acetic acid (Found : N, 11·5. $C_{21}H_{22}ON_3Cl$ requires N, 11·4%); and the 4-p-*di-β-chloroethylamino*-analogue, similarly obtained from *p*-di-β-chloroethylaminobenzaldehyde (7·1 g.) and the pyrazolone (5 g.), formed red needles, m. p. 167°, from acetic acid (Found : N, 10·5. $C_{22}H_{21}ON_3Cl_2$ requires N, 10·45%).

Condensations with Indoxyls.—6-Ethoxythioindoxyl (3 g.) and *p*-methyl-β-chloroethylaminobenzaldehyde (3 g.) were dissolved in ethanol (50 c.c.) with concentrated hydrochloric acid (3 c.c.), and the solution refluxed for 1 hr. After cooling, the reddish-brown crystals were recrystallised from benzene or acetic acid. 6-*Ethoxy*-2-p-*methyl-β-chloroethylaminobenzylidenethioindoxyl* had m. p. 152° (yield, 3·5 g.) (Found : N, 3·5; Cl, 9·9. $C_{20}H_{20}O_2NSCl$ requires N, 3·5; Cl, 9·5%). 6-Chloro-4-methylthioindoxyl (4 g.) and *p*-di-β-chloroethylaminobenzaldehyde (5 g.) were refluxed for 1 hr. with acetic anhydride (50 c.c.); on cooling 6-*chloro*-4-*methyl*-2-p-*di-β-chloroethylaminobenzylidenethioindoxyl* (5·2 g.) separated; it was filtered off, washed with acetic acid, and recrystallised from anisole, forming red prisms, m. p. 191° (Found : N, 3·3; Cl, 24·3. $C_{20}H_{18}ONCl_3S$ requires N, 3·3; Cl, 25·0%).

Condensations with α-Picoline Ethiodide.—*p*-Ethyl-β-chloroethylaminobenzaldehyde (7 g.) was refluxed in ethanol (50 c.c.) with α-picoline ethiodide (7 g.) and piperidine (3 drops) for 4 hrs. 2-p-*Ethyl-β-chloroethylaminostyrylpyridine ethiodide* (8 g.) crystallised on cooling, and was recrystallised from ethanol; it formed red needles, m. p. 154° (Found : N, 6·55. $C_{19}H_{24}N_2ClI$ requires N, 6·35. 0·1795 G. gave 0·1533 g. of mixed silver halides. $C_{19}H_{24}N_2ClI$ requires 0·1560 g.). *p*-Di-β-chloroethylaminobenzaldehyde (8 g.), α-picoline ethiodide (8 g.), piperidine (2 c.c.), and ethanol (50 c.c.) were refluxed for 3½ hrs., and so much dye had then crystallised that boiling was discontinued. The main product, 2-p-*di-β-chloroethylaminostyrylpyridine ethiodide* (12 g.), was sparingly soluble in ethanol and was recrystallised from acetic acid; it formed a red solid, m. p. 191° (decomp.) (Found : N, 5·9. $C_{19}H_{23}N_2Cl_2I$ requires N, 5·9%. 0·1550 G. gave 0·1702 g. of mixed silver halides. $C_{19}H_{23}N_2Cl_2I$ requires 0·1697 g.). It was accompanied by 0·5 g. of a water-soluble, yellow powder which became red on boiling with ethanol; m. p. 300° (decomp.) (Found : N, 5·45%).

p-*Ethyl-β-chloroethylaminostyrylquinoline Methiodide.*—Quinaldine methiodide (5 g.) and *p*-ethyl-β-chloroethylaminobenzaldehyde (5 g.) were boiled for 5 mins. with acetic anhydride (50 c.c.), the solution cooled, and then poured into water (500 c.c.). On recrystallisation from ethanol, the dye was obtained in dark violet crystals, m. p. 191° (Found : N, 5·85. $C_{22}H_{24}N_2ClI$ requires N, 5·85%). Light absorption (ethanol) : max. 5080 A.

Condensations with 2-*Methylbenzthiazole Methiodide.*—The methiodide (6 g.) and *p*-methyl-β-chloroethylaminobenzaldehyde (4 g.) were refluxed for 1 hr. in acetic anhydride (75 c.c.). The cooled solution was poured into water (700 c.c.), and the dye (6 g.) allowed to crystallise at 0°; 2-p-*methyl-β-chloroethylaminostyrylbenzthiazole methiodide* separated from ethanol in dark red prisms with a green lustre, m. p. 138° (Found : N, 6·0. $C_{19}H_{20}N_2SClI$ requires N, 5·95%). Light absorption (ethanol) : max. 5020 A. 2-Methylbenzthiazole methiodide (3 g.) and *p*-ethyl-β-chloroethylaminobenzaldehyde (2·1 g.) were refluxed for 4 hrs. with ethanol (30 c.c.) containing piperidine (3 drops). The warm solution was poured into 10% aqueous sodium iodide (300 c.c.), the whole cooled to 0° overnight, and the dye collected. 2-p-*Ethyl-β-chloroethylaminostyrylbenzthiazole methiodide*, after several crystallisations from ethanol, formed brownish-red needles (3 g.), m. p. 198° (decomp.) (Found : N, 5·5. $C_{20}H_{22}N_2SClI$ requires N, 5·8%. 0·1431 G. gave 0·1134 g. of mixed halides. $C_{20}H_{22}N_2SClI$ requires 0·1153 g.).

Condensations with 2 : 3 : 3-*Trimethylindolenine Methiodide.*—The iodide (3 g.) and *p*-methyl-β-chloroethylaminobenzaldehyde (2 g.) were refluxed in ethanol (30 c.c.) containing piperidine (3 drops) for 4 hrs., and the dark red solution poured into 10% sodium iodide solution (300 c.c.). After keeping at 0°, the dye was washed with ether and then with water, and finally crystallised several times from 60% ethanol. 2-p-*Methyl-β-chloroethylaminostyryl*-3 : 3-*dimethylindolenine methiodide* (2 g.) formed red needles with a green sheen, m. p. 148° (Found : N, 5·6. $C_{22}H_{26}N_2ClI$ requires N, 5·8%. 0·1429 G. gave 0·1095 g. of mixed silver halides. $C_{22}H_{26}N_2ClI$ requires 0·1124 g.). The indolenine methiodide (4·5 g.) was condensed for 4 hrs. with *p*-di-β-chloroethylaminobenzaldehyde (3 g.) in boiling ethanol (40 c.c.) and piperidine (3 drops). The crude dye was salted out with 400 c.c. of 10% sodium iodide, dissolved in chloroform, and the solution filtered and precipitated with 10 vols. of ether. 2-p-*Di-β-chloroethylaminostyryl*-3 : 3-*dimethylindolenine methiodide* recrystallised from 70% ethanol in red needles with a green lustre, m. p. 127° (Found : N, 5·0. $C_{23}H_{27}N_2Cl_2I$ requires N, 5·3%. 0·1129 G. gave 0·1119 g. of mixed silver halides. $C_{23}H_{27}N_2Cl_2I$ requires 0·1116 g.).

2-Methyl-3 : 4-dihydroquinazolone methiodide (3·6 g.) and *p*-methyl-β-chloroethylaminobenzaldehyde (2·5 g.) were heated to 145—150° in acetic anhydride (80 c.c.) for 20 mins. The deep brown solution was cooled, and the product (1·9 g.) recrystallised from formic acid. 2-p-*Methyl-β-chloroethylaminostyryl*-3 : 4-*dihydroquinazolone methiodide* formed brick-red crystals, m. p. 220° (decomp.) (Found : N, 8·5. $C_{20}H_{21}ONClI$ requires N, 8·7%. 0·1106 G. gave 0·0878 g. of mixed silver halides. $C_{20}H_{21}ONClI$ requires 0·0870 g.).

Condensations with Quinoxalines.—2-Aminodiphenylamine (9·2 g.) in ethanol (40 c.c.) was treated slowly with diacetyl (4·3 g.) with cooling and stirring. After 5 mins., hydriodic acid (13 g., *d* 1·7) was slowly added, and the crystalline 1-*phenyl*-2 : 3-*dimethylquinoxalinium iodide* (9 g.) collected and repeatedly crystallised from 90% ethanol; m. p. 204° (decomp.) (Found : N, 7·5; I, 35·5. $C_{16}H_{15}N_2I$ requires N, 7·7; I, 35·1%). When this iodide (1·9 g.) was heated in acetic anhydride (10 c.c.) at 100° for 10 mins. with *p*-methyl-β-chloroethylaminobenzaldehyde (1 g.), and the cooled solution poured into ether (100 c.c.), 1-*phenyl*-2-p-*methyl-β-chloroethylaminostyryl*-3-*methylquinoxalinium iodide* was formed; it was dissolved in ethanol, salted out with aqueous sodium iodide, and finally recrystallised from ethanol (yield, 0·6 g.); m. p. 150° (Found : N, 7·5. $C_{26}H_{25}N_3ClI$ requires N, 7·7%. 0·1818 G. gave 0·1287 g. of mixed silver halides. $C_{26}H_{25}N_3ClI$ requires 0·1271 g.). Light absorption (ethanol) : max. *ca.* 6250 A. 1-Phenyl-2 : 3-dimethylquinoxalinium iodide (3 g.) was condensed with *p*-ethyl-β-chloroethylaminobenzaldehyde (2 g.) in tetrachloroethane (30 c.c.) containing acetic anhydride (2 c.c.) and pyridine (1 c.c.) at 100° for 15 mins. The product was poured into ether (300 c.c.), the dye filtered off, dissolved in ethanol, and salted out with excess of aqueous potassium iodide (yield, 3·5 g.). 1-*Phenyl*-2-p-*ethyl-β-chloroethylaminostyryl*-3-*methylquinoxalinium iodide*, recrystallised from ethanol, had m. p. 170° (Found : C, 58·1; H, 5·0. $C_{27}H_{27}N_3ClI$ requires C, 58·3; H, 4·9%. 0·1670 G. gave 0·1105 g. of mixed silver halides. $C_{27}H_{27}N_3ClI$ requires 0·1137 g.). By replacing the phenyl iodide by 2 : 3-dimethylquinoxaline methiodide in the preceding preparation, 2-p-*ethyl-β-chloroethylaminostyryl*-3-*methylquinoxaline methiodide* was obtained; it separated from ethanol in needles, m. p. 130° (Found : C, 53·6; H, 5·4. $C_{22}H_{25}N_3ClI$ requires C, 53·5; H, 5·1%. 0·1251 G. gave 0·0955 g. of mixed silver halides. $C_{22}H_{25}N_3ClI$ requires 0·0986 g.). 2-p-*Methyl-β-chloroethylaminostyryl*-3-*methylquinoxaline methiodide* was prepared similarly; it separated from ethanol and had m. p. 135° (Found : C, 52·6; H, 5·3. $C_{21}H_{23}N_3ClI$ requires C, 52·6; H, 4·8%. 0·1466 G. gave 0·1092 g. of mixed silver halides. $C_{21}H_{23}N_3ClI$ requires 0·1119 g.). Light absorption (ethanol) : max. 6200 A.

Condensations with 2-*Methyl*-3 : 4-*dihydro*-3-*quinoxalone.*—The quinoxalone (4 g.) was heated with methyl sulphate (9 g.) for 10 mins. at 140°, the product cooled, and excess of methyl sulphate removed by washing with ether. To the residue, acetic anhydride (30 c.c.) was added, followed by *p*-methyl-β-chloroethylaminobenzaldehyde (5 g.) and pyridine (1 c.c.). The solution was heated to boiling, cooled, and the dye precipitated with ether (300 c.c.). The solid was taken up in ethanol, salted out by pouring into 10 vols. of aqueous 10% sodium iodide solution, and the resulting dye (8·5 g.) crystallised from 60% formic acid, affording fine green needles. 2-p-*Methyl-β-chloroethylaminostyryl*-3 : 4-*dihydro*-3-*quinoxalone methiodide* had m. p. 214° (decomp.) and gave intensely blue solutions (Found : C, 49·4; H, 4·2.

$C_{20}H_{21}N_3ClI$ requires C, 49·8; H, 4·4%. 0·1378 G. gave 0·1099 g. of mixed silver halides. $C_{20}H_{21}N_3ClI$ requires 0·1083 g.). Light absorption (ethanol): max. 5900 A. The quinoxalone (7 g.) was made into a paste with methyl sulphate (15 g.) and heated for 10 mins. at 140°. The product was dissolved in acetic anhydride (30 c.c.), treated with di-β-chloroethylaminobenzaldehyde (10 g.) in the same solvent (30 c.c.), and the whole boiled for 15 mins. The solution was cooled, poured into water (600 c.c.), and the solid extracted with boiling acetic acid; the undissolved residue had no dyeing properties, and the crystalline deposit (2·5 g.) from the acetic acid contained two constituents separated by fractional crystallisation from ethanol. The less soluble 2-p-*di-β-chloroethylaminostyryl*-3 : 4-*dihydro*-3-*quinoxalone methosulphate* separated as a dark blue, microcrystalline powder with a green lustre, m. p. 198° (Found: N, 8·05; Cl, 14·2. $C_{22}H_{25}O_5N_3Cl_2S$ requires N, 8·15; Cl, 13·8%). Light absorption (ethanol): max. 6000 A. The second constituent, possibly the *dimethosulphate* of the same cyanine base, separated in blue needles, m. p. 146° (Found: N, 6·3, 6·4. $C_{24}H_{31}O_9N_3S_2Cl_2$ requires N, 6·55%).

Condensations with 2 : 4-*Dimethyl*-3 : 4-*dihydro*-3-*quinoxalone*.—The quinoxalone (1·8 g.) was quaternised with methyl sulphate (1·3 g.) at 140° for 10 mins., the product dissolved in acetic anhydride (10 c.c.), and a solution of *p*-methyl-β-chloroethylaminobenzaldehyde (2 g.) in the same solvent (10 c.c.) added. The whole was boiled under reflux for 5 mins., cooled, and poured into 10% aqueous sodium iodide (200 c.c.). 2-p-*Methyl-β-chloroethylaminostyryl*-4-*methyl*-3 : 4-*dihydro*-3-*quinoxalone methiodide* (2 g.) was filtered off and crystallised from ethanol; it had m. p. 161° (Found: N, 8·7. $C_{21}H_{23}ON_3ClI$ requires N, 8·5%. 0·1466 G. gave 0·1092 g. of silver halides. $C_{21}H_{23}ON_3ClI$ requires 0·1119 g.). Light absorption (ethanol): max. 6170 A. The quinoxalone (8 g.) was quaternised with methyl sulphate (6 g.) as above, the product dissolved in acetic anhydride (40 c.c.), and *p*-di-β-chloroethylaminobenzaldehyde (12 g.) in pyridine (20 c.c.) added. The whole was boiled for 5 mins., poured into water (400 c.c.), and the dye salted out with sodium chloride; it was crystallised from acetic acid, or from ethanol in which it was less soluble; 2-*di-β-chloroethylaminostyryl*-4-*methyl*-3 : 4-*dihydroquinoxalone methochloride* had m. p. 192° (decomp.) (Found: N, 9·5; Cl, 23·4. $C_{22}H_{24}ON_3Cl_3$ requires N, 9·3; Cl, 23·6%). Light absorption (ethanol): max. 5750 A.

Condensations with 4-*Phenyl*-2-*methyl*-3 : 4-*dihydro*-3-*quinoxalone*.—Methyl sulphate (2·5 g.) and the quinoxalone (5 g.) were heated to 140° for 20 mins., the product taken up in acetic anhydride (30 c.c.), a solution of *p*-methyl-β-chloroethylaminobenzaldehyde (4·5 g.) in acetic anhydride (10 c.c.) added, and the whole heated under reflux for 15 mins.; the mixture was then poured into water (400 c.c.), and the solid was filtered off. 4-*Phenyl*-2-p-*methyl-β-chloroethylaminostyryl*-3 : 4-*dihydro*-3-*quinoxalone methosulphate* crystallised from ethanol and had m. p. 189° (decomp.) (Found: Cl, 6·65. $C_{27}H_{28}O_5N_3SCl$ requires Cl, 6·55%). Light absorption (ethanol): max. 6200 A. 4-*Phenyl*-2-p-*di-β-chloroethylaminostyryl*-3 : 4-*dihydro*-3-*quinoxalone methosulphate*, prepared similarly, crystallised from ethanol and had m. p. 170° (decomp.) (Found: N, 7·4; Cl, 12·3. $C_{28}H_{29}O_5N_3Cl_2S$ requires N, 7·1; Cl, 12·0%). Light absorption (ethanol): max. 6000 A.

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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S.W. 7.

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