131. *Pyrrole Trimethincyanines.*

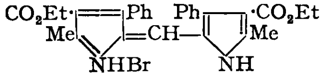
By A. H. Cook and J. R. Majer.

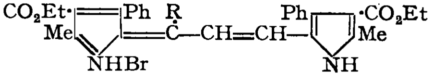
Pyrroles containing at least one α-free position have been found to condense with ketones and orthoformic ester in presence of mineral acid. The intensely coloured products have been proved by alternative syntheses to be cyanines with a substituted trimethin chain. Similar dyes with an unsubstituted chain have been prepared by condensing pyrroles either with β-ethoxyacraldehyde acetal or with acetal and orthoformic ester in presence of mineral acid. These reactions are general ones for pyrroles containing an imino-group, but there appear to be limitations when the nitrogen atom bears a substituent.

Cyanine dyes have been prepared in which the terminal heterocyclic nuclei have covered a wide range; pyrrole nuclei, however, have not hitherto figured in compounds of this type if the very numerous class of dipyrromethene salts is excepted. The present work to some extent remedies this deficiency, although most of the compounds described below were prepared by an unexpected and novel route.*

The need arose in another connection for certain dipyrromethenes which it was hoped to prepare by the interaction of appropriate α-free pyrroles and ethyl orthoformate in presence of mineral acid. This reaction was readily realised and several applications are described in the present paper. It was noted, however, that the pyrroles gave quite different colours if the condensations were carried out in presence of carbonyl compounds of varied kinds. Thus, when ethyl 4-phenyl-2-methylpyrrole-3-carboxylate was kept in presence of ethyl orthoformate and cold hydrobromic acid, a red crystalline *pyrromethene hydrobromide* (I) was formed, whereas in presence of acetone the solution became intensely blue and scintillating green crystals separated. Comparative experiments indicated that the optimum proportions of reactants were two molecular parts of pyrrole, one molecular part of acetone, and one molecular part of orthoformic ester. Analysis of this and similar com-

(I.)





(II.)

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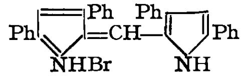
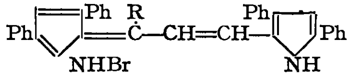
* Patent protection pending.

pounds showed that the blue compound was indeed formed by elimination of two molecules of water and three of ethanol with addition of one of hydrogen bromide. Only constitution (II; R = Me) explains these facts satisfactorily and the products must be formulated as *trimethincyanines*. Exactly similar compounds were prepared, in every case in the form of green or steely blue crystals, by replacing acetone by acetophenone, *p*-methoxyacetophenone, β-acetonaphthone, or methyl ethyl ketone; analyses were in good agreement with their formulation as compounds of type (II) where R = an alkyl or aryl residue. Small-scale experiments indicate that the reaction may also be carried out with any mineral acid and *cyclo*pentanone, *cyclo*hexanone, benzyl methyl ketone, propiophenone, chloroacetone, *o*-benzylacetophenone, and indeed with any normal simple ketone containing the group $\cdot CO\cdot CH_2\cdot$; it failed completely with di*iso*propyl ketone, as would be anticipated from the limitations imposed by the above structure.

These reactions are not limited to the above pyrrole. The more highly arylated 2 : 4-diphenylpyrrole, ethyl orthoformate, and hydrogen bromide in cold acetic acid afforded the red pyrromethene (III); the same reagents with added acetone, however, gave the blue trimethin salt (IV; R = Me), and (IV; R = Ph) arose by the use of acetophenone:

(III.)



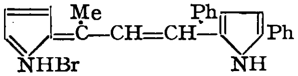


(IV.)

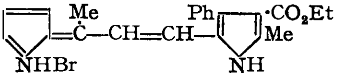
On the other hand, 4-phenyl-2-methyl-, 2 : 4-dimethyl-, 2-triphenylmethyl-pyrrole and even pyrrole itself gave similar colours, so the reaction is clearly a general one for pyrroles which do not bear a substituent on the nitrogen atom.

The structures suggested above are the only possible ones when account is taken of the general properties of the products, analytical data, and the substitution which is permissible without hindering reaction. They were nevertheless confirmed by the following findings:

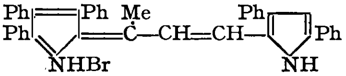
(*a*) 2 : 4-Diphenylpyrrole-5-aldehyde condensed with 2 : 4-diphenylpyrrole, acetone, and hydrobromic acid to give the same product as was obtained from 2 : 4-diphenylpyrrole, acetone, orthoformic ester and hydrobromic acid. Unsymmetrical dyes were similarly prepared from ethyl 4-phenyl-2-methylpyrrole-3-carboxylate, pyrrole, and acetone, from 2 : 4-diphenylpyrrole-5-aldehyde, pyrrole, and acetone, and from 2 : 4-diphenylpyrrole-5-aldehyde, 2 : 3 : 4-triphenylpyrrole and acetone:



(V*a*.)



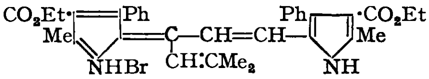
(V*b*.)

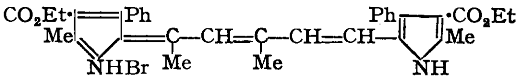


(V*c*.)

(*b*) Pyrroles containing a free α-position condensed with β-ethoxyacraldehyde acetal in presence of mineral acid to give dyes which must contain an unsubstituted trimethin chain. The very similar light absorption of these dyes to that of products obtained by using ketones and orthoformic ester left no doubt that these must contain the same conjugated chain between the nuclei. Ethyl 4-phenyl-2-methylpyrrole-3-carboxylate condensed also with mesityl oxide and ethyl orthoformate. The light absorption showed that the product was again a substituted trimethincyanine (VI) and not the pentamethin compound (VII) which might have arisen:

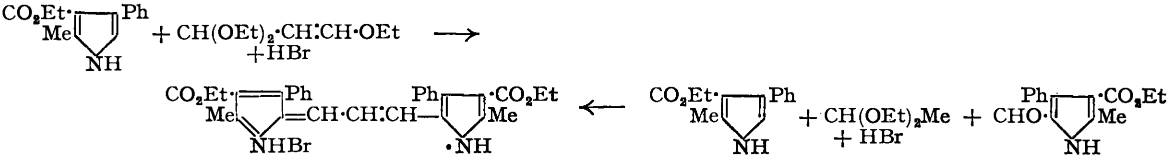
(VI.)



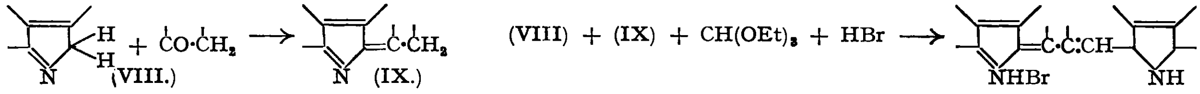


(VII.)

The possibility of linking unsubstituted trimethin chains to pyrroles by condensing aldehydes with pyrroles and orthoformic ester was also investigated. Simple tests showed that colours were indeed formed but that reaction was not so ready as with ketones. It was possible, however, to identify the product of interaction of ethyl 4-phenyl-2-methylpyrrole-3-carboxylate, acetal, orthoformic ester and hydrobromic acid with that from the same pyrrole, β-ethoxyacraldehyde acetal and hydrobromic acid:



It might be thought that the reaction between pyrroles, ketone, and orthoformic ester consisted in the intermediate formation of a formyl ketone or a nearly related compound. Formylacetone has been proposed to supply a trimethin chain in linking pyrazolone nuclei (B.P. 515,998) and, as was shown in the present work, it can be used to link pyrrole nuclei. There is, however, evidence to show that the prime reaction is the condensation of ketone with the pyrrole, the latter probably reacting in a pyrrolenine form:



(VIII.) (IX.)

So, although alkylated pyrroles appeared less ready to undergo reaction than arylpyrroles, dye formation was achieved in these cases by first submitting the pyrrole and ketone in presence of mineral acid to moderate heating and then completing condensation with orthoformic ester in the cold. Moreover, in such cases, preliminary condensation was also required even when condensation was completed by standing with a pyrrole-α-aldehyde.

All the preceding compounds differ from other cyanines not only in the heterocyclic systems but also in their containing no *N*-alkyl or *N*-aryl groups. *N*-Phenylpyrrole appeared to react as readily as pyrrole itself with acetone or other ketones and orthoformic ester, but ethyl 4-phenyl-1 : 2-dimethylpyrrole-3-carboxylate has so far failed to give trimethincyanines, although formation of pyrromethene presented no difficulty; there appear to be limitations among *N*-substituted pyrroles, therefore, which remain to be defined.

The absorption spectra of these cyanines present one interesting feature. Trimethincyanines from mono- or di-phenylpyrroles were intensely blue, but those from unsubstituted or more simply substituted pyrroles were shades of red. The colours were practically unaffected by substitution on the trimethin chain, but it is clear that aryl residues in the pyrrole rings have a very pronounced chromophoric effect, which is unexpected in view of the fact that they are only linked and not fused to the heterocyclic residues.

During the course of this work ethyl 4-anisyl-2-methylpyrrole-3-carboxylate, 2-diphenylmethylpyrrole, and ethyl 4-β-naphthyl-2-methylpyrrole-3-carboxylate were prepared by orthodox methods and shown qualitatively to undergo condensation in the same manner as the simpler pyrroles.

EXPERIMENTAL.

2 : 4-*Diphenylpyrrole Cyanines.*—2 : 4-Diphenylpyrrole (2·2 g.) was warmed with ethyl orthoformate (1·65 g.), 50% hydrobromic acid in acetic acid (0·8 c.c.), and acetic acid (20 c.c.) for 1 hour at 100°. *Bis*-2-(3 : 5-*diphenylpyrrole*)*monomethincyanine bromide* (2·0 g.) was filtered from the deep red solution. It separated from ethanol in greenish needles with a brown reflex, m. p. 262° (decomp.) (Found : Br, 15·3. $C_{33}H_{25}N_2Br$ requires Br, 15·1%); light absorption (chloroform), max., 5510 A.

A solution of 2 : 4-diphenylpyrrole (2·2 g.) in ethyl acetate (15 c.c.) was quickly cooled and then treated with acetone (1·5 c.c.) and 1 drop of 5% hydrobromic acid in acetic acid. After 5 mins., ethyl orthoformate (1·65 c.c.), followed by 50% hydrobromic acid in acetic acid (0·81 c.c.), was added and the green dye (0·91 g.) filtered off after 12 hours. *Bis*-2-(3 : 5-*diphenylpyrrole*)-α-*methyltrimethincyanine bromide* separated from ethyl acetate–ether in grass-green plates, m. p. 225° after softening at 215° (Found : C, 75·8; H, 5·3; N, 4·6. $C_{36}H_{29}N_2Br$ requires C, 75·9; H, 5·1; N, 4·9%). The same compound was obtained when 2 : 4-diphenylpyrrole (1·1 g.), acetone (0·35 c.c.), and 50% hydrobromic acid in acetic acid (0·81 c.c.) were warmed on the water-bath for 15 mins., and 2 : 4-diphenylpyrrole-5-aldehyde (1·25 g.) in acetic acid (10 c.c.) added. After 2 hrs. on the water-bath the green crystals were collected and washed with a little chloroform and then with much acetone to remove a little of the dipyrromethene. The residue crystallised from chloroform–acetone in green plates, m. p. 225° after softening at 215°, which gave no depression with the dye previously described (yield, 1·5 g.) (Found : C, 75·8; H, 5·1%). The light absorption (chloroform) of the two preparations was identical; max. 7050 A.

2 : 4-Diphenylpyrrole (2·2 g.), acetophenone (0·6 g.), acetic acid (3 c.c.), and 50% hydrobromic acid in acetic acid (0·81 c.c.) were warmed on the water-bath for 20 mins. Ethyl orthoformate (1·65 c.c.) was then added, and heating continued for 20 mins. more. After standing overnight, the solid was separated from the deep blue solution and washed with methanol to remove a small amount of the dipyrromethene. *Bis*-2-(3 : 5-*diphenylpyrrole*)-α-*phenyltrimethincyanine bromide* crystallised from chloroform in octahedra with a brass-like lustre, m. p. 245° (decomp.) (yield, 1·4 g.) (Found : C, 78·3; H, 5·0; N, 4·7. $C_{41}H_{31}N_2Br$ requires C, 78·0; H, 5·0; N, 4·4%). Light absorption (chloroform) : max. 7050 A.

Freshly distilled pyrrole (0·35 g.), acetone (0·35 c.c.), acetic acid (10 c.c.), and 50% hydrobromic acid in acetic acid (0·81 c.c.) were warmed together, 2 : 4-diphenylpyrrole-5-aldehyde (1·25 g.) in acetic acid (10 c.c.) then added, and the whole warmed gently on the water-bath for 2 hrs. 2-*Pyrrole*-2′-(3′ : 5′-*diphenylpyrrole*)-α-*methyltrimethincyanine bromide* (V*a*) separated when the intensely purple solution was poured into water. The dye, crystallised from methanol–ether, decomposed above 300° without melting (Found : C, 68·9; H, 4·9. $C_{24}H_{21}N_2Br$ requires C, 69·1; H, 5·1%); light absorption (chloroform), max. 6080 A.

2 : 3 : 4-Triphenylpyrrole (1·5 g.) was condensed with acetone (0·35 c.c.) in acetic acid (11 c.c.) containing hydrobromic acid (0·4 g.) for 5 minutes on a water-bath; 2 : 4-diphenylpyrrolealdehyde (1·25 g.) in acetic acid (10 c.c.) was added, and the solution warmed for 1 hour. The blue solution was poured into water, and the precipitated dye crystallised from methanol. 2-(3 : 4 : 5-*Triphenylpyrrole*)-2′-(3′ : 5′ : *diphenylpyrrole*)-α-*methyltrimethincyanine bromide* (V*c*) separated in green needles, m. p. 148° (Found : C, 78·1; H, 5·3. $C_{42}H_{33}N_2Br$ requires C, 78·1; H, 5·2%).

4-*Phenyl*-2-*methylpyrrole Cyanines.*—Ethyl 4-phenyl-2-methylpyrrole-3-carboxylate (2·3 g.) in boiling acetic acid (10 c.c.) was treated with ethyl orthoformate (1·65 g.) and 50% hydrobromic acid in acetic acid (0·8 c.c.). After 2 hours, the orange needles were collected, washed with acetic acid, and recrystallised from ethanol. *Bis*-2-(4-*carbethoxy*-3-*phenyl*-5-*methylpyrrole*)*monomethincyanine bromide* formed long oranges needles with a blue reflex, m. p. 196° (Found : C, 63·3; H, 5·3. $C_{29}H_{29}O_4N_2Br$ requires C, 63·4; H, 5·3%); light absorption (chloroform), max., 4890 A.

Ethyl 4-phenyl-2-methylpyrrole-3-carboxylate (1·15 g.), acetone (0·7 c.c.) and ethyl orthoformate (1·65 c.c.) were mixed with glacial acetic acid (3 c.c.) and treated with 50% hydrobromic acid in acetic acid (1 c.c.). After 12 hours the deep blue solution deposited a green felt of needles, which was collected and washed with methanol and with ether. *Bis*-2-(4-*carbethoxy*-3-*phenyl*-5-*methylpyrrole*)-α-*methyltrimethincyanine bromide* separated from formic acid in matted grass-green needles (0·5 g.), m. p. 198° (decomp.) (Found : C, 65·4; H, 5·8; N, 4·6. $C_{32}H_{33}O_4N_2Br$ requires C, 65·2; H, 5·6; N, 4·7%); light absorption (chloroform), max. 6090 A.

Bis-2-(4-*carbethoxy*-3-*phenyl*-5-*methylpyrrole*)-α-*ethyltrimethincyanine bromide*, obtained similarly from methyl ethyl ketone, formed matted green needles, m. p. 199°, separating from formic acid (Found : C, 65·9; H, 6·0. $C_{33}H_{35}O_4N_2Br$ requires C, 65·7; H, 5·9%); light absorption (chloroform), max. 6100 A.

By using an equivalent quantity of mesityl oxide in place of acetone, *bis*-2-(4-*carbethoxy*-3-*phenyl*-5-*methylpyrrole*)-α-iso*butenyltrimethincyanine bromide* was obtained; it separated in long green rods, m. p. 212°, from formic acid (Found : C, 66·9; H, 6·1. $C_{35}H_{37}O_4N_2Br$ requires C, 66·8; H, 5·9%); light absorption (chloroform), max. 6100 A.

Methylformanilide (12 c.c.) and phosphorus oxychloride (52 c.c.) were mixed and kept for 1 hour and then cooled to 0·5°. Ethyl 4-phenyl-2-methylpyrrole-3-carboxylate (21 g.) was slowly added, and the mixture stirred for 2 hours.

Decomposition with water gave 3-*carbethoxy*-4-*phenyl*-2-*methylpyrrole*-5-*aldehyde*, which separated in needles, m. p. 149°, from light petroleum (Found: C, 69·8; H, 5·8. $C_{15}H_{15}O_3N$ requires C, 70·0; H, 5·9%).

Ethyl 4-phenyl-2-methylpyrrole-3-carboxylate (1·15 g.) in acetic acid (5 c.c.) was treated with acetal (0·6 c.c.) and 50% hydrobromic acid in acetic acid (0·8 c.c.) at 20°. After 5 minutes the preceding aldehyde (1·3 g.) in acetic acid (5 c.c.) was added. On standing, green prisms of *bis*-2-(4-*carbethoxy*-3-*phenyl*-5-*methylpyrrole*)*trimethincyanine bromide*, m. p. 199°, appeared. The same compound was obtained by warming the same pyrrole (1·15 g.), β-ethoxyacraldehyde-acetal (0·45 g.), and 10% hydrobromic acid in acetic acid (6 c.c.). On standing the dye separated; it was washed with methanol and with ethyl formate and finally crystallised from formic acid to form prisms, m. p. 200°, giving no depression with the compound prepared previously (Found: C, 64·5; H, 5·3. $C_{31}H_{31}O_4N_2Br$ requires C, 64·3; H, 5·4%); light absorption (chloroform), max. 6010 A.

Pyrrole (0·35 g.), acetone (0·35 c.c.), and acetic acid (11 c.c.) containing hydrobromic acid (0·5 g.) were warmed together for 15 minutes, and the solution treated with 3-carbethoxy-4-phenyl-2-methylpyrrole-5-aldehyde (1·25 g.) in acetic acid (10 c.c.). After 2 hours on a water-bath the brilliant red solution was poured into water and 2-*pyrrole*-2′-(3′-*carbethoxy*-4′-*phenyl*-5′-*methylpyrrole*)-α-*methyltrimethincyanine bromide* (Vb) was collected. It had m. p. above 300° and was purified by solution in methanol and precipitation with ether (Found: C, 61·7; H, 5·5. $C_{22}H_{23}O_2N_2Br$ requires C, 61·8; H, 5·4%); light absorption (chloroform), max. 5060 A.

The same pyrrole (2·3 g.), acetophenone (1·2 g.), acetic acid (5 c.c.), and 50% hydrobromic acid in acetic acid (1·6 c.c.) were warmed on the steam-bath for 20 mins., and then treated with a further quantity of the pyrrole (2·3 g.), ethyl orthoformate (1·65 g.), and acetic acid (5 c.c.). A deep blue-green colour appeared at once and needles began to separate. After 12 hours these were collected and recrystallised from ethyl formate. *Bis*-2-(4-*carbethoxy*-3-*phenyl*-5-*methylpyrrole*)-α-*phenyltrimethincyanine bromide* separated in green needles, m. p. 202° (decomp.) (Found: C, 68·4; H, 5·5. $C_{37}H_{35}O_4N_2Br$ requires C, 68·2; H, 5·4%). Light absorption (chloroform): max. 6180 A.

When the same pyrrole (1·15 g.), β-naphthyl methyl ketone (0·8 g.), acetic acid (5 c.c.), ethyl orthoformate (1·5 c.c.) and 50% hydrobromic acid in acetic acid (1 c.c.) were brought together, vigorous reaction set in. The green crystalline product (1·0 g.) was recrystallised from ethyl formate. *Bis*-2-(4-*carbethoxy*-3-*phenyl*-5-*methylpyrrole*)-α-2′-*naphthyltrimethincyanine bromide* separated in needles, m. p. 186° (Found: C, 70·2; H, 5·4. $C_{41}H_{37}O_4N_2Br$ requires C, 70·2; H, 5·3%); light absorption (chloroform), max. 6210 A.

Bis-2-(4-*carbethoxy*-3-*phenyl*-5-*methylpyrrole*)-α-p-*methoxyphenyltrimethincyanine bromide*, prepared similarly from *p*-methoxyacetophenone, separated from formic acid in green needles, m. p. 210° (Found: C, 67·3; H, 5·4; N, 4·1. $C_{38}H_{37}O_5N_2Br$ requires C, 67·0; H, 5·4; N, 4·1%); light absorption (chloroform), max. 6200 A.

4-Phenyl-2-methylpyrrole (1·57 g.), acetophenone (0·6 g.), and 50% hydrobromic acid in acetic acid (0·8 c.c.) were mixed to a homogeneous product at 40°, and ethyl orthoformate (1·65 c.c.) added. On standing, a mixture of dark green octahedra and yellow prisms formed and was separated by washing with ethyl formate. The residual *bis*-2-(3-*phenyl*-5-*methylpyrrole*)-α-*phenyltrimethincyanine bromide*, crystallised from ethyl formate, had m. p. 221° (Found: C, 74·6; H, 5·1. $C_{31}H_{27}N_2Br$ requires C, 74·5; H, 5·1%); light absorption (chloroform), max. 6210 A.

2 : 4-Dimethylpyrrole (0·5 g.), acetophenone (0·6 g.), and 5% hydrobromic acid in acetic acid (10 c.c.) were warmed at 100° for 15 minutes and then treated with the same pyrrole (0·5 g.), acetic acid (5 c.c.), and ethyl orthoformate (1·65 g.). After warming for 2 hours, the blue solution was poured into water, and the dye collected and crystallised from toluene–light petroleum. *Bis*-2-(3 : 5-*dimethylpyrrole*)-α-*phenyltrimethincyanine bromide* formed black crystals with a copper-like sheen, m. p. above 300° (Found: C, 65·7; H, 6·1. $C_{21}H_{23}N_2Br$ requires C, 65·8; H, 6·05%); light absorption (chloroform), max. 5990 A.

Miscellaneous Pyrroles and their Derivatives.—ω-Amino-*p*-methoxyacetophenone hydrochloride (22·7 g.), anhydrous sodium acetate (15·4 g.), ethyl acetoacetate (16 c.c.), water (20 c.c.), and acetic acid (83 c.c.) were heated on the water-bath for 1 hour and then poured into ice-water (1 l.). The precipitate (20 g.) was crystallised from dilute ethanol and from light petroleum. *Ethyl* 4-*anisyl*-2-*methylpyrrole*-3-*carboxylate* formed needles m. p. 124°, which sublimed in a high vacuum (Found: C, 69·9; H, 6·9. $C_{15}H_{17}O_3N$ requires C, 69·5; H, 6·5%).

Pyrrole (6·7 g.), diphenylcarbinol (9·2 g.), and acetic acid (50 c.c.) were heated to boiling, and potassium hydrogen sulphate (13·6 g.) added. After the vigorous reaction, the product was cooled and crude 2-*diphenylmethylpyrrole* was collected; it was purified by distillation at 100° in a high vacuum and crystallisation from light petroleum, being then obtained in long columns, m. p. 267° (Found: C, 87·7; H, 6·35. $C_{17}H_{15}N$ requires C, 87·55; H, 6·5%).

ω-Chloro-β-acetonaphthone (75 g.) in chloroform (100 c.c.) was kept with hexamine (30 g.) in the same solvent (100 c.c.) for 1 day. The cream-coloured solid (80 g.) was collected and kept for 3 days with ethanol (500 c.c.) and concentrated hydrochloric acid (72 c.c.); ammonium chloride was then removed, and the filtrate evaporated to dryness. The residue was crystallised from hot water and finally from acetic acid to give ω-*amino*-β-*acetonaphthone hydrochloride*, m. p. 248° (Found: C, 65·1; H, 5·5. $C_{12}H_{12}ONCl$ requires C, 65·2; H, 5·4%).

The preceding amino-compound (11 g.) was heated for 1 hour on the steam-bath with anhydrous sodium acetate (4 g.), ethyl acetoacetate (6·5 g.), and acetic acid (100 c.c.) and then poured on ice. The precipitate was distilled in a high vacuum, and the distillate crystallised from light petroleum (b. p. 100—120°); *ethyl* 4-β-*naphthyl*-2-*methylpyrrole*-5-*carboxylate* formed needles, m. p. 114° (Found: C, 77·5; H, 6·3. $C_{18}H_{17}O_2N$ requires C, 77·4; H, 6·1%).

Ethyl 4-phenyl-2-methylpyrrole-3-carboxylate (1·2 g.) was ground with benzotrichloride (1·0 g.), and the mixture heated for 1 hour at 100°. The intense purple product was cooled and poured into water, and the solid triturated with aqueous ammonia and ethanol. The light base, *bis*-2-(4-*carbethoxy*-3-*phenyl*-5-*methylpyrrole*)-α-*phenylmonomethincyanine*, crystallised from ethanol in needles (0·5 g.), m. p. 226° (Found: C, 77·4; H, 5·9. $C_{35}H_{32}O_4N_2$ requires C, 77·3; H, 5·9%).

Ethyl 4-phenyl-2-methylpyrrole-3-carboxylate (11·5 g.) was stirred at 0° with ether (100 c.c.) and excess of dry sodium carbonate while bromine (2·5 c.c.) in a little ether was added dropwise; stirring was then continued for 15 mins., and the solution filtered and evaporated in a stream of nitrogen and eventually in a vacuum. The residue was crystallised repeatedly from light petroleum to give *ethyl* 5-*bromo*-4-*phenyl*-2-*methylpyrrole*-3-*carboxylate* as pale yellow octahedra, m. p. 120°, which readily blackened on standing in air or heating (Found: C, 54·7; H, 4·2. $C_{14}H_{14}O_2NBr$ requires C, 54·6; H, 4·6%).

Ethyl 4-phenyl-2-methylpyrrole-3-carboxylate (1·2 g.) in acetic acid (5 c.c.) at 50° was treated with 40% formalin (1 c.c.). After 1 hour the precipitate was collected and recrystallised from ethanol; *bis*-2-(4-*carbethoxy*-3-*phenyl*-5-*methylpyrryl*)*methane* formed slender needles (0·4 g.), m. p. 231° (Found: C, 74·0; H, 6·3. $C_{29}H_{30}O_4N_2$ requires C, 74·1; H, 6·4%).

Ethyl 4-phenyl-2-methylpyrrole-3-carboxylate (4·5 g.) in acetic acid (40 c.c.) was added as rapidly as possible to bromine (2·5 c.c.) in acetic acid (15 c.c.). After standing overnight, the purple solution was cooled until it was semi-solid, then filtered, and the acetic acid removed with cold water. The residual dye was chromatographed in chloroform on alumina and then precipitated from chloroform with light petroleum. 2-(3-*Carbethoxy*-4-*phenylpyrrole*)-2′-(3′-*carbethoxy*-4′-*phenyl*-5′-*methylpyrrole*)*monomethincyanine bromide* crystallised from light petroleum in red needles, m. p. 160° (decomp.);

it gave a bromine-free base on trituration with aqueous ammonia and an intensely yellow fluorescent solution in chloroform, especially in ultra-violet light (Found : C, 63·3; H, 5·1. $C_{28}H_{27}O_4N_2Br$ requires C, 62·9; H, 5·1%).

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