



solvents but dissolved in nitrobenzene or pyridine giving a magenta solution. Analysis suggested the formula  $C_{20}H_{14}O_2N_2$  which rules out the possibility of its belonging to the dipyrroazamethin class of dye. It is also readily prepared in low yield from  $\beta$ -benzoylpropionamide by a different method, and the proposed structure and mechanism of formation are discussed later. The non-identity of these dyes with dipyrroazamethins was disappointing, and work on the preparation of (II;  $R' = H$ ) was about to be abandoned when, by chance, an unusual reaction was observed. Whilst engaged on the preparation of various derivatives of the  $\beta$ -aroylpropionitriles (I;  $R' = H$ ) for their characterisation, difficulty was encountered in the formation of their oximes. Thus,  $\beta$ -benzoylpropionitrile (I;  $R = Ph$ ,  $R' = H$ ) failed to give an oxime with either hydroxylamine acetate or the base itself on refluxing in ethyl alcohol, most of the original nitrile being recovered unchanged. On refluxing an alcoholic solution of the nitrile with hydroxylamine hydrochloride, however, the mixture darkened and a brilliant blue coloration developed. When a large excess of the hydroxylamine salt was employed the dye crystallised during the refluxing, giving an almost solid mass of needles. The dye was slightly soluble in boiling water, the solution giving an immediate precipitation of silver chloride on addition of silver nitrate. It was soluble in alcohols, acetone, and pyridine. Analysis suggested the formula  $C_{20}H_{15}N_3 \cdot 2HCl$ . Its alcoholic solution when poured into water gave magenta flocks soluble in alcohol to a blue solution and which on purification gave a second blue dye of the formula  $C_{20}H_{15}N_3 \cdot HCl$ . Attempts to isolate the base were fruitless since, although it had some stability in solution, it readily decomposed on attempted isolation. The dye salts were very stable to boiling concentrated hydrochloric acid, dissolved in concentrated sulphuric acid to give a blue solution, and were reduced to a colourless leuco-compound by sodium dithionite. The leuco-compound was reoxidised by aerial oxygen to a blue dye. The salts did not sublime on heating under reduced pressure. Apart from the last property (which might be expected of the salts) the behaviour of these dyes is similar to that of Rogers's dye (II;  $R = R' = Ph$ ), and the analysis agrees well with their being the *dihydrochloride* and *monohydrochloride* of bis-2-(5-phenylpyrrole)azamethin (II;  $R = Ph$ ,  $R' = H$ ). Degradation experiments with hydriodic acid, and with an acetic anhydride-sodium acetate mixture which discharged the colour, did not lead to any definite products. Rogers (*loc. cit.*) proved the constitution of his dyes by an alternative synthesis which consisted in the condensation of 3:5-diphenylpyrrole with 2-nitroso-3:5-diphenylpyrrole. Nitrosation of 2-phenylpyrrole, however, either with nitrous acid or with alkaline amyl nitrite, failed to give a pure nitroso-derivative. The dark green solid obtained when employing nitrous acid gave a magenta dye on heating with 2-phenylpyrrole in acetic anhydride-acetic acid mixtures but not in sufficient quantities for isolation. Since 2-phenylpyrrole is readily converted into a magenta dye in the presence of mineral acids and acetic anhydride, it is possible that the green solid causes dye formation by virtue of its being a hydrochloride. Alternatively, if nitrosation occurs in the  $\beta$ -position, as is usual with pyrroles (cf. Fischer and Orth, "Die Chemie des Pyrrols," Vol. I, p. 104), the interaction of 4-nitroso-2-phenylpyrrole hydrochloride with 2-phenylpyrrole might well lead to a magenta dye. The structure of the dye was proved beyond reasonable doubt, however, by obtaining analogously bis-2-(3:5-diphenylpyrrole)azamethin (II;  $R, R' = Ph$ ) from  $\beta$ -benzoyl- $\alpha$ -phenylpropionitrile and hydroxylamine hydrochloride. The reaction proceeded best in boiling butanol to give the unstable dye salt, or in ethylene glycol at  $120^\circ$  to give the dye base. It was also found to proceed rapidly to give a low yield of dye on using formamide as solvent. The salt rapidly lost hydrogen chloride on contact with the atmosphere. The base had all the properties of the dye prepared according to Rogers (*loc. cit.*) and analysis confirmed the identity.

The instability of the new dye base may explain the non-formation of dye on heating  $\gamma$ -nitrobutyrophenone and ammonium formate (Rogers, *loc. cit.*), although further attempts at dye formation by this reaction in the presence of salts such as ammonium chloride or hydroxylamine hydrochloride also failed.

$\beta$ -Benzoylpropionitrile and hydroxylamine sulphate gave *bis-2-(5-phenylpyrrole)azamethin sulphate*.

The reaction was then applied to a variety of  $\beta$ -cyclopropionitriles in order to determine its scope. In every case  $\beta$ -aroylpropionitriles gave the required dye.  $\beta$ -2-Thienoylpropionitrile (I;  $R = 2-C_4H_3S$ ,  $R' = H$ ) gave the corresponding dye in low yield, but  $\beta$ -2-furoylpropionitrile and 2-benzofuryl 2-cyanoethyl ketone gave only brown solutions on similar treatment.

On heating  $\alpha$ -cyano- $\beta$ -benzoylpropionic acid (I;  $R = Ph$ ,  $R' = CO_2H$ ) with alcoholic hydroxylamine hydrochloride a blue, alkali-insoluble dye resulted. Its analysis, and physical



The precipitation of the dihydrochloride, which is more soluble in alcohol than the mono-hydrochloride, is difficult to explain, since it is unlikely that the dye is a stronger base than hydroxylamine.

Rogers (*loc. cit.*) found that 2-amino-3 : 5-diphenylpyrrole is readily oxidised to the azamethin, but such a mechanism for dye formation cannot be applied here, since no oxygen is present. He found also that 2-nitroso-3 : 5-diphenylpyrrole gives the azamethin on heating, and it is possible that (VIII) may also undergo self-condensation with the elimination of water and hydroxylamine.

All the dye salts gave similar blue solutions in organic solvents but differed in colour in the crystalline state. Striking differences, however, were shown in their behaviour towards concentrated sulphuric acid. The different colours given in hot and cold sulphuric acid and on precipitating the dye from the latter with water allow the identification of nearly all the dyes so far prepared (see Table I).

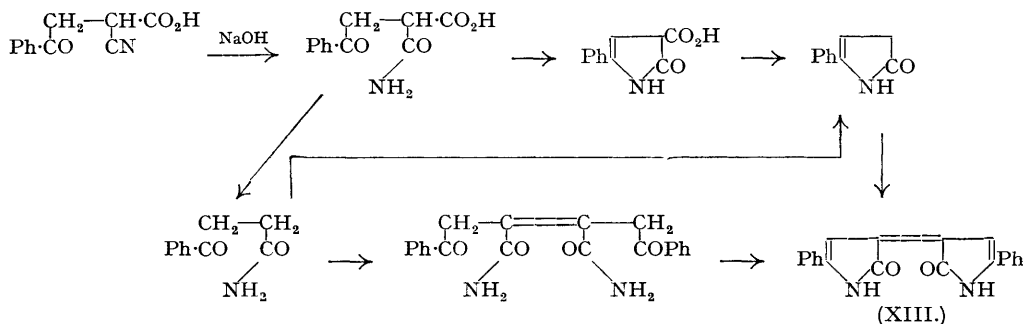
TABLE I.

II.	Cold H <sub>2</sub> SO <sub>4</sub> .	Addition to water.	Hot H <sub>2</sub> SO <sub>4</sub> .
R' = H, R =			
Phenyl .....	Blue *	Magenta	Green → yellow
<i>p</i> -Tolyl .....	Green	Blue	Yellow → brown
<i>p</i> -Chlorophenyl .....	Blue	Blue	Green → yellow → brown
<i>p</i> -Bromophenyl.....	Blue	Blue	Yellow → red-yellow
<i>p</i> -Hydroxyphenyl.....	Orange	Magenta	Red
<i>p</i> -Methoxyphenyl .....	Orange	Blue-green	Red
<i>m</i> -Hydroxyphenyl .....	Purple	Magenta	Blue → yellow
<i>m</i> -Methoxyphenyl .....	Purple → blue	Magenta	Blue → yellow
3 : 4-Dimethoxyphenyl .....	Orange	Blue	Brown → red → brown
1-Naphthyl .....	Yellow → purple → blue	Blue	Blue → green → yellow
2-Naphthyl .....	Green " " "	Blue	Blue " " "
2-Thienyl .....	Green " " "	Blue	Red " " "
R = R' = Phenyl .....	Blue	Blue	Green → yellow

\* Sulphate gave green solution.

As stated above, the dye obtained by Klobb from  $\alpha$ -cyano- $\beta$ -benzoylpropionic acid does not belong to the azamethin class. Apart from the analysis figures, the pale colour it gives in concentrated sulphuric acid is quite different from the deep colours given by (II). An alternative synthesis was found whilst experimenting with  $\beta$ -benzoylpropionamide with a view to the preparation of the dye observed on fusing the latter. Whereas alcoholic hydroxylamine salts did not give any dye on refluxing them with the amide, yet on replacing the alcohol by formamide and heating to 120° the latter reacted suddenly with the hydroxylamine hydrochloride (shown by separate experiment) with the evolution of ammonia, probably due to the formation of a hydroxamic acid (cf. Hoffmann, *Ber.*, 1889, **22**, 2854), and a secondary reaction caused the separation of a crystalline dye. The same dye was formed in very small amounts when the hydroxylamine hydrochloride was omitted. The dye had all the properties of Klobb's dye and analysis confirmed the identity.

Insufficient data have been collected on the dye to prove its structure, but it is suggested that it belongs to the isoindigotin class (cf. Wahl and Bagnard, *Bull. Soc. chim.*, 1909, **5**, 1039 ;



1914, **15**, 329). Analysis agrees with its being *bis-3-(2-keto-5-phenyl-2 : 3-dihydropyrrolylidene)* (XIII). Its formation from (I; R = Ph, R' = CO<sub>2</sub>H) can be explained by hydrolysis by

alkali to the amide, followed by cyclisation, decarboxylation, and oxidation, or by decarboxylation, oxidation, and cyclisation as shown. The hydroxylamine salt-formamide process involves oxidation at one stage and it is not clear how this takes place.

The same dye is also readily formed from  $\beta$ -benzoylpropionamide, acetamide, and hydroxylamine hydrochloride, and the  $\beta$ -benzoylpropionamide may be replaced by the acid or ester. Lævulic acid did not give any dye under similar conditions.

## EXPERIMENTAL.

(Microanalyses are by Drs. Weiler and Strauss, Oxford; m. p.s are uncorrected.)

*Bis-2-(5-phenylpyrrole)azamethin Dihydrochloride.*—(a)  $\beta$ -Benzoylpropionitrile (15.9 g., 0.1 mol.), hydroxylamine hydrochloride (28 g., 0.4 mol.), and industrial methylated spirit (150 c.c.) were refluxed for 2 hours. After the semi-solid reaction mixture had cooled, the dye was collected and washed well with acetone. The yield of crude solid (16.2 g.) was 87.7%. The filtrate gave hydroxylamine hydrochloride (10.1 g.) on concentration. If boiling butanol is used as the solvent a magenta dye is also formed. It is readily removed, however, by washing with acetone. The dye, recrystallised from pyridine, formed purple needles of no definite m. p. (Found: C, 64.4; H, 5.05; N, 11.2; Cl, 20.2.  $C_{20}H_{17}N_3Cl_2$  requires C, 64.85; H, 4.6; N, 11.35; Cl, 19.15%). The *monohydrochloride* was obtained as short needles from butanol or pyridine by pouring an alcoholic solution of the dihydrochloride into water (Found: C, 71.73; H, 4.8; N, 12.5; Cl, 10.5.  $C_{20}H_{16}N_3Cl$  requires C, 71.95; H, 4.8; N, 12.6; Cl, 10.65%). The *sulphate*, obtained in low yield (37%) from the nitrile and hydroxylamine sulphate, was very insoluble in most organic solvents. It was obtained as small bronze needles (Found: N, 10.5.  $C_{20}H_{17}O_4N_3S$  requires N, 10.65%).

(b)  $\alpha$ -Cyano- $\beta$ -benzoylpropionic acid hydrate (2.2 g., 0.01 mol.), hydroxylamine hydrochloride (1.4 g., 0.02 mol.), and industrial methylated spirit (10 c.c.) were refluxed for 90 minutes. The dye (1.0 g., 54%) was collected after cooling and recrystallised from pyridine. It formed alkali-insoluble purple needles (Found: C, 64.25; H, 5.0; N, 11.5%).

*Bis-2-(3:5-diphenylpyrrole)azamethin.*—(a)  $\beta$ -Benzoyl- $\alpha$ -phenylpropionitrile (4.7 g., 0.02 mol.), hydroxylamine hydrochloride (1.4 g., 0.02 mol.), and ethylene glycol (20 c.c.) were heated at 120° in an oil-bath for 2 hours. The dye separated as coppery crystals. These were collected when cold, and recrystallised from nitrobenzene forming short needles (0.3 g., 6.7%), m. p. 286° (Found: C, 84.9; H, 5.05; N, 9.5. Calc. for  $C_{32}H_{23}N_3$ : C, 85.5; H, 5.1; N, 9.4%). (b) With the same procedure as in (a) but using *n*-butyl alcohol (20 c.c.) as solvent and refluxing for 2 hours, the deep blue solution deposited the dye salt on chilling. The purple solid rapidly acquired a coppery sheen on standing in the atmosphere, owing to hydrolysis to the base (m. p. 286°) (1.2 g.; 26.7%). (c) The nitrile (4.7 g.), hydroxylamine hydrochloride (1.4 g.), and formamide (20 c.c.) were placed in an oil-bath at 120°. The temperature of the mixture rose to 90°, then with evolution of gas the temperature rose to 150° and the dye separated. It (0.8 g., 17.8%) was collected after dilution with alcohol, ground with alcohol, and washed with alcohol and water. It had m. p. 286° and was identical with the sample prepared according to (a).

TABLE II.

II; R' = H, R =	Yield, %	Solvent.	Crystal form.	Formula.	Analysis, %.	
					Found.	Requires.
<i>p</i> -Tolyl .....	49.8	Acetic acid	Short bronze needles	$C_{22}H_{21}N_3Cl_2$	N, 10.4	10.55
<i>p</i> -Bromophenyl.....	41.5	Acetic acid	Short gold-green needles	$C_{20}H_{15}N_3Cl_2Br_2$	N, 7.5	7.95
<i>p</i> -Chlorophenyl .....	55	Acetic acid	Fine purple needles	$C_{20}H_{15}N_3Cl_4$	N, 9.5	9.6
<i>p</i> -Hydroxyphenyl *	—	Pyridine	Short green needles	$C_{20}H_{17}O_2N_3Cl_2$	C, 60.05 H, 4.2 N, 10.9 Cl, 17.1	59.7 4.25 10.45 17.65
<i>p</i> -Methoxyphenyl ...	57	Pyridine	Short coppery needles	$C_{22}H_{21}O_2N_3Cl_2$	C, 60.65 H, 5.3 N, 9.55 Cl, 16.15	61.4 4.9 9.75 16.5
<i>m</i> -Hydroxyphenyl †...	40	Pyridine	Short green needles	$C_{20}H_{17}O_2N_3Cl_2$	N, 10.55	10.45
<i>m</i> -Methoxyphenyl ...	46.5	Acetic acid	Short coppery needles	$C_{22}H_{21}O_2N_3Cl_2$	N, 9.45	9.75
3:4-Dimethoxyphenyl	52	Pyridine	Coppery needles	$C_{24}H_{25}O_4N_3Cl_2$	N, 8.5	8.55
1-Naphthyl .....	44.5	Pyridine	Purple threads	$C_{28}H_{21}N_3Cl_2$	C, 71.55 H, 4.65 N, 9.15	71.5 4.45 8.95
2-Naphthyl .....	37	Pyridine	Purple needles	$C_{28}H_{21}N_3Cl_2$	N, 9.2	8.95
2-Thienyl .....	23	Acetic acid	Short green needles	$C_{16}H_{13}N_3S_2Cl_2$	N, 10.45 S, 16.35	11.0 16.8

\* Soluble in alkali to green solution.

† Soluble in alkali to blue solution.

*Hydroxylamine Hydrochloride and  $\beta$ -Benzoylpropionamide.*—The amide (7.08 g., 0.04 mol.), hydroxylamine hydrochloride (2.8 g., 0.04 mol.), and formamide (20 c.c.) were placed in an oil-bath at 120°. After a while the evolution of gas commenced and the dye separated rapidly. After 5 minutes the melt was diluted with alcohol, and the dye collected, and washed with alcohol until the washings were

colourless. It (0.5 g.) formed brassy, irregular plates from pyridine, in which it gives a magenta solution. It sublimed with some decomposition, giving red vapours. It was readily decolorised in pyridine solution with aqueous sodium dithionite (Found: C, 75.7; H, 4.6; N, 9.0.  $C_{20}H_{14}O_2N_2$  requires C, 76.45; H, 4.45; N, 8.9%).

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[Received, November 28th, 1946.]

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