156. 2 : 4-*Diarylpyrroles. Part I. Synthesis of* 2 : 4-*Diarylpyrroles and* 2 : 2′ : 4 : 4′-*Tetra-arylazadipyrromethines.*

By Maurice A. Thorold Rogers.

The intense blue colour formed when ketones of the type Ar·CH(CH_2·NO_2)·CH_2·$COAr^1$ (I) or Ar·CH(CN)·CH_2·$COAr^1$ (II) or some of their simple derivatives and related compounds are heated with ammonium formate or with certain other nitrogen-containing compounds has been shown to be due to the formation of 2 : 2′ : 4 : 4′-tetra-arylazadipyrromethines (III), which constitute a new chromophoric system, having a formal relationship to the phthalocyanines. (III, Ar = Ar^1 = Ph) has been shown to have the structure assigned to it by degradation with hydriodic acid to 2 : 4-*diphenylpyrrole* (IV, Ar = Ar^1 = Ph), which is capable of reconversion into (III, Ar = Ar^1 = Ph) by nitrous acid, *via* 5-*nitroso*-2 : 4-*diphenylpyrrole* (V, Ar = Ar^1 = Ph), which condenses with a further molecule of (IV, Ar = Ar^1 = Ph).

(V, Ar = Ar^1 = Ph) has been reduced catalytically to give 5-*amino*-2 : 4-*diphenylpyrrole* (VII, Ar = Ar^1 = Ph), which differs from the known 3-amino-2 : 4-diphenylpyrrole (VIII).

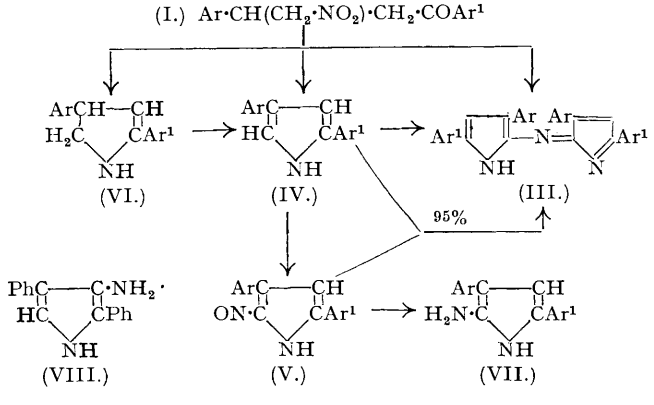
Certain metallic complexes of (III, Ar = Ar^1 = Ph) and a few analogues of types (III) and (IV) are described.

In the course of experiments made with the object of synthesising the compound

Ph·CH(CH_2·NO_2)·CH_2·CHPh·NH_2,

the action of ammonium formate and formamide on the nitrobutyrophenone Ph·CH(CH_2·NO_2)·CH_2·COPh (I, Ar = Ar^1 = Ph) (Kohler, *J. Amer. Chem. Soc.*, **1916**, **38**, 889) was tried, the conditions of the Leuckart reaction (Ingersoll, Brown, Kim, Beauchamp, and Jennings, *ibid.*, **1936**, **58**, 1808) being used. In place of the expected formyl derivative of the amine there was formed an intensely blue compound. The nitrobutanone was heated with 3—5 times its weight of formamide (under reflux) or ammonium formate (under distillation conditions) to 180—200°, at which temperature it was maintained for a further ¼ hour. The first sign of colour appeared at about 120°, the oily droplets of the nitrobutanone acquiring a blue tint; this rapidly increased in intensity, and after 5—10 minutes' boiling the surface of the liquid acquired a coppery sheen, due to the separation of the blue material in crystalline form. After cooling, the melt was extracted with alcohol, leaving a dark microcrystalline powder, which was purified by crystallisation from nitrobenzene or β-ethoxyethyl alcohol. Analysis suggested the formula $C_{32}H_{23}N_3$. Molecular weight determinations eliminated the possibility of a molecule of double this weight.

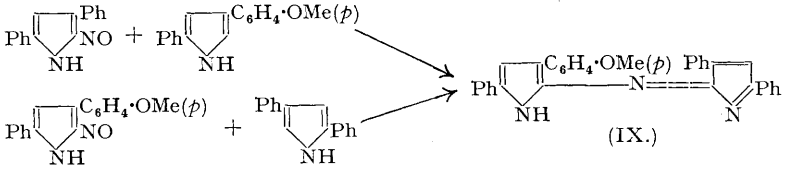
Interest in the new blue compound was enhanced by two observations: (1) its stability was such that it could be sublimed with little decomposition merely by heating at atmospheric pressure, giving violet vapours which condensed on a cool surface to yield the original blue compound; (2) a solution of the blue compound in moist dioxan, pyridine or β-ethoxyethyl alcohol was reduced by alkaline sodium hydrosulphite to a nearly colourless leuco-compound, which was readily reoxidised by air to the original material. The high melting point (287—288°) and intense colour of the material and its tendency to sublime near the melting point made mixed melting points unreliable, and identity of samples was established by the reproducibility of the two phenomena just referred to; by the formation of characteristic short needles when a β-ethoxyethyl-alcoholic solution was allowed to evaporate on a microscope slide; by the appearance of the solution in, for example, nitrobenzene, which was deep blue to reflected, but intense crimson to transmitted light; and finally by the bleaching of the colour when a solution in pyridine was boiled for ¼—½ hour with hydroxylamine hydrochloride (a reaction which will be discussed in a later paper).



Experiments conducted to establish the structure of this compound, consisting of variations of one or other of the constituents of the melt process, eliminated some possibilities, but failed to show the actual structure, which was proved to be 2 : 2′ : 4 : 4′-*tetraphenylazadipyrromethine* (III, Ar = Ar^1 = Ph) by the following steps: on boiling with 55% hydriodic acid, the blue compound was decomposed to a colourless compound, $C_{16}H_{13}N$, which was also isolated in small yield as a by-product in the ammonium formate reaction. That this compound was 2 : 4-*diphenylpyrrole* (IV, Ar = Ar^1 = Ph) was shown by its preparation from the

pyrroline (VI, Ar = Ar¹ = Ph) (Sonn, *Ber.*, 1935, **68**, 148; Rupe and Gisiger, *Helv. Chim. Acta*, 1925, **8**, 338) by selenium dehydrogenation. Nitrosation of pyrroles usually occurs in the β-position (cf. Fischer and Orth, "Die Chemie des Pyrroles," vol. I, p. 104), but 2 : 4-diphenylpyrrole was nitrosated readily by the action of nitrous acid in the α-position, for reduction (catalytic) of the nitroso-compound (V, Ar = Ar¹ = Ph) gave an aminopyrrole (VII, Ar = Ar¹ = Ph) which differed from the known 3-amino-2 : 4-diphenylpyrrole (VIII) (Gabriel, *Ber.*, 1908, **41**, 1138; Gabriel did not consider the constitution of his 3-amino-compound as proved, but the investigations described in Part III leave no doubt that his formula is correct), and was therefore considered to be the 5-*amino*-compound. This 5-*nitroso*-2 : 4-*diphenylpyrrole* (V, Ar = Ar¹ = Ph) condensed readily with a further molecule of 2 : 4-diphenylpyrrole (IV, Ar = Ar¹ = Ph) to give high yields of the blue compound (III, Ar = Ar¹ = Ph).

There remains only the remote possibility that the compound is asymmetric, the α-nitroso-compound condensing with the β-position of the second molecule of the diarylpyrrole. That this was not the case was shown by preparing the methine (IX) by the two routes shown; the identity of the two preparations was established by examination of the *X*-ray diffraction patterns.



(IX.)

The formation of (III) from the nitrobutyrophenones (I) or from the cyano-ketones Ar·CH(CN)·CH_2·COAr¹ (II) constitutes a remarkable reaction, the mechanism of which will be discussed in a later communication. The reaction is not appreciably affected by substituents in either of the aryl nuclei; the azamethines listed in Table I have been prepared.

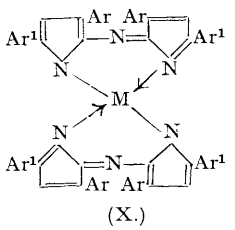
TABLE I.

Reaction of ammonium formate on compounds (I) *and* (II).

(I).		(II).		Azamethine (III).	
Ar.	Ar.¹	Ar.	Ar¹.	M. p.	Reflex colour of crystals.
C_6H_4·NO_2(*m*)	Ph	—	—	330°	Bright green
C_6H_4·OH(*m*)	Ph	—	—	304—306	Violet
C_6H_4·NMe_2(*p*)	Ph	—	—	276—278	Copper
C_6H_3·O_2CH_2(3 : 4)	—	—	—	258—259	Copper-brown
Ph	C_6H_4·OMe(*p*)	Ph	C_6H_4·OMe(*p*)	239—242	Dull blue
C_6H_4·OMe(*p*)	Ph	C_6H_4·OMe(*p*)	Ph	288—290	Bright green
C_6H_4·OMe(*p*)	C_6H_4·OMe(*p*)			281—282	Bluish-copper
		C_6H_4·NHAc(*p*)	Ph	(*ca.*) 370°	Dull violet

These azamethines are very similar in colour in solution, but the reflex colour of the crystals varies over a wide range. Where the substituent is salt-forming, the azamethine shows some water solubility at the appropriate pH," and the dimethylamino-substituted azamethine gives a water-soluble quaternary salt with methyl iodide. The majority of the substituted azamethines have lower solubility than the parent compound.

The reaction calls to mind the " urea melt " process of B.P. 464,126, in which metal phthalocyanines are made by heating phthalic anhydride and a metal salt with urea [urea does actually give some azamethine when fused with (I)]. Indeed, the azamethine bears a certain formal relationship to phthalocyanine, which is an azaporphyrin. The resemblance to phthalocyanines is further pointed by the formation from the azadipyrromethines of metallic complexes, which give analytical figures agreeing well with structure (X). *Zinc, copper, nickel* and *cobalt* complexes have been made, and it is noteworthy that, whereas the compound (III) is not fast to light when rubbed out as a print, the copper complex (X, M = Cu) has an excellent light fastness, being equal to Prussian-blue in this respect. A similar disparity is shown between metal-free phthalocyanine and its copper complex.



(X.)

No earlier examples of the azadipyrromethine series appear to have been made and the system constitutes a new chromophore. The ease of formation and stability seem largely to be accounted for by the reactivity conferred on the α-position by the two suitably placed phenyl groups. There does not seem to be any corresponding increase in reactivity of the β-position, and it is noteworthy that, whereas 3-amino-2 : 4-diphenylpyrrole (Gabriel, *loc. cit.*) is a stable compound, the corresponding 5-amino-compound (VII, Ar = Ar¹ = Ph) is very reactive, and is readily oxidised by air, tetraphenylazadipyrromethine being among the products.

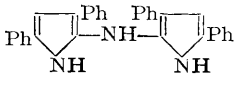
The isolation of the two " halves " of the azamethine makes available two new reactive systems capable of reacting with a wide variety of substances: 5-nitroso-2 : 4-diphenylpyrrole (V, Ar = Ar¹ = Ph) with compounds which contain a reactive methylene group and 2 : 4-diphenylpyrrole itself with compounds which normally react with reactive methylene groups. Examples of such condensations, which occur in acetic acid–acetic anhydride, are given in the following paper.

Attention has been directed to the preparation of 2 : 4-diphenylpyrrole in good yield; β-benzoyl-α-phenylpropionitrile, which can be made in yields of 96% by the method of Allen and Kimball (*Org. Synth.*, Vol. X, 80), can be reduced to 2 : 4-diphenylpyrroline catalytically with Raney nickel in yields exceeding 95% (compare Rupe and Gisiger, *Helv. Chim. Acta*, 1925, **8**, 338). The selenium dehydrogenation of 2 : 4-diphenylpyrroline, already referred to, presents some unusual features; only traces of hydrogen selenide are evolved and the bulk of the selenium can be recovered unchanged at the end of the reaction, which is quite rapid at 250°. No other examples of selenium-catalysed dehydrogenations have been traced. Yields higher than 55% could not be obtained, owing to the formation of by-products, among them a hydrocarbon, which is probably $CHPhMe{\cdot}CH_2{\cdot}CH_2Ph$. The mechanism of the formation of this compound is obscure, but the missing nitrogen atom can be detected as ammonia in the issuing gases. Dehydrogenation can also be effected with Raney nickel in the liquid phase (350°); again the yield is 55%, and ammonia is evolved. A more satisfactory process for the dehydrogenation of the pyrroline has been worked out by my colleague Dr. P. V. Youle, who obtained yields exceeding 80% by passing the pyrroline over a nickel catalyst on a pumice substrate at 350°.

Syntheses of 2 : 4-diarylpyrroles with substituents in the aryl nuclei proceed satisfactorily by this series of reactions, and 2-*phenyl*-4-p-*anisylpyrrole* (IV; Ar^1 = Ph, Ar = $C_6H_4{\cdot}OMe$) and 4-*phenyl*-2-p-*anisylpyrrole* (IV; Ar = Ph, Ar^1 = $C_6H_4{\cdot}OMe$) have thus been made.

2 : 4-Diphenylpyrrole is a very weak base, but its 5-nitroso-derivative is a relatively strong base, forming salts with strong acids. The free base is a typical green nitroso-compound, which causes dermatitis in some subjects.

Tetraphenylazadipyrromethine is slightly basic; it forms a perchlorate which can be isolated, but dissociates rapidly in solution. The nature of the unstable reduction products obtained by treating the azamethine with various reducing agents is obscure. When the pigment, *e.g.*, in aqueous dioxan, is treated with an alkaline solution of glucose, a red reduction product is obtained, which is readily reoxidised in air. This red " leuco "-compound is further reduced by sodium hydrosulphite to a substance with a pale yellowish-pink colour, which is also obtained direct from the azamethine by hydrosulphite. The oxidation, even when the reduction has been carried out by hydrosulphite alone, can frequently be observed to pass through a red stage. Dilution with water at the colourless stage precipitates a white solid, which rapidly becomes blue when exposed to the air. The view is held that the glucose reduction product is the true leuco-compound (annexed formula) and the hydrosulphite reduction product is an addition complex with the reducing agent. The metallic complexes can also be reduced to colourless leuco-compounds, but the metal atom is removed by the process.



This work is the subject of pending patent applications.

Experimental.

Analyses by Mr. E. S. Morton. M. p.'s are uncorrected.

A. *Tetra-arylazadipyrromethines by the Ammonium Formate Melt Process.*—2 : 2′ : 4 : 4′-*Tetraphenylazadipyrromethine* (III, Ar = Ar^1 = Ph). γ-Nitro-β-phenylbutyrophenone (Kohler, *loc. cit.*) (150 g.) and ammonium formate (430 g.) were heated during ¼ hr. to 180°, and then at 190° for a further ¼ hr. Ammonia was evolved, followed, suddenly, at 180°, by formic acid (condensate decolourised potassium permanganate) and a little solid, probably diphenylpyrrole, steam-distilled out of the flask. After cooling to 70°, the mixture was triturated with methyl alcohol, the liquid filtered, and the residue washed thoroughly with methyl alcohol, the total filtrates being worked up as described below, and dried at 100° (54 g.). Recrystallisation from nitrobenzene gave short, dark copper-coloured needles (32 g., with a further 8·7 g. from the filtrate by concentration). The uncrystallised material probably contained other strongly coloured compounds, not isolated by any method tried (including chromatographic analysis).

The *azamethine* was very sparingly soluble in water, methyl or ethyl alcohol (very pale blue-violet colour), and petrol; addition of a drop of a strong acid to an alcoholic suspension produced a deep greenish-blue solution, from which the azamethine was reprecipitated by alkali. It was slightly soluble in hot butanol, benzene or acetone, more soluble in hot nitrobenzene, β-ethoxyethyl alcohol, xylene, pyridine, dioxan, formodimethylamide or camphor. It was also readily soluble in cold concentrated sulphuric acid, being reprecipitated unchanged if the solution was diluted immediately, but if it was kept for 2—3 hours and then poured on ice, a clear olive-green solution was obtained, which on boiling deposited a brilliant green powder; this contained sulphur, was soluble in dilute alkali and ammonia, to a pale olive-green solution, and was reprecipitated by acids. The azamethine sublimed without decomposition at 5 mm. and with slight decomposition at atmospheric pressure; the vapours were violet. M. p. 287—288° [Found: C, 85·65; H, 4·9; N, 9·35; *M* (Menzies–Wright differential method, using benzene), 430, 460. $C_{32}H_{23}N_3$ requires C, 85·5; H, 5·1; N, 9·4%; *M*, 449].

2 : 4-*Diphenylpyrrole from the ammonium formate reaction.* The permanganate-coloured methanol extract from the previous experiment was poured into water and the solid was collected, dried, and dissolved in benzene (charcoal). The filtered solution was concentrated until, on cooling, solid crystallised; this was collected, and the concentration and crystallisation of the filtrate repeated. The combined solids were dissolved in ethyl alcohol (charcoal), filtered, and fractionally precipitated by the addition of water. The first fraction was blue (m. p. 172°) and was discarded. The main fraction, after drying, crystallised from benzene in long, white, flattened needles (0·62 g.), m. p. 178—179°, identical with 2 : 4-diphenylpyrrole prepared synthetically.

2 : 2′-*Diphenyl*-4 : 4′-*di*-(m-*nitrophenyl*)*azadipyrromethine* (III; Ar = $C_6H_4{\cdot}NO_2$, Ar^1 = Ph). 3-Nitrochalkone (Sorge, *Ber.*, 1902, **35**, 1068) (25·3 g.) was dissolved in hot methyl alcohol (200 c.c.), cooled to 35°, nitromethane (9·1 g.) added, a solution of sodium (3·45 g.) in methyl alcohol (100 c.c.) run in and the mixture warmed on the steam-bath under reflux for 10 minutes. The cooled solution (0°) was acidified with acetic acid (20 c.c.); the precipitated oil rapidly solidified. Crystallised from methyl alcohol, γ-*nitro*-β-(m-*nitrophenyl*)*butyrophenone* formed needles, m. p. 74—77° (Found: N, 9·05. $C_{16}H_{14}O_5N_2$ requires N, 8·95%). This nitro-ketone (10 g.) was heated with ammonium formate (30 g.) to 180° during ¼ hr. The cooled melt was extracted with alcohol, and the residual greenish solid crystallised

from nitrobenzene; the *azamethine* formed needles with a bright green reflex (2·8 g.), m. p. 330° (Found: C, 71·15; H, 4·05; N, 13·05. $C_{32}H_{21}O_4N_5$ requires C, 71·25; H, 3·9; N, 13·0%). It was less soluble than the parent azamethine. It was reduced by sodium hydrosulphite in aqueous dioxan to a pink leuco-compound.

2 : 2′-*Diphenyl*-4 : 4′-*di*-(m-*hydroxyphenyl*)*azadipyrromethine* (III; Ar = C_6H_4·OH, Ar^1 = Ph). 3-Hydroxychalkone (Bablich and Kostanecki, *Ber.*, 1896, **29**, 235) (22·4 g.) in methyl alcohol (100 c.c.), nitromethane (9·1 g.), and a solution of sodium (6·9 g.) in methyl alcohol (20 c.c.), added during 1 hour, gave a deep yellow solution. Ice (200 g.) was added and the solution was cooled to − 5° and acidified with acetic acid (20 c.c.). Addition of water precipitated an oil, which was extracted in ether, dried (calcium chloride), and recovered. It slowly solidified, forming hard prisms, but some oily material remained. A sample was pressed on a porous tile and recrystallised from benzene, from which *γ-nitro-β-*(m-*hydroxyphenyl*)*butyrophenone* separated very slowly in pale yellow-brown prisms, m. p. 96—98° (Found: C, 67·7; H, 5·0; N, 4·95. $C_{16}H_{15}O_4N$ requires C, 67·35; H, 5·25; N, 4·9%). The crude oily nitrobutyrophenone was heated to 160° with ammonium formate (5 parts). Colour formation was very rapid. The residual *azamethine* after alcohol extraction crystallised from nitrobenzene in short needles with a violet reflex, m. p. 304—306° (Found: C, 79·6; H, 4·8; N, 8·85. $C_{32}H_{33}O_2N_3$ requires C, 79·8; H, 4·8; N, 8·7%). A paste with dioxan, treated with a little 2N-sodium hydroxide and diluted with water, gave a deep blue aqueous solution, which was reduced reversibly to a colourless solution with sodium hydrosulphite.

2 : 2′-*Diphenyl*-4 : 4′-*di*-(p-*dimethylaminophenyl*)*azadipyrromethine* (III; Ar = C_6H_4·NMe_2, Ar^1 = Ph). Into 4-dimethylaminochalkone (MacLean and Widdows, J., 1914, **105**, 2173) (10 g.), methyl alcohol (100 c.c.), and nitromethane (3·6 g.), heated to solution and cooled to 25°, was run a solution of sodium (1·4 g.) in methyl alcohol (50 c.c.); the mixture was refluxed for 1 hour on the steam-bath, cooled to 5°, and acidified with acetic acid (5 c.c.). The yellow oil obtained rapidly solidified and after crystallisation from alcohol *γ-nitro-β-*(p-*dimethylaminophenyl*)*butyrophenone* (8·5 g.) separated in pale yellow needles, m. p. 114—115° (Found: N, 9·25. $C_{18}H_{20}O_3N_2$ requires N, 9·0%). The *oxime* crystallised from alcohol in colourless needles, m. p. 121—123° with formation of a yellow liquid (Found: N, 13·05. $C_{18}H_{21}O_3N_3$ requires N, 12·85%). The nitrobutyrophenone, on heating with ammonium formate (5 parts), gave the *azamethine*, which separated from β-ethoxyethyl alcohol in flat needles with curved edges, with a bright coppery reflex, m. p. 276—278° (Found: C, 80·8; H, 6·05; N, 12·7. $C_{36}H_{35}N_5$ requires C, 80·45; H, 6·5; N, 13·0%). It was slightly soluble in dilute acids. On standing with methyl iodide in nitrobenzene solution for 24 hours, it formed a *dimethiodide*, which was soluble in water and in alcohol to form deep blue solutions, and insoluble in acetone (Found for the ether-washed product: N, 8·75; I, 29·25. $C_{38}H_{39}N_5I_2$ requires N, 8·55; I, 31·0%). The quaternary salt is a wool dye.

2 : 2′-*Diphenyl*-4 : 4′-*di*-(3 : 4-*methylenedioxyphenyl*)*azadipyrromethine* (III; Ar = $C_6H_3{:}O_2CH_2$, Ar^1 = Ph). γ-Nitro-β-(3 : 4-methylenedioxyphenyl)butyrophenone (50 g.), obtained as an oil (Kohler and Drake, *J. Amer. Chem. Soc.*, **1923**, **45**, 2144, give m. p. 95—96°), was heated with ammonium formate (75 g.) as previously described. After extraction of the melt with alcohol and crystallisation of the residue from β-ethoxyethyl alcohol, the *azamethine* was obtained in copper-brown needles, m. p. 258—259° (Found: C, 75·9; H, 4·25; N, 7·9. $C_{34}H_{23}O_4N_3$ requires C, 76·0; H, 4·3; N, 7·8%).

2 : 2′-*Di*-p-*anisyl*-4 : 4′-*diphenylazadipyrromethine* (III; Ar = Ph, Ar^1 = C_6H_5·OMe). Into benzylidene-*p*-methoxyacetophenone (Stockhauser and Gattermann, *Ber.*, 1892, **25**, 3536) (23·8 g.) and nitromethane (9·2 g.) in methyl alcohol (100 c.c.) was run sodium (3·0 g.) in methyl alcohol (100 c.c.); the mixture was warmed at 50° for ½ hour, cooled, and acidified with acetic acid, and water added. *γ-Nitro-β-phenyl*-p-*methoxybutyrophenone* separated slowly in prisms or thick plates, m. p. 92—93° after recrystallisation from alcohol (Found: C, 68·15; H, 5·7; N, 4·65. $C_{17}H_{17}O_4N$ requires Cl, 68·2; H, 5·7; N, 4·7%). The *azamethine*, prepared from it by heating with ammonium formate, formed dull blue, broad flat needles or plates with a tendency to show curved edges, m. p. 239—242° (Found: C, 79·65; H, 5·05; N, 8·3. $C_{34}H_{27}O_2N_3$ requires C, 80·1; H, 5·3; N, 8·2%).

2 : 2′-*Diphenyl*-4 : 4′-*di*-p-*anisylazadipyrromethine* (III; Ar = C_6H_4·OMe, Ar^1 = Ph). 4-Methoxychalkone was converted into *γ-nitro-β-*p-*anisylbutyrophenone* by the method described for the isomeric compound (above). It was crystallised with difficulty from alcohol and then from benzene; m. p. 66° after previous sintering (Found: C, 67·45; H, 5·45; N, 4·5. $C_{17}H_{17}O_4N$ requires C, 68·2; H, 5·7; N, 4·7%). The *azamethine* crystallised from nitrobenzene in large needles with a bright greenish metallic reflex, m. p. 288—290° (Found: C, 79·7; H, 5·7; N, 8·55. $C_{34}H_{27}O_2N_3$ requires C, 80·15; H, 5·3; N, 8·25%). From the alcoholic filtrates of the ammonium formate melt process a little 2-phenyl-4-*p*-anisylpyrrole was obtained, which crystallised from benzene in silvery plates, m. p. 198—200°, identical with a synthetic specimen.

2 : 2′ : 4 : 4′-*Tetra*-p-*anisylazadipyrromethine* (III, Ar = Ar^1 = C_6H_4·OMe). To anisylidene-*p*-methoxyacetophenone (Stauss, *Annalen*, 1910, **374**, 139) (52 g.) and nitromethane (18·5 g.) in methyl alcohol (500 c.c.) was added sodium (7·1 g.) in methyl alcohol (220 c.c.). When reaction was complete, and the temperature began to fall, the mixture was cooled below 0° and acidified with acetic acid. The oil obtained on addition of water was extracted with ether and dried over calcium chloride, and the ether distilled; γ-nitro-β-anisyl-*p*-methoxybutyrophenone was left as an oil. The *azamethine* made from it crystallised from pyridine in flat bluish-coppery needles, m. p. 281—282° (Found: C, 76·2; H, 5·6. $C_{36}H_{31}O_4N_3$ requires C, 75·95; H, 5·5%).

2 : 2′-*Diphenyl*-4 : 4′-*di*-(p-*acetamidophenyl*)*azadipyrromethine* (III; Ar = C_6H_4·NHAc, Ar^1 = Ph). *p*-Acetamidochalkone was made by condensing *p*-acetamidobenzaldehyde and acetophenone in alcohol with sodium hydroxide as catalyst. It had m. p. 180—182° (cf. Kauffman and Burckhardt, *Ber.*, 1913, **46**, 3811). The chalkone (34·4 g.) in methyl alcohol (500 c.c.) and powdered sodium cyanide (25·5 g.) were heated under reflux, and a mixture of acetic acid (24 c.c.) and water (65 c.c.) run in during 20 mins. After a further 20 mins.' boiling, the solution was cooled and poured into ice and water, and the white solid collected and washed until the filtrate was free from cyanide; *β-benzoyl-α-*(p-*acetamidophenyl*)*propionitrile* formed very pale yellow prisms or needles (12·2 g.), m. p. 163—164·5°, from ethanol (Found: C, 73·9; H, 5·4; N, 9·6. $C_{18}H_{16}O_2N_2$ requires C, 74·0; H, 5·5; N, 9·6%). When heated with ammonium formate for 10 minutes at 190°, the nitrile gave the *azamethine*, which formed dull violet needles, m. p. *ca.* 370°, from nitrobenzene (Found: C, 76·6; H, 5·05; N, 12·6. $C_{36}H_{29}O_2N_5$ requires C, 76·7; H, 5·15; N, 12·4%).

B. *Metallic Complexes of the Azamethines.—Copper bis-*(2 : 2′ : 4 : 4′-*tetraphenylazadipyrromethine*) (X) was obtained by refluxing the azamethine (1·0 g.) and copper acetate (0·5 g.) in butyl alcohol (50 c.c.) for ½ hour. The coppery-brown precipitate (1·0 g.), which appeared as minute, diamond-shaped prisms under the microscope, crystallised from formodimethylamide in well-formed prisms (Found: C, 80·1; H, 4·4; N, 8·75; Cu, 6·5. $C_{64}H_{44}N_6Cu$ requires C, 80·05; H, 4·6; N, 8·75; Cu, 6·6%). The complex was somewhat soluble in nitrobenzene, dioxan and pyridine, but less soluble than the azamethine in butyl alcohol and β-ethoxyethyl alcohol. The solutions were blue to transmitted light, in contrast to the crimson colour of solutions of the azamethine. *Cobalt bis-*(2 : 2′ : 4 : 4′-*tetraphenylazadipyrromethine*), from the azamethine and cobalt acetate in butyl alcohol, was not readily crystallised; it was dissolved in nitrobenzene, and the filtered solution concentrated to small volume. The complex formed small hexagonal prisms (Found: C, 78·95; H, 4·55; N, 9·1; Co, 5·9. $C_{64}H_{44}N_6Co$ requires C, 80·4; H, 4·6; N, 8·8; Co, 6·2%). The *nickel* (Found: C, 80·95; H, 4·6; N, 9·15; Ni, 6·3. $C_{64}H_{44}N_6Ni$ requires C, 80·4; H, 4·6; N, 8·8; Ni, 6·2%) and the *zinc*

complex (Found: C, 80·0; H, 4·75; N, 8·65; Zn, 7·1. $C_{64}H_{44}N_6Zn$ requires C, 79·9; H, 4·6; N, 8·7; Zn, 6·8%) were prepared.

C. 2 : 4-*Diarylpyrroles*.—2 : 4-*Diphenylpyrrole* (IV, Ar = Ar¹ = Ph). β-Benzoyl-α-phenylpropionitrile (120 g.), suspended in methyl alcohol or ethyl acetate (800 c.c.), and Raney nickel (about 20 g.) were shaken rapidly in a hydrogenator at atmospheric temperature and pressure. If less catalyst was used, reduction was very slow; if more, reduction tended to continue, with no very noticeable break in the curve, to the pyrrolidine, recognised as its phenylthiourea (Rupe and Gisiger, *loc. cit.*). When the theoretical amount of hydrogen had been absorbed (23 l.), the solution was filtered, and the solvent distilled. The residue was distilled in a vacuum, giving 2 : 4-diphenylpyrroline, m. p. about 40°; yield, 105 g. (95%). Rupe and Gisiger obtained 15—16 g. from 30 g. of the nitrile.

Dehydrogenation. (a) Traces of the pyrrole were obtained on prolonged heating of the pyrroline at 350°. (b) The pyrroline (5·0 g.) was heated with selenium (5·0 g.) in a Kjeldahl flask fitted with an inlet tube reaching to just above the surface of the contents, through which a very slow stream of nitrogen or carbon dioxide was passed. The flask was heated at 250° for 3 hours and the issuing vapours were passed into lead nitrate solution. On cooling, the pyrrole solidified on the button of selenium as a light grey solid, and was extracted with hot toluene. The residual selenium weighed 4·5 g., and from the lead selenide solution 0·43 g. of lead selenide was obtained. From the toluene extract 2·7 g. (55%) of 2 : 4-diphenylpyrrole were obtained. When the experiment was conducted on a larger scale (the lead nitrate solution was dispensed with when the experiment was conducted for purely preparative purposes) there was obtained from the toluene mother-liquors by repeated concentration and crystallisation a small oily residue, which was distilled in a vacuum, b. p. 175°/17 mm., 228°/760 mm., giving a colourless oil with a pleasant smell. This b. p. accords reasonably well with that given by Stobbe and Posnjak (*Annalen*, 1909, **371**, 297) for αγ-diphenylbutane and analysis also suggests this structure (Found: C, 91·05; H, 8·2; N, 0·5. Calc. for $C_{16}H_{18}$: C, 91·4; H, 8·6%). (c) *By Raney nickel* (liquid phase). This was carried out as in (b) except that the temperature was maintained at 350°. Yields were of the order of 50%, and the toluene portion had the same sweet smell as had the αγ-diphenylbutane isolated from the selenium dehydrogenation. (d) *Vapour phase dehydrogenation* (P. V. Youle). Various catalysts were tried, each held in a Pyrex tube (3 cm. in diameter, 30 cm. long) heated in an electric furnace. The best results were obtained from a nickel-on-pumice catalyst, made by igniting pumice fragments (16—32 mesh) impregnated with nickel nitrate. Before use the catalyst was reduced with hydrogen at 400—450°. At 350°, diphenylpyrroline was passed over the reduced catalyst (2 mols./hr./l. catalyst, the pyrroline being either molten or dissolved in its own weight of benzene). During and after the addition a rapid flow of carbon dioxide was used to blow out the product. Yield of pure diphenylpyrrole, m. p. 176—178° after one recrystallisation from toluene, 83%. 2 : 4-Diphenylpyrrolidine was dehydrogenated as readily as the pyrroline in all the dehydrogenation processes.

2 : 4-*Diphenylpyrrole* crystallised from toluene or ligroin (b. p. 100—120°) in long, white, flattened needles, m. p. 180° (Found: C, 86·5, 86·5, 87·2; H, 5·75, 5·75, 5·7; N, 6·45, 6·7, 6·45. $C_{16}H_{13}N$ requires C, 87·7; H, 5·9; N, 6·4%. The low value for carbon is remarkable, especially as the solvent in each case was a hydrocarbon). It was soluble in most hot organic solvents; the solution in acetic acid became blue on heating. It dissolved in concentrated sulphuric acid to give a canary-yellow solution; the colour faded on heating, became strongly violet on stronger heating, and then disappeared on dilution. The diphenylpyrrole gave a blue colour with Ehrlich's reagent. It coupled (in alcoholic solution, acidified with hydrochloric acid) with diazo-compounds (with diazotised-2 : 5-dichloroaniline, dull brick-red; with diazotised-*p*-nitroaniline, reddish-violet; with diazotised-5-chloro-*o*-toluidine, wine-red). A very sensitive test for 2 : 4-diarylpyrroles is the rapid formation of the blue azamethine when the diarylpyrrole is treated in the cold with a solution of 5-nitroso-2 : 4-diphenylpyrrole hydrochloride in acetic anhydride. 2 : 4-Diphenylpyrrole formed a picrate and a platinichloride, but both dissociated on attempted recrystallisation.

4-*Phenyl*-2-p-*anisylpyrrole* (IV; Ar¹ = C_6H_4·OMe, Ar = Ph). β-*p*-Anisoyl-α-phenylpropionitrile (Kohler and Leers, *J. Amer. Chem. Soc.*, 1934, **56**, 981) was reduced with Raney nickel as described for the unsubstituted compound. 4-*Phenyl*-2-p-*anisylpyrroline* b. p. 235—250°/7 mm., crystallised from ether in large, pale yellow, waxy prisms, m. p. 74—75° (Found: C, 81·15; H, 6·45; N, 5·75. $C_{17}H_{17}ON$ requires C, 81·3; H, 6·8; N, 5·6%). It gave a picrate, long canary-yellow needles from alcohol, m. p. 180—181° (Found: N, 12·05. $C_{17}H_{17}ON,C_6H_3O_7N_3$ requires N, 11·7%). The pyrroline was dehydrogenated by selenium as described for the unsubstituted compounds; the *pyrrole* crystallised from benzene or toluene in white plates or thin broad needles, m. p. 205—207° (Found: C, 81·6; H, 5·95; N, 5·8. $C_{17}H_{15}ON$ requires C, 81·9; H, 6·05; N, 5·65%). It dissolved in concentrated sulphuric acid to a yellow solution, the colour of which faded on warming, then darkened, and finally became olive-green.

2-*Phenyl*-4-p-*anisylpyrrole* (IV; Ar¹ = Ph, Ar = C_6H_4·OMe.) β-Benzoyl-α-*p*-anisylpropionitrile was made by the method of *Organic Syntheses* (Coll. Vol. I, 71), the appropriate amount of anisaldehyde being used in place of benzaldehyde; yield 76·5%, m. p. 114—116° (Robertson and Stephens, J., 1931, 963, give m. p. 118°). Catalytic reduction with Raney nickel gave 2-*phenyl*-4-p-*anisylpyrroline*, b. p. 232—238°/7 mm., s. p. 27° (Found: N, 6·05. $C_{17}H_{17}ON$ requires N, 5·6%). The pyrroline was probably contaminated with a little of the pyrrolidine, as hydrogen absorption continued beyond the theoretical end-point (cf. Rupe and Gisiger, *loc. cit.*). The pyrroline gave a *picrate*, pale yellow leaflets from alcohol, m. p. 156—158° (Found: N, 11·7. $C_{17}H_{17}ON,C_6H_3O_7N_3$ requires N, 11·7%). Dehydrogenation was effected with selenium at 250°, whereby the *pyrrole* was obtained in leaflets, m. p. 197—199°, identical with the material isolated as a by-product in the corresponding ammonium formate melt process (Found: C, 81·55; H, 5·75; N, 5·9. $C_{17}H_{15}ON$ requires C, 81·9; H, 6·05; N, 5·6%). It was soluble in cold concentrated sulphuric acid to give a yellow solution, which became progressively green and then violet-blue on warming.

D. *Nitrosation of* 2 : 4-*Diarylpyrroles*.—(1) A solution of 2 : 4-diphenylpyrrole (5·0 g.) in hot alcohol (250 c.c.) was cooled and to the suspension concentrated hydrochloric acid was added, followed by sodium nitrite (1·8 g.) in water (20 c.c.) during 10 minutes. The deep red-brown solution was filtered, and concentrated hydrochloric acid (25 c.c.) added, whereupon 5-*nitroso*-2 : 4-*diphenylpyrrole hydrochloride* crystallised in long, hair-like, brown needles. These were washed with acetone [yield, 5·8 g.; m. p. 190° (decomp.) with formation of the azamethine] and purified for analysis by dissolution in the minimum quantity of warm alcohol and dilution of the filtered solution with acetone, the hydrochloride separating in orange-brown needles (Found: C, 67·2; H, 4·45; N, 9·4. $C_{16}H_{12}ON_2,HCl$ requires C, 67·1; H, 4·55; N, 9·85%). The *base* (V, Ar = Ar¹ = Ph) was obtained from the hydrochloride in alcoholic solution by addition of alcoholic sodium acetate until the colour changed to yellow. The mixture was poured into cold water containing a little caustic soda or ammonia, and kept until the base had separated as a green solid; this was collected, washed with water, dried in a vacuum, and crystallised from alcohol, benzene or ether–petrol, forming green needles, m. p. 139—140° (Found: C, 77·2; H, 4·8; N, 11·05. $C_{16}H_{12}ON_2$ requires C, 77·4; H, 4·85; N, 11·3%). The *picrate* formed scarlet needles from benzene, m. p. 188° (decomp.) (Found: N, 14·6. $C_{16}H_{12}ON_2,C_6H_3O_7N_3$ requires N, 14·7%).

Nitrosation of diphenylpyrrole was also carried out by dissolving it (5·0 g.) in sulphuric acid (20 c.c.), running the yellow solution slowly into stirred ice and water, and treating the mixture with 5% sodium nitrite solution until a permanent positive nitrous acid test showed to starch–iodide paper (excess of nitrous acid does not seem to have any deleterious effect on the product). The crystalline paste was collected, and the orange sulphate dissolved in alcohol and converted into the green nitroso-base as described above. Yield, 5·0 g.

(2) A solution of 2-phenyl-4-*p*-anisylpyrrole (6·0 g.) in hot acetic acid (100 c.c.) was cooled, concentrated hydrochloric acid (5·0 c.c.) added, and nitrosation carried out with sodium nitrite (1·8 g.) in water. From the deep permanganate-purple solution, 5-*nitroso*-2-*phenyl*-4-*anisylpyrrole hydrochloride* separated on addition of concentrated hydrochloric acid (10 c.c.). It was collected, washed with a mixture of acetic acid (5 c.c.) and concentrated hydrochloric acid (1 c.c.), and crystallised from alcohol by cautious addition of ether, separating in small diamond-shaped prisms, red to transmitted light, or elongated prisms or needles (Found : N, 8·75. $C_{17}H_{14}O_2N_2$,HCl requires N, 8·9%). The free *base* (V; Ar^1 = Ph, Ar = C_6H_4·OMe) was obtained from the hydrochloride as described for the unsubstituted compound; a yellow precipitate, which rapidly became green, was formed on pouring into water. From alcohol it formed green needles, m. p. 176—177° (decomp.) (Found : N, 10·0. $C_{17}H_{14}O_2N_2$ requires N, 10·1%).

(3) 4-Phenyl-2-*p*-anisylpyrrole was nitrosated as was the unsubstituted pyrrole. 5-*Nitroso*-4-*phenyl*-2-p-*anisylpyrrole hydrochloride* formed yellow felted needles from methyl alcohol, probably containing 1MeOH of crystallisation. It decomposed without melting at 170° (Found : N, 8·0. $C_{17}H_{14}O_2N_2$,HCl requires N, 8·9%. $C_{17}H_{14}O_2N_2$,HCl,MeOH requires N, 8·1%).

E. 5-*Amino*-2 : 4-*diphenylpyrrole*.—5-Nitroso-2 : 4-diphenylpyrrole (2·0 g.) in methyl alcohol (50 c.c.) was completely reduced catalytically with Adams's catalyst in 1¼ hours, the hydrogen absorption being almost theoretical. The solution was filtered rapidly from the catalyst, and the alcohol distilled off, leaving a brown crystalline solid. Half of this was crystallised from benzene, but during the crystallisation the solution, and the stout needles which separated, became strongly blue. A sample dried in a vacuum had m. p. 155—156° (Found : C, 81·05; H, 6·4; N, 11·5. $C_{16}H_{14}N_2$ requires C, 82·0; H, 6·0; N, 12·0%). The other half of the crude amine was dissolved in acetic acid and refluxed for ¼ hour with excess of acetic anhydride. The solution was poured on ice, giving a blue solid, which was collected, dissolved in alcohol, filtered from a little azamethine, treated with charcoal, filtered, and allowed to crystallise. The *acetyl* compound separated in bundles of short white needles, m. p. 171—172° (Found : C, 78·25; H, 5·6; N, 10·1. $C_{18}H_{16}ON_2$ requires C, 78·1; H, 5·8; N, 10·15%). This compound exists in at least two modifications, and a form, m. p. 192°, may be isolated; on long heating at 180°, the lower-melting is transformed into the higher-melting form.

The nitroso-compound was also reduced by zinc dust and acetic acid, but the amine was not obtained owing to the rapid formation of the azamethine during the working-up process.

F. *Formation of Azadipyrromethines by Condensation of* 5-*Nitroso*-2 : 4-*diarylpyrroles with* 2 : 4-*Diarylpyrroles*.—(a) *Condensation of* 5-*nitroso*-2 : 4-*diphenylpyrrole and* 2 : 4-*diphenylpyrrole*. Nitrosodiphenylpyrrole (1·25 g.) and diphenylpyrrole (1·1 g.) in acetic acid (25 c.c.) and acetic anhydride (5 c.c.) were heated on the steam-bath for ½ hour. The cooled mixture was filtered, the filtrate being practically colourless, and the residue of azamethine washed with acetic acid and methyl alcohol, and dried; yield, 2·15 g. (95%).

Condensation can also be effected without acetic anhydride, if the hydrochloride of the nitroso-compound is used, but the yields are less satisfactory.

(b) 2 : 2′ : 4-*Triphenyl*-4′-p-*anisylazadipyrromethine* (IX) *by two routes*. (1) A mixture of 5-nitroso-2 : 4-diphenylpyrrole hydrochloride (2·0 g.), 2-phenyl-4-*p*-anisylpyrrole (1·75 g.), and acetic acid (25 c.c.) was refluxed for 1 hour, kept for 16 hours, diluted with alcohol (25 c.c.), and filtered. The residue of *azamethine* crystallised from aqueous pyridine in small copper-coloured prisms, m. p. 256—257° (Found : C, 83·2; H, 5·1; N, 8·8. $C_{33}H_{25}ON_3$ requires C, 82·7; H, 5·05; N, 8·5%). (2) 5-Nitroso-2-phenyl-4-*p*-anisylpyrrole hydrochloride (2·0 g.) was condensed with diphenylpyrrole (1·2 g.) exactly as described under (1). The products of the two experiments were kindly examined by Dr. Bunn of I.C.I. (Alkali) Ltd., who reported that the *X*-ray diffraction patterns were identical.

G. *Action of Formamide and Ammonium Formate on Compounds related to* γ-*Nitro*-β-*phenylbutyrophenone*.—(1) Methyl γ-nitro-β-phenylpropyl ketone (Kohler and Drake, *J. Amer. Chem. Soc.*, 1923, **45**, 2147), when heated with formamide (3 parts) for ½ hour, gave a deep red-brown solution, and a brown oil which solidified on cooling. It could not be crystallised, nor did it show any of the typical reactions of the azamethine of the diphenylpyrrole series.

(2) γ-Nitro-αε-dibenzoyl-ββδ-diphenylpentane, NO_2·CH(CHPh·CH_2·COPh)$_2$, was prepared by Worrall and Bradway's method (*J. Amer. Chem. Soc.*, 1936, **58**, 1607); only the higher-melting [230° (decomp.)] of the two forms claimed by these authors was obtained. During the preparation a considerable amount of blue colour developed, and, although no azamethine was isolated, traces of it were probably responsible for the colour. The dione itself gave no sign whatever of any blue colour with formamide or ammonium formate.

(3) γ-Nitro-β-phenylvalerophenone (Kohler, *J. Amer. Chem. Soc.*, 1916, **38**, 889) was obtained in the form, m. p. 101—103°. This gave no colour with ammonium formate.

(4) γ-*Nitro*-β-*phenylhexophenone*, made from α-nitropropane and chalkone by the method described by Kohler (*loc. cit.*) for the pentanone, was isolated in two forms; one had m. p. 156—158° (Found : C, 72·5; H, 6·35; N, 4·85. $C_{18}H_{19}O_3N$ requires C, 72·75; H, 6·4; N, 4·7%). This form was only slightly soluble in cold toluene, and crystallised from it in long needles. The other form, m. p. 88—90° (Found : N, 5·0%), was soluble in cold toluene and separated from *cyclo*hexane in clusters of short needles. Neither form gave any sign of coloured material on heating with formamide.

(5) When γ-nitrobutyrophenone (Reichert and Posmann, *Arch. Pharm.*, 1937, **275**, 75) was heated with formamide, the mixture became blue, greenish-blue, and finally red-brown. A red-brown amorphous solid which separated on cooling, was soluble in alcohol and insoluble in benzene, and bore no obvious relation to the tetraphenylazadipyrromethines. It was not further examined.

(6) γ-*Nitro*-β-*phenylbutyrophenoneoxime*, m. p. 108—110°, decomposed to a gum on storing (Found : N, 9·55. $C_{16}H_{16}O_3N_2$ requires N, 9·85%). It gave the azamethine readily with ammonium formate or with formamide. When solutions of the oxime in formic or acetic acid were evaporated, and the residues heated, considerable amounts of the azamethine were formed. A small quantity of the azamethine was also formed during the preparation of the oxime by the usual method.

(7) A detailed account of the action of formamide and ammonium formate on β-benzoyl-α-phenylpropionitrile (II, Ar = Ar^1 = Ph) and related compounds will be communicated later. At present it may be recorded that, whereas with ammonium formate this class of compound gives the azamethine (cf. p. 594), with formamide very little, or no blue colour is formed, and in its place a colourless compound is produced which gives the azamethine with ammonium formate and has been shown to be a formylated 5-amino-2 : 4-diphenylpyrrole.

H. *Action of Nitrogen Compounds, other than Formamide or Ammonium Formate, on the Nitrobutyrophenone* (I, Ar = Ar^1 = Ph) —(1) *Ammonia*. The nitrobutyrophenone (0·5 g.) and aqueous ammonia (25 c.c., *d* 0·88) were heated in a Pyrex tube during 5 hours to 160—170°. When the tube was opened, there was no residual pressure and there remained a clear aqueous layer and a brown tar. From a solution of the latter in β-ethoxyethyl alcohol, after several hours, a small amount of the azamethine was gradually precipitated. When alcoholic ammonia was used in place of aqueous ammonia, a reddish tar was obtained, from which no blue compound was isolated.

(2) *Other agents*. The nitrobutyrophenone (I, Ar = Ar^1 = Ph) gave low yields of the azamethine on heating with urea or thiourea. No colour was formed on heating with acetamide, butyramide, or hexamethylenetetramine. With lauramide, a dull red colour was obtained. The formates of primary aliphatic amines (methylamine, benzylamine,

hexamethylenediamine) (cf. Novelli, *J. Amer. Chem. Soc.*, 1939, **61**, 520) gave the azamethine in low yield, but this was thought to be due to the liberation of ammonia by the strong heating of the formate; this is supported by the observation that aniline formate gave no colour. No colour was produced by the action of formodimethylamide.

I. *Degradation Reactions of* 2 : 2′ : 4 : 4′*-Tetra-arylazadipyrromethines.*—(1) *Hydriodic acid reduction.* The tetraphenylazamethine (III, Ar = Ar^1 = Ph) (0·5 g.) was refluxed with 65% hydriodic acid (25 c.c.) for ¾ hour; the blue colour was lost, and a dark solid formed. After cooling, the product was poured into water and the solid was collected, washed well, dissolved in alcohol, filtered, and poured slowly into a well-stirred solution of sodium thiosulphate. The light grey solid obtained was collected, washed, and dried. It crystallised from chloroform (charcoal) in steely-grey needles of 2 : 4-diphenylpyrrole, m. p. 177—179°, which did not depress the m. p. of an authentic specimen.

(2) *Potassium permanganate oxidation.* (a) *Neutral.* The azamethine (1·0 g.), potassium permanganate (2·0 g.), magnesium sulphate (2·0 g.), and water (100 c.c.) were rolled in a ball mill for 24 hours, and then kept for 48 hours. Excess of sodium bisulphite solution was added, and the mixture gently warmed (at this stage there was a distinct smell of benzaldehyde). The mixture was extracted with ether, and the purple solution dried with magnesium sulphate and decolorised with the minimum quantity of charcoal. On removal of the ether, an oil remained which rapidly solidified and was identified as benzoic acid (0·13 g.). (b) *Acid.* Acid oxidation was rapid; the decolorised solution was steam-distilled and an ethereal extract of the distillate gave benzoic acid.

Oxidation of 2 : 2′-diphenyl-4 : 4′-di-*p*-anisylazadipyrromethine, and of the isomer, 4 : 4′-diphenyl-2 : 2′-di-*p*-anisylazadipyrromethine (III; Ar^1 = Ph, Ar = C_6H_4·OMe; and Ar^1 = C_6H_4·OMe, Ar = Ph respectively) gave mixtures of acids, from which anisic acid was obtained in each case by crystallisation from water. These results provided confirmation that aryl groups in the nitrobutanone (I) did not take part in any cyclisation process, but remained as pendant aryl groups in the blue pigment.

(3) *Other degradations of* (III, Ar = Ar^1 = Ph). (*a*) With ceric sulphate complex results were obtained, and there were isolated, surprisingly, two aldehydes (or ketones) as their 2 : 4-dinitrophenylhydrazones, m. p. 156—157° and 159—160°; these depressed each other's m. p., but the latter compound did not depress the m. p. of acetaldehyde-2 : 4-dinitrophenylhydrazone. (*b*) With lead tetra-acetate in acetic acid or benzene, decoloration was rapid, but no crystalline product was obtained. (*c*) With hydroxylamine in pyridine, a crystalline product was obtained, $C_{32}H_{23}ON_3$. The nature of this compound will be discussed in a later communication. (*d*) Thionyl chloride in large excess decolorised the azamethine on boiling, but no crystalline product was obtained. (*e*) With concentrated nitric acid, complex yellow degradation products were obtained.

The author thanks Mr. C. Paine for constant encouragement and much valuable advice; also his many colleagues in the Research Department of I.C.I. (Dyestuffs) Limited, for help and advice; and I.C.I. (Dyestuffs) Limited for permission to publish this work.

I.C.I. (Dyestuffs) Limited, Manchester, 9. [*Received, April 28th*, 1943.]