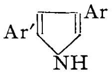
157. 2 : 4-*Diarylpyrroles. Part II. Methines.*

By Maurice A. Thorold Rogers.

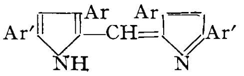
2 : 4-Diarylpyrroles readily form *methines* of type (II) either by condensation with ethyl orthoformate or other suitable agents, or by conversion into the *aldehyde* (IV) and further condensation with a second molecule of the diarylpyrrole. meso-*Phenylmethines* of type (V) have also been prepared. Metallic derivatives of the methines are described.

In Part I (preceding paper) the preparation of a new class of compound, the azadipyrromethines, from a new class of pyrrole, 2 : 4-diarylpyrroles, is described. A few of the reactions of diarylpyrroles for which there is some analogy in the alkylpyrrole series are now described.

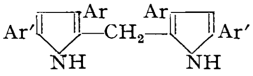
2 : 4-Diphenylpyrrole (I, Ar = Ar′ = Ph) condenses readily in acetic acid with ethyl orthoformate or with diphenylformamidine (Imperial Chemical Industries, Ltd., Piggott, and Rodd, B.P. 344,409, 354,898. No intermediate of the type there described was obtained) to give the red, crystalline *methine* (II, Ar = Ar′ = Ph). The same methine is formed from the pyrrole and formic acid, or formaldehyde in the presence of air. The methane (III) is presumably very unstable, as it has not been isolated.



(I.)



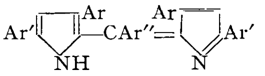
(II.)



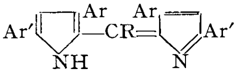
(III.)

The same methine was made very readily from the *aldehyde* (IV) by condensation with one molecule of (I). The aldehyde (IV) has been very conveniently prepared by the methylformanilide–phosphorus oxychloride method (Vilsmeier and Haak, *Ber.*, 1927, **60**, 119; cf. Fieser, *Org. Synth.*, XX, 11; B.P. 311,208, 343,570, 456,534, and 524,696)—apparently its first application to the pyrrole series.

(IV.)



(V.)



(VI.)

With benzotrichloride, the pyrrole (I) condenses readily in acetic acid to give meso-*phenylmethines* of type (V). The same product is obtained by condensing benzoic acid with the pyrrole in, for example, phosphorus oxychloride. As might be expected, the *meso*-phenylmethine is most sensitive to pH.

Diarylpyrroles dissolve in hot acetic acid, and the solution becomes blue on boiling. There is little doubt that this colour can be attributed to the *meso*-alkyl-methine (VI).

The *copper* complex of the methine (II) was of the normal type, 2 methine = 1 Cu; but the copper complex from the *meso*-phenylmethine, a somewhat intractable compound, appeared to be of the type 1 methine = 1 Cu.

This work is the subject of pending patent applications.

EXPERIMENTAL.

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

2 : 2′ : 4 : 4′-*Tetraphenyldipyrromethine* (II, Ar = Ar′ = Ph).—(1) 2 : 4-Diphenylpyrrole (4·0 g.) in acetic acid (50 c.c.) was refluxed with ethyl orthoformate (3 c.c.); the solution almost immediately became intensely crimson, and soon set to a crystal paste. After cooling, the crystals were collected, washed with acetic acid and with methyl alcohol, and dried (3·5 g.). The *methine* crystallised from nitrobenzene in red needles, m. p. 284—286° (Found : C, 88·65; H, 5·3; N, 6·4. $C_{33}H_{24}N_2$ requires C, 88·4; H, 5·35; N, 6·25%). (2) Similar yields were obtained by refluxing diphenylpyrrole (5·0 g.), acetic anhydride (25 c.c.), and diphenylformamidine (4·5 g.) for 1 hour.

2 : 4-*Diphenylpyrrole*-5-*aldehyde*.—A mixture of methylformanilide (24 c.c.) and phosphorus oxychloride (105 c.c.) was kept at room temperature for 1 hour, then cooled below 5°, and the pyrrole (20 g.) added during 1 hour. The mixture was stirred below 5° for 2 hours, allowed to warm to room temperature, and poured on ice, with agitation; the phosphorus oxychloride decomposed, leaving a red gum. At 50° the gum hydrolysed with formation of a yellow solid. This was collected, washed with aqueous sodium acetate and with water, and dried at 40°; the *aldehyde* crystallised from toluene in short, biscuit-coloured or pink needles. It was purified for analysis by recrystallisation from toluene, giving white needles, m. p. 187—188° (Found : C, 82·55; H, 5·0; N, 5·8. $C_{17}H_{13}ON$ requires C, 82·6; H, 5·25; N, 5·65%). On strong heating the aldehyde formed a red mass, probably containing the methine.

It formed an *oxime*, fluffy white needles from toluene, m. p. 202° (slow decomp.), which was probably a mixture of two forms (Found : C, 77·85; H, 5·05; N, 10·75. $C_{17}H_{14}ON_2$ requires C, 77·85; H, 5·35; N, 10·7%). With *p*-nitrophenylhydrazine in acetic acid it formed a p-*nitrophenylhydrazone*, dark red, saw-edged needles, m. p. 241—242° (sintering at 235°) from acetic acid (Found : N, 14·25. $C_{23}H_{18}O_2N_2$ requires N, 14·7%). Condensed with 2 : 4-dinitrotoluene (0·9 g.) and piperidine (3 drops), the aldehyde (1·25 g.) gave, after 1 hour at 130° and 3 hours at 170°, α-(2 : 4-*dinitrophenyl*)-β-(2 : 4-*diphenyl*-5-*pyrrolyl*)*ethylene*, dark hair-like needles, m. p. 254—255°, from moist pyridine or from butanol (Found : N, 10·35. $C_{24}H_{17}O_4N_3$ requires N, 10·0%).

Catalytic reduction of the aldehyde (Raney nickel in methanol) readily gave 2 : 4-*diphenylpyrrole*-5-*carbinol*, which was very unstable. With acids, or even on long standing, or on heating, it gave the methine, with loss of formaldehyde (smell and dinitrophenylhydrazone). It was recrystallised from benzene; m. p. 170° (decomp.) approx. (Found : C, 81·85; H, 5·8. $C_{17}H_{15}ON$ requires C, 82·0; H, 6·05%). An attempt to acylate the carbinol with acetic anhydride in pyridine resulted in the formation of the methine.

2-*Phenyl*-4-p-*anisylpyrrole*-5-*aldehyde*, prepared from the corresponding pyrrole (this vol., p. 594) exactly as described for diphenylpyrrolealdehyde, formed white felted needles from toluene, m. p. 158—159°, turning red on strong heating (Found : C, 78·1; H, 5·5. $C_{18}H_{15}O_2N$ requires C, 78·0; H, 5·4%). It gave an *oxime*, m. p. 196—198°, from toluene, which was obviously a mixture of *syn*- and *anti*-forms, as both long, hair-like and short thick needles were visible (Found : C, 74·25; H, 5·5. $C_{18}H_{16}O_2N_2$ requires C, 74·0; H, 5·5%).

2 : 2′ : 4-*Triphenyl*-4′-p-*anisyldipyrromethine*.—Diphenylpyrrolealdehyde (1·0 g.) and 2-phenyl-4-*p*-anisylpyrrole (1·0 g.) were refluxed with acetic acid (20 c.c.) and acetic anhydride (5 c.c.). After 1 hour the liquid was poured into water, and the product dried; it crystallised from aqueous pyridine in fiery copper-coloured platelets, m. p. 240—247° (Found : C, 85·4; H, 5·1; N, 6·0. $C_{34}H_{26}ON_2$ requires C, 85·4; H, 5·45; N, 5·85%).

Copper Bis-(2 : 2′ : 4 : 4′-*tetraphenyldipyrromethine*).—The methine (1·0 g.) in butanol (50 c.c.) was refluxed with copper acetate (0·5 g.). The crimson colour was replaced by magenta and platelets with a coppery sheen were formed. These were collected, and crystallised from pyridine–methyl alcohol (Found : C, 82·7; H, 4·45; N, 6·15; Cu, 6·35. $C_{66}H_{46}N_4Cu$ requires C, 82·9; H, 4·6; N, 5·85; Cu, 6·65%).

2 : 2′ : 4 : 4′-*Tetraphenyl*-meso-*phenyldipyrromethine*.—(1) Diphenylpyrrole (1·0 g.), benzotrichloride (1·0 c.c.), and acetic acid (25 c.c.) were refluxed for 1 hour, and the blue solution poured into water. This was made alkaline with sodium hydroxide and kept overnight. The solid product was collected and dried; it crystallised from β-ethoxyethyl alcohol in brown-red flattened needles, m. p. 268—270° (Found : C, 88·8; H, 5·2; N, 5·7. $C_{39}H_{28}N_2$ requires C, 89·3; H, 5·35; N, 5·35%).

(2) Diphenylpyrrole (4·4 g.) was dissolved in phosphorus oxychloride (20 c.c.), and benzoic acid (1·3 g.) added. The mixture was warmed on the steam-bath for 1 hour, cooled, poured on ice, and, when the phosphorus oxychloride had decomposed, heated to boiling. The coppery tar was washed by decantation and dissolved in the minimum quantity of alcohol, and the bright green solution poured into dilute sodium hydroxide solution. The red solid was collected, washed with water, dried, and crystallised from β-ethoxyethyl alcohol; yield, quantitative.

The meso-*phenylmethine* showed remarkable colour sensitivity to a variety of factors. Its solutions were generally red in alkaline and green in acid conditions; but a red ethereal solution of the base with a little acetic, formic or benzoic acid showed no change until the ether was allowed to evaporate on, for example, filter-paper. As the solvent evaporated, the colour became bright green. Spotting with ether gave a red mark, but methyl alcohol gave no change in colour. Other solvents showed intermediate, purplish, colour changes. Even the vapour of ether immediately and reversibly turned such a green test paper a dull purple.

Copper 2 : 2′ : 4 : 4′-*Tetraphenyl*-meso-*phenyldipyrromethine*.—The methine (0·5 g.), copper acetate (0·25 g.), and butyl alcohol (35 c.c.) were refluxed for 1 hour. A purple colour was formed, and the solution gradually became bluer and paler, and a mass of small prisms separated. These were collected, and crystallised with difficulty from nitrobenzene–methanol, giving needles (Found : C, 79·55; H, 5·0; N, 5·1; Cu, 9·85. $C_{39}H_{27}N_2Cu$ requires C, 79·9; H, 4·6; N, 4·8; Cu, 10·7. $C_{78}H_{54}N_4Cu$ requires C, 84·3; H, 4·85; N, 5·05; Cu, 5·75%).

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