

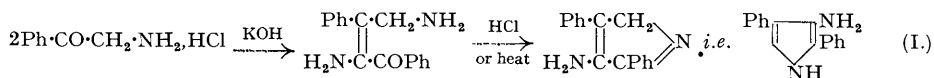
158. 2 : 4-Diarylpyrroles. Part III. 3-Amino-2 : 4-diphenylpyrrole.

By MAURICE A. THOROLD ROGERS.

The blue compound obtained by Gabriel by the action of benzaldehyde and air on 3-amino-2 : 4-diphenylpyrrole (I) is shown to have the structure (III). Benzoylation of (I) under Schotten-Baumann conditions gave 3-benzamido-2 : 4-diphenylpyrrole (IV) and a red compound, shown to be 3 : 3'-dibenzamido-2 : 2' : 4' : 4'-tetraphenyl-*meso*-phenyldipyrromethine (V) by synthesis from (IV) and benzotrichloride.

THE interesting properties of 2 : 4-diarylpyrroles discussed in Parts I and II (preceding papers) led to a search for earlier examples of diarylpyrroles of this orientation. The only recorded cases are 3-amino-2 : 4-diphenylpyrrole * (Gabriel, *Ber.*, 1908, 41, 1138) and its derivatives, and the *p*-tolyl analogue (Rüdenburg, *Ber.*, 1913, 46, 3558).

Gabriel's synthesis left some doubt whether the compound was a pyrrole, and Gabriel himself used the alternative name " bisanhydro-phenacylamine "; the synthesis was



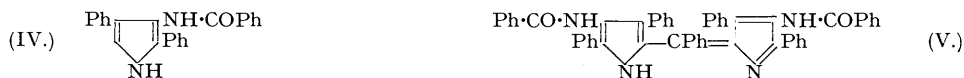
The present work leaves little doubt that the pyrrole structure is correct.

In the first place, Gabriel described the formation of an intensely blue compound (" Gabriel's blue ") when the pyrrole (I) was heated with benzaldehyde in a stream of air. He did not give an exact structural formula, but inferred that the blue compound was represented by (II), though he noted that the nitrogen analyses were unsatisfactory. Repetition of the work has shown that in fact it was the carbon analysis which was unsatisfactory, and new analyses are in good agreement with the more probable structure (III).



Confirmation of these analyses was obtained by using anisaldehyde in place of benzaldehyde; Zeisel determination of methoxy-groups showed conclusively that three aldehyde residues were incorporated in " Gabriel's blue." Both compounds showed the sensitivity of colour to pH expected of a *meso*-phenylmethine (preceding paper).

Gabriel described the benzoylation of (I) under Schotten-Baumann conditions. It has now been found more convenient to prepare the benzoyl compound (IV) by acylation with benzoyl chloride in pyridine; for under Schotten-Baumann conditions a bright red compound is also formed, to which the structure (V) was attributed.



This structure has been confirmed by independent synthesis from the benzoyl compound (IV) and benzotrichloride (cf. preceding paper).

This work is the subject of pending patent applications.

EXPERIMENTAL.

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

3-Amino-2 : 4-diphenylpyrrole (I).—This was made according to Gabriel's instructions (*loc. cit.*). It was found inadvisable to attempt to purify the " Monoanhydrophenacylamine " by recrystallisation from benzene, as considerable decomposition resulted; the crude material was quite satisfactory for conversion into the hydrochloride of (I).

" Gabriel's Blue."—The table shows the analyses obtained by the present author, and the figures calculated for Gabriel's formula (II) and for the *meso*-phenylmethine formula (III) now favoured.

	Found.		Required.	
	Gabriel.	Present work.	II, (C ₂₃ H ₁₇ N ₂) ₂ .	III, C ₅₃ H ₃₆ N ₄ .
C, %	85.74	87.3	86.0	87.4
H, %	5.37	5.65	5.3	4.9
N, %	7.78	7.55	8.7	7.7

" Gabriel's blue " is therefore given the constitution : 3 : 3'-dibenzylideneamino-2 : 2' : 4' : 4'-tetraphenyl-*meso*-phenyldipyrromethine (III).

3 : 3'-(Di-*p*-anisylideneamino)-2 : 2' : 4' : 4'-tetraphenyl-*meso*-*p*-anisylidipyrromethine (" Methoxy-Gabriel's blue ").—3-Amino-2 : 4-diphenylpyrrole (0.6 g.) and anisaldehyde (3 c.c.) were heated under reflux in the steam-bath in a slow stream of air. The product was triturated with methyl alcohol, and the dark residue recrystallised from nitrobenzene [Found: N, 6.95; OMe, 11.85. C₅₃H₃₃N₄(OMe)₃ requires N, 6.85; OMe, 11.35%].

3-Benzamido-2 : 4-diphenylpyrrole (IV).—(1) As described by Gabriel, under Schotten-Baumann conditions. When reaction was complete, the benzene was distilled off, and the reddish solid residue collected and dried. It was

* Fischer and Orth (" Chemie des Pyrroles," 1934, Vol. I, p. 112) give a second reference, F. Angelico and A. Angeli, R.A.L. (5), 14, I, 701 (1905); reference to the abstract (*Centr.*, 1905, II, 900) shows that the compound referred to is 3-amino-2 : 5-diphenylpyrrole.

extracted with alcohol, leaving a small scarlet residue which was shown to be identical with (V) prepared from benzotrichloride. From the alcoholic filtrate greenish prisms were obtained, m. p. 220—222° (Gabriel gives m. p. 218—219°); 0.5 g. from 2.0 g. of the base.

(2) *In pyridine.* To 3-amino-2 : 4-diphenylpyrrole (2.0 g.) in pyridine (25 c.c.) was added benzoyl chloride (3 c.c.) dissolved in pyridine (15 c.c.). The mixture became warm; after an hour it was poured into water, and made alkaline with sodium carbonate. The solid, recrystallised from alcohol, formed biscuit-coloured prisms (2.25 g.), m. p. 222—223°.

3 : 3'-Dibenzamido-2 : 2' : 4 : 4'-tetraphenyl-meso-phenyldipyrromethine (V).—3-Benzamido-2 : 4-diphenylpyrrole (1.15 g.) in acetic acid (15 c.c.) was refluxed with benzotrichloride (0.75 g.) for 1 hour, the mixture cooled, and the blue-green solution poured into dilute sodium hydroxide solution. The purple precipitate was collected, dried, and crystallised from nitrobenzene containing a trace of triethylamine, sufficient to form a deep red solution. On cooling, the meso-phenylmethine crystallised in short scarlet needles, m. p. 345° (decomp.) (Found : C, 82.55; H, 4.95; N, 7.55. $C_{53}H_{38}O_2N_4$ requires C, 83.3; H, 5.0; N, 7.35%).*

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