777. *The Preparation and Structure of Some Derivatives of 3-Hydroxypyrrole.*

By J. Davoll.

2 : 5-Dimethyl-4-oxo-1-phenyl-Δ^2-pyrroline is prepared by decarboxylation of its 3-carboxylic acid, and also by condensation of aniline with 3-hydroxyhexane-2 : 5-dione. Air or potassium ferricyanide oxidises it to 5-hydroxy-2 : 5-dimethyl-4-oxo-1-phenyl-Δ^2-pyrroline. It is shown from a consideration of spectral and chemical properties that most derivatives of 3-hydroxypyrrole exist in the oxopyrroline form; however, derivatives of 3-hydroxy-1-phenylpyrrole in which the α-positions are unsubstituted so that interannular conjugation is possible, appear to exist in the enolic hydroxypyrrole form.

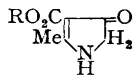
Grob and Ankli have recently (*Helv. Chim. Acta*, 1949, **32**, 2010) shown that most of the compounds previously described as 2-hydroxypyrroles (as, for example, in Fischer and Orth, "Die Chemie des Pyrrols," Akad. Verlags' G.m.b.H., Leipzig, 1934, Vol. I, p. 125) are better formulated as 5-oxo-Δ^2-pyrrolines. It would be expected, in view of the general chemical similarity between the α- and the β-positions in pyrrole, that derivatives of 3-hydroxypyrrole (I) would tend to exist in the 4-oxo-Δ^2-pyrroline form (II), and the present communication is concerned with the preparation and properties of a relatively simple derivative of 3-hydroxypyrrole, and with the structure of some previously known derivatives of this compound.

In view of the evidence set out below, it is considered that the reactions of most of these compounds are best represented by the oxopyrroline structure (II), and, with one or two exceptions, this formulation will be used in the following account.

It was desired to study a 3-hydroxypyrrole in which the disturbing effects of other functional groups (*e.g.*, alkoxycarbonyl) were absent. Among the few such compounds known are 3-hydroxy-1 : 2 : 4-tri- (Widman and Almström, *Annalen*, 1913, **400**, 86) and 3-hydroxy-2 : 5-di-phenylpyrrole (von Meyer, *J. pr. Chem.*, 1914, **90**, 1); but the properties of these compounds do not give a clear indication as to which of their possible tautomeric forms is the more stable, and attention was turned to the preparation of a less heavily substituted 3-hydroxypyrrole.


(I)


(II)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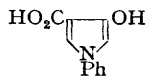
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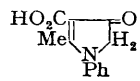

(V)

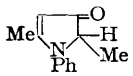
The most obvious approach to such a compound was by decarboxylation of one of the readily available 4-oxo-Δ^2-pyrroline-3-carboxylic acids. Benzyl 2-methyl-4-oxo-Δ^2-pyrroline-3-carboxylate (III; R = CH_2Ph) was prepared from benzyl β-aminocrotonate by Benary and Silbermann's method (*Ber.*, 1913, **46**, 1363) and hydrogenated, to give the acid (III; R = H); this could not, however, be decarboxylated. Benary and Konrad (*Ber.*, 1923, **56**, 44) failed to obtain hydroxypyrroles by heating the acids (IV) and (V), but we found that 2 : 5-dimethyl-4-oxo-1-phenylpyrroline-3-carboxylic acid (VI; R = H), prepared by cyclisation of methyl β-anilino-α-α'-chloropropionylcrotonate to (VI; R = Me), followed by hydrolysis, lost carbon dioxide at its melting point, to give 2 : 5-dimethyl-4-oxo-1-phenylpyrroline (VII). The methoxy-acid (VIII) similarly gave 3-methoxy-2 : 5-dimethyl-1-phenylpyrrole.

A more convenient preparation of (VII) (66% yield) was to heat aniline and 3-hydroxyhexane-2 : 5-dione at 100°. 1-Benzyl-2 : 5-dimethyl-4-oxopyrroline was similarly prepared from benzylamine and the hydroxy-diketone at room temperature; the lower yield (27%) in this case may be due to decomposition of the hydroxy-diketone by the strongly basic amine.

2 : 5-Dimethyl-4-oxo-1-phenylpyrroline was insoluble in dilute alkali and did not react with ethereal diazomethane. Diazomethane in ether–methanol converted it into an

intractable dark syrup. Addition of ferric chloride solution to the oxopyrroline in ethanol gave a transient red colour, which became permanent when sufficient ferric chloride (which presumably oxidises the compound) had been added. Treatment with benzoyl chloride–pyridine converted it in good yield into the benzoate (IX; R = Ph), and (IX; R = CH_2Ph) was similarly obtained. No derivatives could be prepared from (VII) by treatment with semicarbazide or 2 : 4-dinitrophenylhydrazine.


(VI)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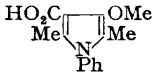
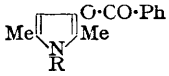

(VIII)

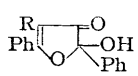

(IX)

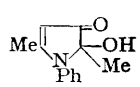
The most striking property of 2 : 5-dimethyl-4-oxo-1-phenylpyrroline was its rapid autoxidation, in air, to a crystalline compound (A), $C_{12}H_{13}O_2N$, m. p. 151—152°, containing one oxygen atom more than the original compound. Very little of A was obtained when an ethanolic solution of the oxopyrroline was shaken in oxygen (although absorption of gas occurred), or by oxidation with hydrogen peroxide or ferric chloride, but potassium ferricyanide in aqueous or aqueous-ethanolic solution readily gave the new compound in *ca.* 50% yield.

It has been shown previously (Kohler, Westheimer, and Tishler, *J. Amer. Chem. Soc.*, 1936, **58**, 264; Kohler and Woodward, *ibid.*, p. 1933; Lutz and his co-workers, *ibid.*, 1936, **58**, 1885; 1937, **59**, 2322; and many other papers) that some derivatives of 3-hydroxyfuran, such as (X; R = H or Ph) absorb oxygen to give peroxides, from which, by reduction, hydroxyfuranones (XI; R = H or Ph) are obtained. The latter compounds may be stable in this form (*e.g.*, XI; R = Ph), or may isomerise to open-chain triketones, such as (XII), derived from (XI; R = H). It seemed possible that the compound A might have a structure (XIII) analogous to (XI), or else one of the structures (XIV) or (XV) to which (XIII) might give rise by isomerisation.

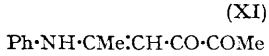
The following evidence indicates that A is, in fact, 5-hydroxy-2 : 5-dimethyl-4-oxo-1-phenylpyrroline (XIII), and exists in this form, although derivatives of an open-chain structure (XIV) or (XV) can be prepared from it under suitable conditions. The compound was hydrolysed by boiling dilute alkali, with liberation of aniline, and by very dilute hydrochloric acid at room temperature; these reactions are probably preceded by isomerisation to (XV). It reacted vigorously with sodium bismuthate (Rigby, *J.*, 1950, 1907), which attacks the CO·C·OH group, but not α-diketones, and with sodium metaperiodate, in the latter case yielding a crystalline product which could not, however, be identified. The compound A did not give derivatives with semicarbazide or 2 : 4-dinitrophenylhydrazine, and this is attributed to the fact that (XIII) is the vinylogue of an amide; in such compounds the ketonic character of the carbonyl group is known to be suppressed (Cromwell, Miller, Johnson, Frank, and Wallace, *J. Amer. Chem. Soc.*, 1949, **71**, 3337). With acetic anhydride–pyridine, A gave a monoacetate. The infra-red spectrum of A in Nujol mull showed strong bands at 3·12, 6·08, and 6·64 μ. The first of these indicates the presence of a hydroxyl group (in XIII), or an NH group (in XIV), and the other two are presumably those characteristic of αβ-unsaturated β-amino-ketones (XIII or XIV) (Cromwell *et al.*, *loc. cit.*). Structures (XIV) and (XV) might be expected to show an acetyl-carbonyl band near 5·75 μ, and this is absent.

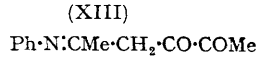

(X)


(XI)


(XIII)

Ph·CO·CH_2·CO·COPh
(XII)

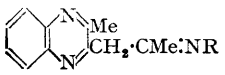

(XIV)


(XV)

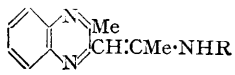
In its reaction with *o*-phenylenediamine, the compound apparently behaves as an α-diketone (XIV) or (XV), affording a yellow product $C_{18}H_{17}N_3$, m. p. 108—109°. On acid hydrolysis this gave 2 : 3-dimethylquinoxaline, indicating a structure (XVI or XVII; R = Ph) rather than (XVIII), derived from the cyclic form of A. Of the first two

structures, the absence of an NH band near 3 μ in the infra-red spectrum of the substance in chloroform solution makes (XVI; R = Ph) the more probable. On some occasions the reaction with *o*-phenylenediamine gave a product of m. p. 120—140°, with an ultra-violet spectrum similar to that of the compound of m. p. 108—109°, and giving 2 : 3-dimethylquinoxaline on acid hydrolysis. This material may have contained a compound (XVI; R = *o*-C_6H_4·NH_2), formed by replacement of aniline by *o*-phenylenediamine during the condensation.

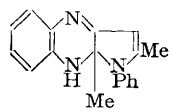
If structure (XVI) is correct, the strong yellow colour of the quinoxaline and its hydrolysis to 2 : 3-dimethylquinoxaline require explanation. Although no satisfactory reasons can at present be given for the former, a similar unexpected orange colour has been noted in a compound of rather similar structure, 3-phenacyl-2-phenylquinoxaline (Lutz and Stuart, *J. Amer. Chem. Soc.*, 1936, **58**, 1885); 3-α-methylphenacyl-2-phenylquinoxaline, on the other hand, is colourless (*idem*, *ibid.*, 1937, **59**, 2316). The acid hydrolysis to 2 : 3-dimethylquinoxaline probably takes place by initial hydrolysis of the anil, followed by a breakdown similar to that of a β-diketone (*e.g.*, benzoylacetone to acetophenone), the C:N group in the quinoxaline ring behaving like a carbonyl group (Bergstrom and Ogg, *ibid.*, 1931, **53**, 245).



(XVI)



(XVII)



(XVIII)

Potassium ferricyanide oxidation of the condensation products of *m*-nitroaniline and α-naphthylamine with 3-hydroxyhexane-2 : 5-dione gave 5-hydroxy-2 : 5-dimethyl-1-*m*-nitrophenyl-4-oxopyrroline and -1-α-naphthyl-4-oxopyrroline respectively, and oxidation of 2 : 5-dimethyl-4-oxo-1-phenylpyrroline-3-carboxylic acid similarly gave its 5-hydroxy-derivative. On oxidation with potassium ferricyanide, ethyl 2-methyl-4-oxo-Δ^2-pyrroline-3-carboxylate gave the indigo previously obtained by Benary and Silbermann by oxidation with ferric chloride, and 2 : 5-dimethyl-1-phenylpyrrole, 3-benzoyloxy-2 : 5-dimethyl-1-phenylpyrrole, and 2-methyl-4-oxo-1-phenylpyrroline-3-carboxylic acid were recovered unchanged.

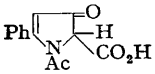
The reactions of various oxopyrroline and hydroxypyrrole derivatives with diazomethane were studied, in order to determine whether enolic hydroxyl groups were present. The reactions were carried out at room temperature in ether–methanol mixtures, which were used in preference to ether alone, partly because the compounds were usually more soluble in methanol than in ether, and partly because diazomethane is a more effective methylating agent in the presence of methanol (Schonberg and Mustafa, *J.*, 1946, 746).

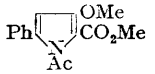
Ethyl 4-hydroxy-1-phenylpyrrole-3-carboxylate reacted slowly, to give a product from which 4-methoxy-1-phenylpyrrole-3-carboxylic acid was obtained in 20% overall yield on alkaline hydrolysis.

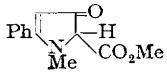
Methyl 2-methyl-4-oxo-1-phenylpyrroline-3-carboxylate gave a 17% yield of a yellow compound, $C_{14}H_{15}O_3N_3$ (*i.e.*, addition of diazomethane had occurred), and the same product was obtained in 19% yield from methyl 4-acetoxy-2-methyl-1-phenylpyrrole-3-carboxylate and diazomethane. It melted with decomposition at 200°, without any evidence of evolution of nitrogen at lower temperatures, and was rapidly hydrolysed by alkali to a colourless acid, $C_{13}H_{13}O_3N_3$, with light absorption characteristics markedly different from those of the ester. These compounds were not investigated further.

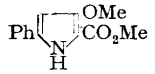
1-Acetyl-4-oxo-2-phenylpyrroline-5-carboxylic acid (XIX) (Madelung and Obermann, *Ber.*, 1930, **63**, 2870) gave two crystalline products, $C_{15}H_{15}O_4N$, m. p. 96—97°, presumably (XX), in 25% yield, and $C_{13}H_{13}O_3N$, m. p. 182—183°, believed to be (XXI) on the basis of its ultra-violet spectrum (see below), in 13% yield. The removal of an *N*-acetyl group by diazomethane is unexpected, and the possibility (not excluded by its method of preparation) that Madelung and Obermann's compound was in fact 3-acetoxy-5-phenylpyrrole-2-carboxylic acid was considered. If this were so, the compound $C_{15}H_{15}O_4N$ would be methyl 3-acetoxy-1-methyl-5-phenylpyrrole-2-carboxylate, and its spectrum should be

similar to that of the starting material, since, in the examples given below, replacement of acetoxy by methoxy and substitution on the imino-nitrogen produce little change in spectrum. The observation that the spectra do, in fact, differ, supports Madelung and Obermann's formulation of the original acid. This difference also indicates, although not conclusively, that (XIX) exists in the oxopyrroline, rather than the hydroxypyrrole, form, and the close similarity in spectra shown by (XIX) and the compound $C_{13}H_{13}O_3N$ supports the structure (XXI) for the latter rather than the alternative possibility (XXII).


(XIX)


(XX)


(XXI)


(XXII)

Ultra-violet and infra-red spectra have been widely used in the study of tautomeric compounds, and often give more reliable information than purely chemical methods. The ultra-violet absorption data (Figs. 1 and 2; Table 1) and infra-red absorption bands in the 2—8 μ region (Table 2) of a number of pyrroles and pyrrolines are set out below. Except where otherwise stated, the ultra-violet spectra were determined in ethanolic solution, with a Unicam S.P. 500 Spectrophotometer or a Cary Spectrophotometer, and the infra-red spectra in Nujol mull on a Beckman IR-2 Spectrophotometer.

TABLE 1.

No.	Compound	$\lambda_{max.}$(mμ)	ε	$\lambda_{max.}$	ε
1	(III; R = H)	239	12,400	291·5	8,300
2	Et ester of (III) [1]	240	13,600	294	9,800
3	Enol acetate of no. 2 [2]	223	18,100	—	—
4	(IV) [3]	243	15,100	249	14,900
		255	14,500	—	—
5	Et ester of (IV)	246	18,000	255	18,500
6	Me enol ether of (IV) [3]	241	16,000	245—247	15,000
7	(V) [3]	246	14,200	309	11,000
8	Me ester of (V)	248	19,200	310	10,500
9	Enol acetate of no. 8	236	17,800	—	—
10	(VI; R = H)	244	14,800	314	9,600
11	(VIII)	238	15,900	—	—
12	Enol acetate of (VI; R = H)	236	14,700	—	—
13	(VII)	246·5	2,800	324·5	16,200
13*a*	(VII) in 0·01N-NaOH	338	10,400	—	—
14	Me enol ether of (VII)	208	16,100	—	—
15	2 : 5-Dimethyl-1-phenylpyrrole [4]	208	15,000	—	—
16	(IX; R = Ph)	230	21,700	—	—
17	(IX; R = CH_2Ph)	227·5	20,600	—	—
18	1-Phenylpyrrole [5]	253	13,500	—	—
19	3-Methoxy-1-phenylpyrrole [3]	271·5	10,800	—	—
20	1-Benzylpyrrole [5]	208	13,700	—	—
21	(XIII)	336	12,900	—	—
22	Acetate of (XIII)	328	12,000	—	—
23	3-CO_2H- deriv. of (XIII)	242	16,300	322	11,100
24	1-Acetyl-4-oxo-2-phenylpyrroline-5-carboxylic acid [6]	224·5	11,200	243	7,100
		312	24,200	—	—
25	Methyl 1-acetyl-3-methoxy-5-phenylpyrrole-2-carboxylate	232	11,100	292·5	16,000
26	Methyl 1-methyl-4-oxo-2-phenylpyrroline-5-carboxylate	230	12,000	—	—
		243	9,900	311	27,800

[1] Benary and Silbermann, *loc. cit.* [2] Küster, *Z. physiol. Chem.*, 1922, **121**, 135. [3] Benary and Konrad, *loc. cit.* [4] Hazlewood *et al.*, *J. Proc. Roy. Soc. N.S.W.*, 1937, **71**, 92 (*Chem. Abs.*, 1938, **32**, 1695). [5] Adkins and Coonradt, *J. Amer. Chem. Soc.*, 1941, **63**, 1563. [6] Madelung and Obermann, *loc. cit.*

Discussion.—A comparison of the ultra-violet spectra of compounds 1—3 with those of compounds 7—9 shows that substitution of the imino-hydrogen by phenyl has little effect on the absorption, apart from a moderate shift of the maxima to longer wave-lengths, and consequently, it seems unlikely that pyrrolenine forms contribute to the structures of the first three compounds. The presence of NH absorption at 3·20 μ in the infra-red spectra of compounds 2 and 3 supports this conclusion.

The ultra-violet spectra of compounds 1—3, 7—14, and 16 clearly indicate that, of

these compounds, those with free potential hydroxy-groups exist in the oxopyrroline, rather than the hydroxypyrrole, form, since the spectra of the methoxy-, acetoxy-, and benzoyloxy-derivatives are very different from those of the unsubstituted compounds. In

TABLE 2.

(Wave-lengths are in μ. vs = very strong, s = strong, m = medium, w = weak band. Compound nos. are from Table 1.)

No.	Absorption bands								
2	3·20 m	5·88 vs	6·18 s.	6·40 s.	6·65 s	6·95 s	7·17 m	7·31 s	7·46 s
3	3·20 w	5·63 s	5·74 s	5·90 vs	6·26 w	6·51 m	7·07 s	7·49 s	7·90 vs
4	3·87 w	5·81 m	6·07 m	6·11 m	6·46 s	7·10 m	7·90 m	—	—
5	5·94 vs	6·42 vs	6·64 s	—	—	—	—	—	—
6	3·80 w	5·99 vs	6·27 w	6·35 m	6·55 vs	6·64 s	7·15 w	7·68 s	—
7	5·82 vs	6·05 m	6·18 m	6·52 s	6·70 m	7·45 m	—	—	—
8	5·99 vs	6·54 vs	6·70 m	6·96 s	7·92 m	—	—	—	—
10	3·03 w	5·77 vs	6·08 m	6·14 s	6·52 vs	6·72 s	7·03 m	—	—
13	(liquid film)		3·08 w	3·22 w	3·32 w	6·02 vs	6·12 vs	6·28 m	—
	—	—	6·52 vs	6·68 vs	7·06 s	7·31 m	7·58 m	7·94 w	—
21	3·12 s	6·08 vs	6·30 m	6·45 w	6·64 vs	6·82 s	7·33 m	7·57 w	—

those compounds with two strong maxima, it seems reasonable to attribute the lower wave-length one (at 240—248 mμ) to the αβ-unsaturated β-(substituted amino)-acid or -ester group, and the other (at 291·5—324·5 mμ) to the αβ-unsaturated β-(substituted

FIG. 1. FIG. 2. FIG. 3.

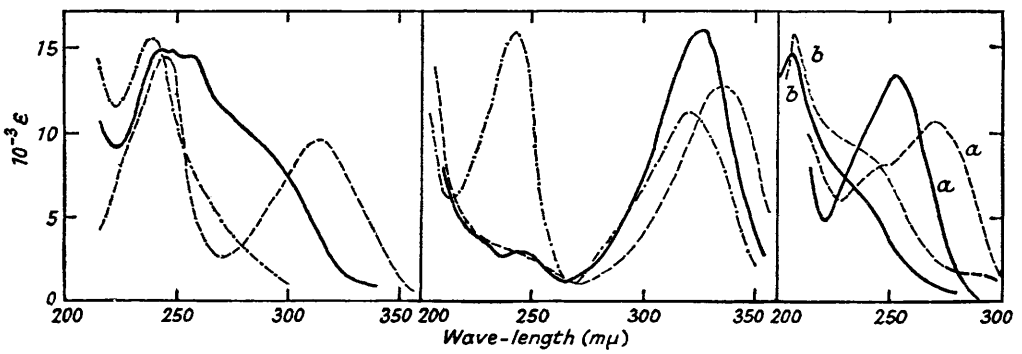


FIG. 1. ———— *4-Hydroxy-1-phenylpyrrole-3-carboxylic acid.*
– – – – – – – *2 : 5-Dimethyl-4-oxo-1-phenylpyrroline-3-carboxylic acid.*
— · — · — *4-Methoxy-2 : 5-dimethyl-1-phenylpyrrole-3-carboxylic acid.*

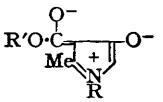
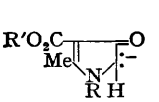
FIG. 2. ———— *2 : 5-Dimethyl-4-oxo-1-phenylpyrroline.*
– – – – – – – *5-Hydroxy-2 : 5-dimethyl-4-oxo-1-phenylpyrroline.*
— · — · — *5-Hydroxy-2 : 5-dimethyl-4-oxo-1-phenylpyrroline-3-carboxylic acid.*

FIG. 3. *a*———— *1-Phenylpyrrole.*
a– – – – – *3-Methoxy-1-phenylpyrrole.*
b———— *2 : 5-Dimethyl-1-phenylpyrrole.*
b– – – – – *3-Methoxy-2 : 5-dimethyl-1-phenylpyrrole.*

amino)-carbonyl group. These assignments, and the oxopyrroline structure on which they are based, are confirmed by a comparison of the spectra of the derivatives of 5-hydroxy-2 : 5-dimethyl-4-oxo-1-phenylpyrroline (compounds 21—23) in which the oxopyrroline structure is fixed, with those of compounds 13 and 10.

The chemical behaviour of compounds 1, 2, 7, 8, 10, and 13 is generally consistent with this formulation. Acyloxypyrroles are presumably formed after a preliminary enolisation, and the same mechanism may account for the solubility of esters such as 2 and 8 in alkali; however, this may be due to contributions from forms such as (XXIII) and (XXIV) (cf. Grob and Ankli, *loc. cit.*, on similar 5-oxo-Δ^2-pyrroline derivatives). 2 : 5-Dimethyl-4-oxo-1-phenylpyrroline, lacking an alkoxycarbonyl group, is insoluble in dilute aqueous alkali, and its spectrum is not greatly altered by the addition of sodium hydroxide. The compounds are not converted into methoxypyrroles by diazomethane, and with methyl

sulphate–sodium hydroxide give either no product (compound 2; Küster, *loc. cit.*) or only a low yield of methoxy-derivative (compound 10). Most of these compounds give colours with ferric chloride solution, but this does not necessarily indicate an enolic hydroxyl group; a red colour is given by some of the αβ-unsaturated β-amino-ketones prepared by Cromwell *et al.* (*loc. cit.*), and also by 5-hydroxy-2 : 5-dimethyl-4-oxo-1-phenylpyrroline. Küster (*loc. cit.*) concluded from a K. H. Meyer titration of ethyl 2-methyl-4-oxo-Δ^2-pyrroline-3-carboxylate that this compound existed entirely in the enolic form, but this result can equally be explained as addition of bromine to the 2 : 3-double bond of the oxopyrroline, followed by reaction of the resulting α-bromo-ketone with acidified potassium iodide in the usual way.

(XXIII)   (XXIV)

The compounds do not show the properties of simple ketones; methyl 2-methyl-4-oxo-1-phenylpyrroline-3-carboxylate, for example, with hydrazine gives the corresponding acid hydrazide, rather than a hydrazone. This suppression of ketonic properties is ascribed to the amide character of the carbonyl group, as discussed earlier, and the infra-red spectra do, in fact, generally show absorption bands at about 6·0 and 6·5 μ similar to those found by Cromwell *et al.* (*loc. cit.*) to be characteristic of the αβ-unsaturated β-amino-carbonyl system. However, the presence of acid or ester carbonyl groups in most of these compounds, and a lack of data on the infra-red absorption of the pyrrole ring system, make deductions from the infra-red spectra of a very questionable value. The weak OH bands at about 3 μ in the spectra of compounds 10 and 13 are considered to be due to the presence of small quantities of 5-hydroxy-derivatives formed by oxidation, rather than to enolic forms of the compounds.

The compounds having a 1-phenyl substituent and no α-methyl groups in the pyrrole ring (compounds 4—6) show markedly different properties. The ultra-violet spectrum of compound 4 is quite different from that of its 2-methyl derivative (compound 7), but closely resembles that of the corresponding methoxy-acid (compound 6), suggesting that the compound exists mainly, at any rate, in the enolic form in ethanolic solution. Moreover, ethyl 4-hydroxy-1-phenylpyrrole-3-carboxylate (compound 5) reacted slowly with diazomethane in methanol–ether, and hydrolysis of the product gave the methoxy-acid (compound 6) in 20% overall yield. A similar methylation with methyl sulphate–sodium hydroxide (Benary and Konrad, *loc. cit.*) gave the same acid in 34% yield. The infra-red spectra of the acid (4) and its ethyl ester (5) in Nujol mull do not show OH bands near 3 μ; possibly the compounds have a different structure in the solid state, or, alternatively, hydrogen bonding may shift the OH band to longer wave-lengths sufficiently for it to be masked by the 3·4 μ Nujol band.

The considerable alteration in chemical and physical properties produced by introducing one or two α-methyl groups into these 1-phenylpyrrole derivatives is almost certainly due to the fact that these groups hinder the coplanarity, and hence the interannular conjugation, of the two ring systems, as has been shown by a study of the diple moments of a number of 1-phenylpyrrole derivatives (Kofod, Sutton, and Jackson, *J.*, 1952, 1467). Presumably in compounds 4 and 5 the additional conjugation stabilises the enolic form with two double bonds in the pyrrole ring, in comparison with those compounds from which the phenyl group is absent (1, 2) or held out of coplanarity with the pyrrole ring (7, 8, 10, and 13). Moreover, the spectrum of 2 : 5-dimethyl-1-phenylpyrrole is similar to that of 1-benzylpyrrole, but differs from that of 1-phenylpyrrole. Introduction of a methoxy-group into the 3-position of 2 : 5-dimethyl-1-phenylpyrrole has little effect on the spectrum, but in the more highly conjugated system of 1-phenylpyrrole produces a marked change.

The structures of compounds 24—26 have already been discussed. Although the ultra-violet spectra and the absence of any colour reaction with ferric chloride support an oxopyrroline structure for 24 and 26, the methylation with diazomethane indicates an enolic structure, and definite conclusions cannot at present be reached.

Experimental

Benzyl β-Aminocrotonate.—Ammonia was passed into benzyl acetoacetate (62 g.), without cooling, for 1½ hr. The mixture was set aside overnight at 0°, then diluted with ether and washed 3 times with sodium chloride solution. Evaporation of the dried (Na_2SO_4) ethereal solution and distillation of the residue afforded *benzyl β-aminocrotonate* (36 g., 58%), b. p. 134—148°/2 mm., m. p. 30—32° (Found: C, 69·1; H, 6·8; N, 7·2. $C_{11}H_{13}O_2N$ requires C, 69·1; H, 6·9; N, 7·3%).

Benzyl β-Amino-α-chloroacetylcrotonate.—Chloroacetyl chloride (11·3 g.) in dry ether (15 c.c.) was added during 20 min. to a solution of the above ester (19·1 g.) in dry ether (50 c.c.) and pyridine (7·9 g.) with stirring and cooling in ice-water. The mixture was stirred for 1 hr. at 0°; then ice-water (30 c.c.) was added and most of the ether was evaporated in a current of air. The crystalline solid was collected and crystallised from ethanol (75 c.c.), to give *benzyl β-amino-α-chloroacetylcrotonate* (12 g., 45%) as colourless needles, m. p. 86—87° (from ethanol) (Found: C, 58·0; H, 5·3; N, 5·4. $C_{13}H_{14}O_3NCl$ requires C, 58·4; H, 5·2; N, 5·2%).

Benzyl 2-Methyl-4-oxo-Δ²-pyrroline-3-carboxylate (III; R = CH_2Ph).—The above chloroacetyl compound (13·4 g.) was added all at once to a vigorously stirred solution of potassium hydroxide (6 g.) in ethanol (50 c.c.). A vigorous reaction ensued, and the flask was at once cooled in ice-water. The crystalline mass was kept for 30 min. at room temperature, then acidified with ice-cold dilute hydrochloric acid, and the crystalline solid (10·2 g., 88%) collected and washed with water. Rapid recrystallisation from ethanol (1200 c.c.) afforded *benzyl 2-methyl-4-oxo-Δ²-pyrroline-3-carboxylate* (7 g., 61%) as fine, buff needles, m. p. 205—206° (decomp., with much previous darkening) (Found: C, 67·0; H, 6·0; N, 6·0. $C_{13}H_{13}O_3N$ requires C, 67·5; H, 5·7; N, 6·1%).

2-Methyl-4-oxo-Δ²-pyrroline-3-carboxylic Acid (III; R = H).—A suspension of the above ester (4·5 g.) in 0·4N-sodium hydroxide (100 c.c.) was hydrogenated at atmospheric temperature and pressure, with 5% palladium–strontium carbonate catalyst. The theoretical amount of hydrogen for removal of the benzyl group was absorbed in 45 min., the compound dissolving. Catalyst was removed and the filtrate acidified with dilute hydrochloric acid, to give *2-methyl-4-oxo-Δ²-pyrroline-3-carboxylic acid* (1·76 g., 64%), which crystallised from water in pale-yellow rods, m. p. 177° (decomp. with darkening above 150°) (Found: C, 51·3; H, 5·2; N, 9·7. $C_6H_7O_3N$ requires C, 51·1; H, 5·0; N, 9·9%). The acid decomposed completely when heated with powdered glass at 180°/0·5 mm.

2-Methyl-4-oxo-1-phenylpyrroline-3-carboxylic Acid.—This compound is described by Benary and Konrad (*loc. cit.*) as colourless needles, m. p. 145° (decomp.), when prepared from the methyl ester by hydrolysis with boiling ethanolic potassium hydroxide for many hours. Obtained by hydrolysis of the ester with 10% aqueous sodium hydroxide at 100° for 30 min., the acid formed pinkish needles, m. p. 174—175° (decomp.) (Found: C, 66·2; H, 5·3; N, 6·6. Calc. for $C_{12}H_{11}O_3N$: C, 66·3; H, 5·1; N, 6·4%).

Methyl 4-Acetoxy-2-methyl-1-phenylpyrrole-3-carboxylate.—Acetylation of methyl 2-methyl-4-oxo-1-phenylpyrroline-3-carboxylate (5 g.; Benary and Konrad, *loc. cit.*) by acetic anhydride and potassium acetate at 100° afforded the *acetoxy*-ester (4·2 g., 71%), colourless crystals (from ethanol), m. p. 101—102° (Found: C, 66·5; H, 5·8; N, 5·3. $C_{15}H_{15}O_4N$ requires C, 65·9; H, 5·5; N, 5·1%).

2-Methyl-4-oxo-1-phenylpyrroline-3-carboxylic Acid Hydrazide.—A solution of methyl 2-methyl-4-oxo-1-phenylpyrroline-3-carboxylate (1 g.) in hot ethanol (3 c.c.) was cooled rapidly to 25° and treated with 90—95% hydrazine hydrate (3 c.c.). The solution was set aside overnight at room temperature, then evaporated to dryness under reduced pressure, and the crystalline residue recrystallised from ethanol, to yield the *hydrazide* (0·54 g., 54%) as slightly yellowish, rectangular crystals, m. p. 146—147° (from ethanol) (Found: C, 62·7; H, 5·9; N, 18·0. $C_{12}H_{13}O_2N_3$ requires C, 62·3; H, 5·7; N, 18·2%). An ethanolic solution of the compound gave a faint brown colour with ferric chloride solution.

Methyl β-Anilino-α-α′-chloropropionylcrotonate.—α-Chloropropionyl chloride (25·4 g.) in dry ether (30 c.c.) was added during 30 min. to a solution of methyl β-anilinocrotonate (38·2 g.; Conrad and Limpach, *Ber.*, 1888, **21**, 1965) in dry ether (130 c.c.) and pyridine (15·8 g.) with stirring and cooling in ice. Stirring was continued for 2 hr. at 0° and 2 hr. at room temperature; then ice-water (75 c.c.) was added, and the ethereal layer was dried (Na_2SO_4) and evaporated under reduced pressure from a bath at 40°. Crystallisation of the residue from ethanol gave *methyl β-anilino-α-α′-chloropropionylcrotonate* (26 g., 46%) as colourless rods, m. p. 73° (from ethanol) (Found: C, 59·6; H, 5·7; N, 5·5. $C_{14}H_{16}O_3NCl$ requires C, 59·7; H, 5·7; N, 5·0%).

2 : 5-*Dimethyl*-4-*oxo*-1-*phenylpyrroline*-3-*carboxylic Acid* (VI; R = H).—A solution of the above chloropropionyl derivative (26 g.) in warm methanol (80 c.c.) was cooled rapidly to 0°, and treated, with shaking and cooling in ice-water, with an ice-cold solution of potassium hydroxide (12·5 g.) in methanol (80 c.c.), added in portions. The mixture was kept at 0° for 20 min., then evaporated under reduced pressure to small volume, and the residue dissolved in water (200 c.c.) and acidified with dilute hydrochloric acid. The crude methyl 2 : 5-dimethyl-4-oxo-1-phenylpyrroline-3-carboxylate (16·8 g., 77%) which separated was isolated by ether-extraction as a stiff, light yellow syrup.

The above ester (3·3 g.) and 2N-sodium hydroxide (30 c.c.) were heated together on the steam-bath for 30 min. Cooling and acidification with dilute hydrochloric acid gave 2 : 5-*dimethyl*-4-*oxo*-1-*phenylpyrroline*-3-*carboxylic acid* (2·7 g., 87%) as a white powder; crystallised from benzene or ethyl acetate it formed colourless needles, m. p. 151—152° (Found: C, 66·9; H, 5·7; N, 6·2. $C_{13}H_{13}O_3N$ requires C, 67·5; H, 5·7; N, 6·1%).

4-*Acetoxy*-2 : 5-*dimethyl*-1-*phenylpyrroline*-3-*carboxylic Acid*.—The above acid was acetylated in the usual way with acetic anhydride–potassium acetate. The *acetoxy-acid* separated from aqueous methanol as short, colourless rods, m. p. 93—95°, which on further recrystallisation yielded colourless blades, m. p. 206—208° (decomp.) (Found: C, 66·2; H, 5·9; N, 4·9. $C_{15}H_{15}O_4N$ requires C, 65·9; H, 5·5; N, 5·1%).

4-*Methoxy*-2 : 5-*dimethyl*-1-*phenylpyrroline*-3-*carboxylic Acid* (VIII).—A solution of crude methyl 2 : 5-dimethyl-4-oxo-1-phenylpyrroline-3-carboxylate (7 g.) in N-sodium hydroxide (75 c.c.) was treated with methyl sulphate (5·5 c.c.). The mixture was shaken for 2 hr., then treated with N-sodium hydroxide (15 c.c.) and methyl sulphate (1 c.c.) and shaken for a further 4 hr., during which a yellow syrup separated. The mixture was made just acid with dilute sulphuric acid, and the product (5·9 g.) isolated by ether as a yellow gum. This was heated under reflux with ethanolic potassium hydroxide (60 c.c.; 10%) for 2 hr.; the solution was then evaporated to dryness under reduced pressure, and a solution of the residue in water (60 c.c.) acidified with dilute sulphuric acid. Crystallisation of the separated material from ethyl acetate gave 4-*methoxy*-2 : 5-*dimethyl*-1-*phenylpyrrole*-3-*carboxylic acid* (0·5 g., 7%) as colourless needles, m. p. 153—155° (decomp.) (<130° on admixture with the unmethylated acid of m. p. 151—152°) (Found: C, 68·7; H, 6·4; N, 5·7. $C_{14}H_{15}O_3N$ requires C, 68·6; H, 6·2; N, 5·7%). A second preparation yielded the methoxy-acid as dense hexagonal prisms, m. p. 162—163°, (decomp.); in admixture with the form of m. p. 153—155°, the m. p. was 154—156° (decomp.) (Found: C, 68·9; H, 6·1; N, 5·6%). The ultra-violet absorption spectra of the two forms were virtually identical.

3-*Methoxy*-2 : 5-*dimethyl*-1-*phenylpyrrole*.—4-Methoxy-2 : 5-dimethyl-1-phenylpyrrole-3-carboxylic acid (0·15 g.) was heated at 155—156°/10 mm. 3-*Methoxy*-2 : 5-*dimethyl*-1-*phenylpyrrole* distilled as a very pale yellow, rather mobile liquid, which darkened rapidly on exposure to air (Found: C, 76·7; H, 7·5; N, 7·4. $C_{13}H_{15}ON$ requires C, 77·6; H, 7·5; N, 7·0%).

2 : 5-*Dimethyl*-4-*oxo*-1-*phenylpyrroline* (VII).—(*a*) Aniline (3·72 g.) and 3-hydroxyhexane-2 : 5-dione (5·20 g.; Henze and Müller, *Z. physiol. Chem.*, 1933, **214**, 281; Schechter and LaForge, U.S.P. 2,574,500) were mixed, the temperature rising spontaneously to about 45°. After 30 min., the mixture was heated for 1 hr. at 100° in an atmosphere of nitrogen, and for a further 3 hr. at 10 mm. (to remove water). Distillation of the residue through a short column afforded 2 : 5-dimethyl-4-oxo-1-phenylpyrroline (4·95 g., 66%) as a viscous, golden-yellow liquid, b. p. 133—134°/0·6 mm., 155—157°/2 mm. The compound rapidly oxidised in air to a crystalline mass (see below), and good analytical figures could not be obtained (Found: C, 75·3; H, 6·9; N, 7·2. Calc. for $C_{12}H_{13}ON$: C, 77·0; H, 7·0; N, 7·5%).

(*b*) 2 : 5-Dimethyl-4-oxo-1-phenylpyrroline-3-carboxylic acid (1 g.) was heated at 148—152°/5 mm. When evolution of carbon dioxide ceased, the pressure was reduced to 1 mm., and the bath temperature raised, finally to 200°. 2 : 5-Dimethyl-4-oxo-1-phenylpyrroline (0·6 g., 74%) distilled, and with benzoyl chloride and pyridine afforded 3-*benzoyloxy*-2 : 5-*dimethyl*-1-*phenylpyrrole*, m. p. 88—90°, alone or mixed with a sample of m. p. 90—91° described below (Found: N, 4·6. $C_{19}H_{17}O_2N$ requires N, 4·8%).

3-*Benzoyloxy*-2 : 5-*dimethyl*-1-*phenylpyrrole* (IX; R = Ph).—A solution of the above 4-oxopyrroline (1·12 g.) in dry pyridine (5 c.c.) was treated with benzoyl chloride (0·88 g., 1·05 mol.) added all at once, at about −40°. The mixture was kept at 0° with occasional shaking for 2 hr., then added to excess of sodium hydrogen carbonate solution, and the product extracted with chloroform. The extract was washed successively with dilute sulphuric acid, sodium hydrogen carbonate solution, and water, dried (Na_2SO_4), and evaporated under reduced pressure. Crystallisation of the residue from ethanol afforded 3-benzoyloxy-2 : 5-dimethyl-1-phenylpyrrole

(1·03 g., 59%) in colourless, hexagonal plates, m. p. 90—91° (Found: C, 78·1; H, 5·7; N, 4·9 Calc. for $C_{19}H_{17}O_2N$: C, 78·3; H, 5·9; N, 4·8%). The compound gave no colour with ferric chloride solution.

3-Benzoyloxy-1-benzyl-2 : 5-dimethylpyrrole (IX; R = CH_2Ph).—Benzylamine (4·28 g.) was cautiously added to 3-hydroxyhexane-2 : 5-dione (5·20 g.) with strong cooling. After 30 min. at 0° and 2 hr. at room temperature the mixture was distilled through a short column, giving crude 1-benzyl-2 : 5-dimethyl-4-oxopyrroline (2·20 g., 27%) as a viscous red liquid, b. p. 162°/1 mm. The compound gave a ferric chloride reaction identical with that of the corresponding 1-phenyl derivative. It (1·52 g.) afforded *3-benzoyloxy-1-benzyl-2 : 5-dimethylpyrrole* (1·40 g., 61%), yellow blades (from ethanol), m. p. 99—100° (Found: C, 79·0; H, 6·4; N, 4·6. $C_{20}H_{19}O_2N$ requires C, 78·7; H, 6·3; N, 4·6%).

5-Hydroxy-2 : 5-dimethyl-4-oxo-1-phenylpyrroline (XIII) *by Oxidation of 2 : 5-Dimethyl-4-oxo-1-phenylpyrroline.*—(a) *With air.* 2 : 5-Dimethyl-4-oxo-1-phenylpyrroline (1 g.) was exposed to air in a thin film for 2 days, being converted into light yellow crystals. Recrystallisation from ethyl acetate afforded *5-hydroxy-2 : 5-dimethyl-4-oxo-1-phenylpyrroline* (0·4 g., 35%) as very pale yellow rectangular prisms, m. p. 151—152°, soluble in cold water and the common organic solvents, except light petroleum [Found: C, 70·5; H, 6·5; N, 7·2%; *M* (Rast), 184. $C_{12}H_{13}O_2N$ requires C, 70·9; H, 6·5; N, 6·9%; *M*, 203]. It did not give a semicarbazone or 2 : 4-dinitrophenylhydrazone. Its ethanolic solution gave an immediate permanent red colour with ferric chloride.

(b) *With potassium ferricyanide.* A suspension of the oxopyrroline (7·5 g.) in water (80 c.c.) was treated with a solution of potassium ferricyanide (26·3 g., 2 mols.) in water (250 c.c.) and kept for 2 hr. at room temperature, with occasional shaking. The clear solution was extracted with chloroform (4 × 60 c.c.) and the extract dried (Na_2SO_4) and evaporated to give, after crystallisation from ethyl acetate (85 c.c.), the hydroxyoxopyrroline (3·74 g., 46%), m. p. 151—152°, alone or in admixture with the material described in (a). Similar yields were obtained from the crude product produced by heating aniline with 3-hydroxyhexane-2 : 5-dione without distillation.

Reactions of 5-Hydroxy-2 : 5-dimethyl-4-oxo-1-phenylpyrroline.—(a) *With alkali.* The compound (0·336 g.), and N-sodium hydroxide (25 c.c.) were boiled together under reflux for 1 hr. The liberated aniline (79%) was distilled in steam into dilute hydrochloric acid, and determined by titration with sodium nitrite solution. In a similar hydrolysis, the aniline formed was identified by conversion into benzanilide.

(b) *With acetic anhydride–pyridine.* A solution of the compound (0·30 g.) in pyridine (3 c.c.) and acetic anhydride (2 c.c.) was kept overnight at room temperature. After addition of ethanol and evaporation under reduced pressure, a solution of the residue in chloroform was washed with dilute sulphuric acid and sodium hydrogen carbonate solution, dried (Na_2SO_4), and evaporated, to yield *5-acetoxy-2 : 5-dimethyl-4-oxo-1-phenylpyrroline* (0·15 g., 41%), colourless prisms (from ethyl acetate), m. p. 128·5—129·5° (decomp.) (Found: C, 68·5; H, 6·1; N, 5·9. $C_{14}H_{15}O_3N$ requires C, 68·6; H, 6·2; N, 5·7%).

(c) *With o-phenylenediamine.* The compound (0·6 g.) and *o*-phenylenediamine (0·3 g.) were heated together at 150° for 15 min. Water was evolved, and after cooling, crystallisation from methanol yielded (?) *3-acetonyl-2-methylquinoxaline anil* (0·24 g., 30%) as fine yellow needles, m. p. 108—109° after two recrystallisations from methanol (Found: C, 78·6; H, 6·2; N, 15·2. $C_{18}H_{17}N_3$ requires C, 78·5; H, 6·2; N, 15·3%). Light absorption in EtOH: Max. at 222, 296, 325, and 426 mμ (ε 31,500, 13,200, 16,000, and 19,550 respectively). In other preparations, material of m. p. 120—140°, similar in appearance to the above, was obtained; this may be a mixture of the above compound and the corresponding 2-amino-anil (Found: C, 76·2; H, 6·0; N, 17·4. Calc. for $C_{18}H_{17}N_3 + C_{18}H_{18}N_4$: C, 76·4; H, 6·2; N, 17·3%). Its ultra-violet absorption spectrum was similar to that of the compound of m. p. 108—109°.

When the condensation was carried out in boiling ethanol (4 hr.) and in boiling 2-ethoxyethanol (1 hr.), the yields of crude condensation product were 9% and 31% respectively.

The above quinoxaline (50 mg.; m. p. 108—109°) and 50% sulphuric acid (4 drops) were heated together at 100° for 1½ hr. The mixture was cooled and made just alkaline with ammonia, giving brownish needles (24 mg., 66%), m. p. 98—100°, which were purified by sublimation at 100—105°/0·5 mm. This was followed by recrystallisation from aqueous ethanol, to give 2 : 3-dimethylquinoxaline as colourless needles, m. p. 104·5—105·5° alone or in admixture with an authentic sample (Found: C, 76·2; H, 6·3; N, 18·1. Calc. for $C_{10}H_{10}N_2$: C, 75·9; H, 6·4; N, 17·7%). The quinoxaline of m. p. 120—140° gave the same product in similar yield.

5-Hydroxy-2 : 5-dimethyl-1-m-nitrophenyl- and -1-α-naphthyl-4-oxopyrroline.—3-Hydroxyhexane-2 : 5-dione (2·60 g.) and *m*-nitroaniline (2·76 g.) were heated together for 2 hr. at 100°. The

crude product was oxidised with potassium ferricyanide as described for the corresponding 1-phenyl derivative, except that 50% ethanol (240 c.c.) was used as solvent, and the mixture was evaporated to half its volume before extraction with chloroform. The 1-m-*nitrophenyl* compound crystallised from ethyl acetate in small yellow rectangular prisms, m. p. 179—181° (Found: C, 57·7; H, 4·9; N, 11·8. $C_{12}H_{12}O_4N_2$ requires C, 58·1; H, 4·9; N, 11·3%).

Similarly prepared from α-naphthylamine, the 1-α-*naphthyl* compound was obtained in almost colourless prisms, m. p. 167—168° (Found: C, 75·5; H, 5·8; N, 5·6. $C_{16}H_{15}O_2N$ requires C, 75·9; H, 6·0; N, 5·5%).

5-Hydroxy-2 : 5-dimethyl-4-oxo-1-phenylpyrroline-3-carboxylic Acid.—2 : 5-Dimethyl-4-oxo-1-phenylpyrroline-3-carboxylic acid (0·5 g.) was oxidised with potassium ferricyanide (2 mols.) in aqueous ethanol, and the product (0·1 g.) isolated by chloroform. Crystallised from ethyl acetate, *5-hydroxy-2 : 5-dimethyl-4-oxo-1-phenylpyrroline-3-carboxylic acid* formed colourless needles, m. p. 197—198° (decomp.) (Found: C, 63·0; H, 5·2; N, 5·9. $C_{13}H_{13}O_4N$ requires C, 63·2; H, 5·3; N, 5·7%).

Reactions with Diazomethane.—The pyrrole was dissolved in methanol (20 c.c. per g.), treated with a 3—4-fold excess of crude ethereal diazomethane (*Org. Synth.*, Coll. Vol. II, p. 166, Note 3), and kept for several days at room temperature, then evaporated under reduced pressure.

(a) *Ethyl 4-hydroxy-1-phenylpyrrole-3-carboxylate.* The ester (1 g.) was methylated for 5 days, and the crude product boiled under reflux with ethanolic potassium hydroxide (10 c.c. of 10%) for 2 hr. Acidification of the cooled mixture with dilute hydrochloric acid gave a brown powder which crystallised, with difficulty, from benzene or ethanol, to give 4-methoxy-1-phenylpyrrole-3-carboxylic acid (0·19 g., 20%) as light brown prisms, m. p. 165—166° (decomp.), after recrystallisation (Found: C, 66·3; H, 5·4; N, 6·1. Calc. for $C_{12}H_{11}O_3N$: C, 66·3; H, 5·1; N, 6·4%). The m. p. was not depressed by admixture with a sample of m. p. 167—168° (decomp.) prepared by Benary and Konrad's method.

(b) *Methyl 2-methyl-4-oxo-1-phenylpyrroline-3-carboxylate.* Methylation of the ester (0·5 g.) for 5 days gave a *compound* (0·1 g., 17%), as yellow needles, m. p. 200° (decomp., with slight darkening at lower temperature) after recrystallisation from ethanol (Found: C, 61·5; H, 5·6; N, 15·3. $C_{14}H_{15}O_3N_3$ requires C, 61·5; H, 5·5; N, 15·4%). Light absorption in EtOH: Max. at 235, 322, and 393 mμ (ε 17,100, 11,700, and 9200 respectively). In ethanolic solution, the compound gave an intense olive-green colour with ferric chloride. The same compound was similarly prepared from methyl 4-acetoxy-2-methyl-1-phenylpyrrole-3-carboxylate (yield, 19%) (Found: N, 15·5%).

The above yellow compound (0·15 g.) and ethanolic potassium hydroxide (2 c.c.; 10%) were heated under reflux for 2 hr. and cooled. The potassium salt (0·15 g.) was collected, dissolved in water, and acidified, to give the *acid* (0·10 g., 69%) as colourless needles, m. p. 216—218° after recrystallisation from benzene. Dried at room temperature, the compound appeared to be a hemihydrate (Found: C, 58·5, 58·3; H, 5·3, 5·3; N, 15·9. $C_{13}H_{13}O_3N_3,\frac{1}{2}H_2O$ requires C, 58·2; H, 5·3; N, 15·7%). Light absorption in EtOH: approx. equal max. at 242 and 305 mμ. The ferric chloride colour was cherry-red.

(c) *1-Acetyl-4-oxo-2-phenylpyrroline-5-carboxylic acid.* The acid (1 g.), suspended in methanol, dissolved rapidly with vigorous evolution of nitrogen on addition of ethereal diazomethane. After 2 days, the solution was evaporated and the residue crystallised from benzene (5 c.c.), to give *methyl 1-methyl-4-oxo-2-phenylpyrroline-5-carboxylate* (0·12 g. 13%) as colourless needles, m. p. 182—183° after recrystallisation (Found: C, 67·1; H, 5·8; N, 6·4. $C_{13}H_{13}O_3N$ requires C, 67·5; H, 5·7; N, 6·1%). Addition of light petroleum (15 c.c.; b. p. 40—60°) to the filtrate from the above compound gave *methyl 1-acetyl-3-methoxy-5-phenylpyrrole-2-carboxylate* (0·25 g., 25%), colourless prisms, m. p. 96—97° after recrystallisation from light petroleum (b. p. 80—100°) (Found: C, 65·7; H, 5·4; N, 5·1. $C_{15}H_{15}O_4N$ requires C, 65·9; H, 5·5; N, 5·1%).

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