559. *The Ultra-violet Absorption Spectra of Some Pyrroles.*

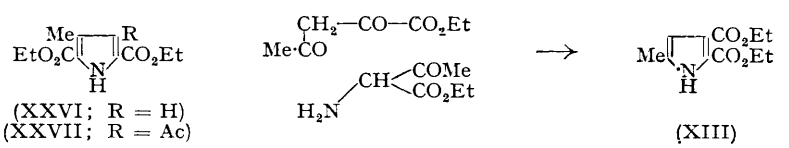
By GERALD H. COOKSON.

The ultra-violet absorption spectra of a number of pyrroles have been measured and their dependence on the position of electron-attracting substituents is illustrated. Consideration of these results has led to the revision of the structures assigned to several compounds. The preparation of some pyrroles fused to a heterocyclic ring in the 2 : 3-positions is described.

THE type of ultra-violet absorption spectrum shown by a pyrrole conjugated with a chromophore is dependent on the position of substitution. The striking contrast between the absorption curves given by pyrroles with an electron-attracting group in the 2- and 3-positions is shown in Fig. 1, and the curves for the various isomers with two such groups are given in Figs. 2 and 3. The spectra of individual examples are summarized in the Table, from which it appears that the general effects observed in the benzene series also apply here (Doub and Vandenbelt, *J. Amer. Chem. Soc.*, 1947, **69**, 2714; 1949, **71**, 2414). Thus, substitution of a nuclear hydrogen by a methyl group shifts the bands 5—10 mμ towards the red, and replacement of a carbethoxyl by a formyl or acetyl group causes a bathochromic shift of *ca.* 20 mμ. A bromo-group has an effect similar to that of methyl.

Very few spectra of pyrroles have been published, and in a recent review (Granick and Gilder, *Adv. Enzymol.*, 1947, **7**, 358) the unjustified generalization, based on a single example (VII) (Pruckner and Dobeneck, *Z. physikal. Chem.*, 1942, **190**, *A*, 43), was made that " the spectrum of a substituted pyrrole consists of a single major band in the region 250—300 mμ."

The application of these results to a structural problem may be illustrated by reference to the condensation between ethyl α-aminoacetoacetate and ethyl acetopyruvate in acetic acid. Two pyrroles are formed, one of which was correctly identified as ethyl 5-carbethoxy-2 : 4-dimethyl-3-pyrrolylglyoxylate (XVIII) by Kordo, Ono, and Sato (*J. Pharm. Soc. Japan*, 1934, **54**, 123, 683). The other product, a (dicarbethoxy)methylpyrrole, m. p. 61°, was said to give no mixed m. p. depression with the ethyl ester of the ester acid, $C_9H_{11}O_4N$, m. p. 207°, which the Japanese chemists obtained when the condensation was carried out in aqueous sodium hydroxide. They obtained the same ester acid, m. p. 207°, by the use of glycine ester instead of ethyl α-aminoacetoacetate in the alkaline condensation, and both samples were decarboxylated to an ethyl methylpyrrolecarboxylate, m.p. 88°. They concluded that the substance, m. p. 61°, was diethyl 3-methylpyrrole-2 : 5-dicarboxylate (XXVI), and hence, by exclusion of the known 2 : 3-isomer, that the compound, m. p. 88°, was ethyl 4-methylpyrrole-2-carboxylate (*ibid.*, 1937, **57**, 1). These results appeared improbable. The Japanese assumed that (XXVI) was formed by hydrolysis of the nuclear acetyl group from the presumed intermediate (XXVII) in which in fact it is firmly attached (Lichtenwald, *Z. physiol. Chem.*, 1942, **273**, 118). Secondly, Fischer, Beyer, and Zaucker (*Annalen*, 1931, **483**, 55) have shown that the way in which acetylpyruvic ester condenses with an amino-ketone is dependent on pH ; at pH < 6 the amino-group condenses exclusively with the acetyl group (leading here to XVIII) and only in strongly alkaline solution does it react with the oxalyl group (which would be required for the formation of XXVII).



(XXVI; R = H)
(XXVII; R = Ac)

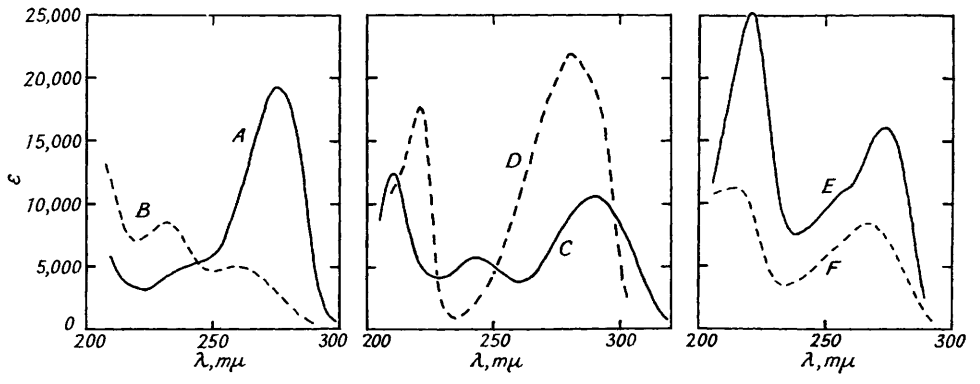
(XIII)

It is evident that the " extra " acetyl group which is lost during the formation of the compound, m. p. 61°, is removed by a reaction of the type discovered by Fischer and Fink (*Z. physiol. Chem.*, 1948, **283**, 152), and that in fact the product is (XIII). Had the amino-group condensed with the oxalyl CO, a similar reaction would have given (XXVI). This is unlikely since, if the amino-group had reacted in two ways, a mixture of all four pyrroles (XVIII), (XIII), (XXVI), and (XXVII) might have been expected, whereas only

(XVIII) and one other were obtained. The true structure (XIII) was proved by the close similarity of its absorption spectrum to that of diethyl 4 : 5-dimethylpyrrole-2 : 3-dicarboxylate (XIV), while the spectrum of a pyrrole with 2 : 5-dicarbethoxy-groups is entirely different. This was later confirmed by bromination of (XIII) to (XV), which was shown by m. p. and mixed m. p. to be different from diethyl 4-bromo-3-methylpyrrole-2 : 5-dicarboxylate (XIX). Although Corwin and Straughn (*J. Amer. Chem. Soc.*, 1948, **70**, 1416) quoted the Japanese results in support of their formulation, diethyl 3-methylpyrrole-2 : 5-dicarboxylate, which melts at 62°, the structure was proved by their own work. If the Japanese experimental data are accepted, it follows from the structure (XIII) by exclusion of the known 2 : 5-isomer that their compound, m. p. 88°, is actually ethyl 5-methylpyrrole-3-carboxylate. The condensations in alkaline solution have not been repeated.

Grob and Ankli (*Helv. Chim. Acta*, 1949, **32**, 2023), in their investigation of the products of the acetylation of 2 : 3-dihydro-2-oxopyrroles, explained the close similarity of the spectra of the compounds they called 2-acetoxy-3-acetyl-4-carbethoxypyrrole and its 5-methyl

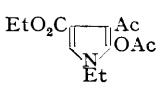
FIG. 1. FIG. 2. FIG. 3.



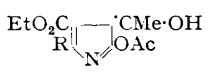
Absorption spectra.

FIG. 1. *A, Ethyl* 3 : 5-*dimethylpyrrole*-2-*carboxylate* (V). *B, Ethyl* 2 : 4-*dimethylpyrrole*-3-*carboxylate* (X).
FIG. 2. *C, Diethyl* 5-*methylpyrrole*-2 : 3-*dicarboxylate* (XIII). *D, Methyl* 5-*carbethoxy*-3-*ethyl*-4-*methyl pyrrole*-2-*carboxylate* (XX).
FIG. 3. *E, Diethyl* 3 : 5-*dimethylpyrrole*-2 : 4-*dicarboxylate* (XVI). *F, Diethyl* 2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylate* (XXII).

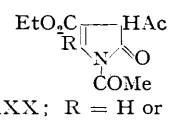
derivative, and their difference from that of 2-acetoxy-3-acetyl-4-carbethoxy-1-ethylpyrrole (XXVIII), by assuming that the first two compounds could tautomerise (XXIX). No evidence of such enolization has been found in the present work. The pyrrolylglyoxylate (XVIII), in which it would be most favoured, gives no colour with ferric chloride, and its ultra-violet spectrum is unaltered by alkali. Its infra-red spectrum in carbon tetrachloride, kindly measured by Dr. L. A. Duncanson, includes two bands at 3440



(XXVIII)



(XXIX; R = H or Me)



(XXX; R = H or Me)

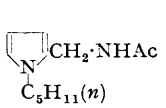
and 3300 cm.$^{-1}$. Their relative intensities vary with concentration in the manner expected for an NH group which is strongly associated in concentrated solutions; *i.e.*, on dilution the 3440 cm.$^{-1}$ band increases and that at 3300 cm.$^{-1}$ decreases in intensity. The spectrum of the solid shows only one NH frequency at 3220 cm.$^{-1}$. There is no sign of an OH frequency near 3500—3600 cm.$^{-1}$ throughout the concentration range studied (*ca.* 0·02—0·0036M). Both bands were present in the chloroform solution of (XVIII) at 3420 and 3290 cm.$^{-1}$, but the lower-frequency band was much weaker than its counterpart in similar concentration in carbon tetrachloride. The same pattern was found for the

spectrum of (XII) in chloroform (0·03M), the two frequencies in this case being 3450 and 3290 cm.$^{-1}$. From the changes with concentration observed in the intensities of the carbonyl bands of these compounds, it is concluded that the intermolecular association which takes place involves N–H···O bonds.

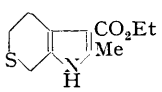
The compound (XXVIII) has an ultra-violet spectrum like that of (XXII) but with maxima shifted *ca.* 20 mμ towards the red, as expected, and its structure seems certain. The very close similarity of those of the other two compounds of Grob and Ankli, both with maxima at 315 mμ, contraindicates tautomerism. One would expect a pure enol (XXIX) with an azafulvene structure to absorb in the visible, so that a slight shift in the keto–enol equilibrium caused by the introduction of a methyl group would cause an appreciable difference between the spectra of the equilibrium mixtures of the two compounds. The compounds, unlike (XXVIII), are rapidly hydrolysed by cold sodium hydroxide to 3-acetyl-4-carbethoxy-2 : 3-dihydro-2-oxopyrroles and their spectra suggest that they still contain this system. They must therefore be the *N*-acetyl derivatives (XXX), the only other possibility (with both acetyl groups at position 3) being precluded by the blue colour produced by ferric chloride. Acetylation in position 1 is not unlikely, since 5-acetyl-4-carbethoxy-2 : 3-dihydro-2-oxopyrrole gives the *N*-methyl derivative with diazomethane.

Pyrrole itself absorbs weakly at 240 mμ (ε 300), in addition to the strong band at 210 mμ (ε 15,000) (in hexane; see Bowden, Braude, and Jones, *J.*, 1946, 948), but no sign of a low-intensity band in the 250-mμ region was observed in any of the alkylpyrroles studied (in alcohol). The absorption curves all fell smoothly with no inflexion, opsopyrrole (I) reaching ε 20 at 270 mμ, and (III) reaching ε 25 at 260 mμ. Low-intensity absorption is less significant in the case of cryptopyrrole (II) without special precautions being taken against its rapid atmospheric oxidation, but ε was less than 200 at 265 mμ.

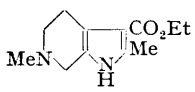
The formation of a salt of cryptopyrrole was observed. The addition of a drop of hydrochloric acid to its alcoholic solution removed the band at 200 mμ and produced a new maximum at 261 mμ (ε 4000) (cf. *cyclo*pentadiene, 238·5 mμ; also Booker, Evans, and Gillam, *J.*, 1940, 1453). The acid solution was stable for at least 10 minutes, and the spectrum reverted to the neutral form on the addition of alkali, although measurements below 225 mμ could no longer be taken. Opsopyrrole (I), which has only two electron-donating alkyl groups, showed only a slight change in spectrum after the addition of much acid, whereas (III) and pyrroles with an electron-attracting group were unaffected.



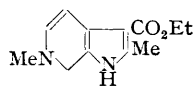
(III)



(XXIII)



(XXIV)



(XXV)

The preparation is described of the bicyclic pyrroles (XXIII—XXV). It had been hoped that useful intermediates for porphyrin syntheses could be obtained by opening the six-membered ring in such compounds.

Experimental

Ultra-violet absorption spectra between ~210 and 400 mμ were measured in ethanolic solution with a Unicam spectrophotometer; 10-mm. cells were used except for (I) and (II), for which 1-mm. cells were used. The concentrations of the solutions employed were such that any maxima with ε > 10% of the most intense band recorded could be measured [except for (I) and (III) which were also examined at much higher concentrations; see above].

Compound (III) was kindly provided by Dr. Niels Elming (Elming and Clauson-Kaas, *Acta Chem. Scand.*, 1952, **6**, 867). Compound (VII) was prepared by hydrogenation of (XVII) in acetic acid containing 1% of concentrated hydrochloric acid over Adams's catalyst at 1 atm. It melted at 89—90° as reported by Signaigo and Adkins (*J. Amer. Chem. Soc.*, 1936, **58**, 709) and not at 96° (Siedel, *Z. physiol. Chem.*, 1935, **231**, 184). Pyrroles with only a 3-carbethoxy-group are hydrogenated to pyrrolines under these conditions. *Methyl 5-carbethoxy-3-ethyl-4-methylpyrrole-2-carboxylate* (XX), prepared from the ester acid with diazomethane, had m. p. 64—65° (Found: C, 60·4; H, 7·2; N, 6·1. $C_{12}H_{17}O_4N$ requires C, 60·2; H, 7·1; N, 5·9%). *4-Ethyl-3-methylpyrrole-2-carboxylic acid* (IV) was obtained by hydrolysis of its ester with

boiling N-sodium hydroxide in 50% ethanol for 45 min. and formed prisms, m. p. *ca.* 180—200° (effervescence) (Found : C, 62·5; H, 7·1; N, 9·2. $C_8H_{11}O_2N$ requires C, 62·7; H, 7·2; N, 9·15%). The aldehyde (XXI) melted at 92—93°, but the m. p. and preparation of the remaining compounds in the Table, apart from those described below, were in accordance with those in the literature (see Fischer and Orth, " Die Chemie des Pyrroles," Leipzig, 1934, Band 1).

Diethyl 5-Methylpyrrole-2 : 3-dicarboxylate (XIII).—Zinc dust (8·4 g.) was added in portions to a stirred solution of ethyl hydroxyiminoacetoacetate (10·2 g.) and ethyl acetopyruvate (11·1 g.) in acetic acid (25 c.c.) with cooling to keep the temperature below 45°. The solution was then refluxed for 50 min., poured into water (300 c.c.) and extracted with benzene. After being washed with sodium hydroxide solution and with water, the extract was dried (Na_2SO_4), and the solvent removed. The residual oil (8·9 g.) was chromatographed on alumina in benzene, which eluted all the Ehrlich-positive reacting material (5 g.). This was again chromatographed on alumina in light petroleum (b. p. 40—60°)—ether (5 : 1). The first fractions yielded the *diester* (XIII), large colourless tablets [from light petroleum (b. p. 60—80°)], m. p. 62—63° (2·25 g., 15·6%) (Found : C, 58·8; H, 6·8; N, 6·2. $C_{11}H_{15}O_4N$ requires C, 58·65; H, 6·7; N, 6·2%). Later fractions from the chromatogram provided ethyl 5-carbethoxy-2 : 4-dimethyl-3-pyrrolylglyoxylate (XVIII) (0·6 g., 3·5%), m. p. 126—127·5° undepressed by admixture with a sample prepared by Fischer and Andersag's method (*Annalen*, 1927, **458**, 137). The 2 : 4-*dinitrophenylhydrazone* of (XVIII) separated in orange crystals (from ethyl acetate), m. p. 205—207° with slight previous softening (Found : C, 51·0; H, 5·0; N, 15·8. $C_{19}H_{21}O_8N_5$ requires C, 51·0; H, 4·7; N, 15·7%).

Diethyl 4-Bromo-5-methylpyrrole-2 : 3-dicarboxylate (XV).—A solution of diethyl 5-methylpyrrole-2 : 3-dicarboxylate (502 mg.) in boiling carbon tetrachloride (5 c.c.) was treated with bromine (1 mol.) in carbon tetrachloride. Hydrogen bromide was immediately evolved and after 1 min. suction was applied to remove the solvent. The *bromopyrrole* (XV), recrystallized twice from alcohol, formed prisms, m. p. 117·5—119° (146 mg., 22%) (Found : C, 43·55; H, 4·7; N, 4·65. $C_{11}H_{14}O_4NBr$ requires C, 43·4; H, 4·6; N, 4·6%). When mixed with its isomer (XIX), its m. p. was depressed to 70—79°.

3-*Hydroxyiminothiacyclohexan-4-one*.—This was not isolated from solution. Attempts to prepare it from 3-carbomethoxythia*cyclo*hexanone with alkali and nitrite (cf. Geissman and Schlatter, *J. Org. Chem.*, 1946, **11**, 771) yielded only thia*cyclo*hexanone ; and reaction between the latter, sodium ethoxide, and ethyl nitrite (1 equiv.) in dry ether (cf. Pezold and Shriner, *J. Amer. Chem. Soc.*, 1932, **54**, 4707) gave a product heavily contaminated with 3 : 5-*bishydroxyiminothia*cyclo*hexan-4-one*, colourless efflorescent needles which charred on being heated (Found : C, 34·3; H, 3·3. $C_5H_6O_3N_2S$ requires C, 34·5; H, 3·45%).

Methyl 4-oxothia*cyclo*hexane-3-carboxylate (16·2 g.) was hydrolysed with potassium hydroxide (6·0 g. in 50 c.c. of water) at −10° for several weeks. Extraction of the solution with ether removed thia*cyclo*hexanone (3 g.), and further extraction with ether after careful acidification at −10° provided the free keto-acid (10 g.). This was dissolved in acetic acid (10 c.c.) and water (5 c.c.) and treated dropwise with concentrated aqueous sodium nitrite. Carbon dioxide was evolved, and the nitrite was rapidly consumed until 2·9 g. had been added. The yellow solution was kept at 0° for 3 hr. before use.

Ethyl 4 : 5 : 6 : 7-Tetrahydro-2-methyl-1-aza-6-thiaindene-3-carboxylate (XXIII).—Ethyl acetoacetate (6·5 g.) was added to the solution of the hydroxyimino-compound described above, and the mixture added in portions to zinc dust (6·5 g.) with mechanical stirring. The temperature was kept below 60° during the addition, after which the mixture was warmed for 30 min. and then poured on ice. The washed and dried precipitate gave a turbid solution in chloroform which was clarified by shaking it with alumina before pouring it through an alumina column. The material recovered from the eluate was further chromatographed in benzene on alumina. The *tetrahydroazathiaindene* (XXIII) (1·3 g., 6·5%) crystallized from ethanol or nitromethane in needles, m. p. 154·5—156°, which were sublimed at 165°/0·2 mm. before analysis (Found : C, 58·5; H, 6·6; N, 5·8. $C_{11}H_{15}O_2NS$ requires C, 58·6; H, 6·7; N, 6·2%). A solution of the compound in warm nitromethane containing methyl iodide soon deposited crystals of the *methiodide* (Found : C, 39·3; H, 5·2. $C_{12}H_{18}O_2NSI$ requires C, 39·2; H, 4·9%), which was converted into the *methopicrate*, golden needles (from ethanol), m. p. 134—137° (decomp.) (Found : C, 46·35; H, 4·3; N, 11·8. $C_{18}H_{20}O_9N_4S$ requires C, 46·2; H, 4·3; N, 12·0%).

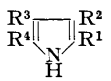
3-Hydroxyimino-1-methyl-4-piperidone was not isolated from solution. Sodium hydroxide (10·75 g. in 20 c.c. of water) was added to a stirred solution of 3-carbethoxy-1-methyl-4-piperidone hydrochloride (25 g.) in water (50 c.c.) at 3°. The mixture was kept at this temperature with occasional shaking for 8—10 days. The temperature was then kept below 0° while first acetic

acid (72 c.c.) and then a solution of sodium nitrite (6·1 g. in 13 c.c. of water) were added. The addition of the nitrite (1 hr.) was accompanied by smooth evolution of carbon dioxide. The solution was set aside for 2 hr. before use.

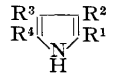
4′-Carbethoxy-1 : 2 : 5 : 6-tetrahydro-1 : 5′-dimethylpyrrolo(2′ : 3′-3 : 4)pyridine (XXIV).—Ethyl acetoacetate (14·6 g.) was added to the solution of the foregoing hydroxyimino-compound, and the mixture gradually (45 min.) added to zinc dust (14·44 g.). The temperature rose to 50°. Stirring was continued while the mixture was refluxed for 4 hr. The product could be extracted with chloroform after the addition of enough 30% sodium hydroxide solution to the ice-cold reaction mixture to redissolve the zinc hydroxide. However, it was more convenient to remove the zinc first, by diluting the solution five times with water and saturating it with hydrogen sulphide. The supernatant liquid was made alkaline and extracted with chloroform. Evaporation of the solvent left a dark brown oil (9 g.) from which the pure product crystallized (2·1 g.). The *tetrahydropyrrolopyridine* (XXIV) separated from chloroform in colourless needles, which lost solvent of crystallization when warmed. The solvent-free base, which was very soluble in the common solvents, melted at 165—166° (Found: C, 65·2; H, 7·9; N, 13·0. $C_{12}H_{18}O_2N_2$ requires C, 64·9; H, 8·1; N, 12·6%). The *picrate* formed canary-yellow crystals (from ethanol), m. p. 180—186° (decomp.) (Found: C, 48·3; H, 4·7; N, 15·4. $C_{18}H_{21}O_9N_5$ requires C, 47·9; H, 4·7; N, 15·5%). A quantitative yield of the *methiodide* rapidly separated from a solution of the base in alcoholic methyl iodide and had m. p. 239—240° (decomp.) (Found: C, 43·0; H, 5·6; N, 7·65. $C_{13}H_{21}O_2N_2I$ requires C, 42·8; H, 5·8; N, 7·7%). The *methopicrate* crystallized from water in golden needles, m. p. 227—229° (Found: C, 48·25; H, 4·8; N, 15·4. $C_{19}H_{23}O_9N_5$ requires C, 49·0; H, 4·95; N, 15·05%).

Hofmann degradation of methiodide of (XXIV). Silver oxide could not be used since it gave a complex with the iodide which was soluble in methanol and deposited a silver mirror when heated. Sodium ethoxide (1 equiv.) was added to the methiodide (500 mg.) in ethanol (10 c.c.), and the solution refluxed for 2 hr. The *methine base* was obtained by removal of the solvent, addition of water, and extraction with benzene. After distillation at 130°/0·2 mm., it crystallized from light petroleum (b. p. 60—80°) in rhombs, m. p. 76—77° (Found: C, 62·9, 63·2; H, 9·1, 9·1; N, 9·6, 10·2%). Its *hydrochloride* separated in laths, m. p. 230—235° (effervescence),

Absorption Characteristics of pyrrole derivatives



	R^1	R^2	R^3	R^4	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{min.}$	$\varepsilon_{min.}$
(I)	H	Et	Me	H	~203	5,670	—	—
(II)	Me	Et	Me	H	~200	7,450	—	—
				(+ HCl)	261	4,000	231	2,000
					Isosbestic point at		241	2,300
(III)			(See text)		220	8,770	—	—
(IV)	CO_2H	Me	Et	H	253 *	9,700	220	2,660
					270	14,500	—	—
(V)	CO_2Et	Me	H	Me	240 *	5,000	221	3,000
					276	19,300	—	—
(VI)	CO_2Et	Me	$CH_2{\cdot}CH(CO_2Et)_2$	Me	247 *	5,950	222·5	3,770
					280	19,200	—	—
(VII)	CO_2Et	Me	Et	Me	250 *	5,900	222	2,800
					283·5	18,900	—	—
(VIII)	Ac	Me	Et	Me	266 *	4,700	235	800
					308	19,600	—	—
(IX)	Me	Me	CO_2Et	H	231·5	9,980	220	7,960
					263·5	3,740	255	3,570
(X)	Me	CO_2Et	Me	H	232	8,480	220	7,100
					259	5,030	250	4,670
(XI)	Me	CO_2Et	Me	Me	232·5	9,400	222·5	8,760
					270	4,700	254	3,800
(XII)	Me	Ac	Me	H	<210	>10,000	—	—
					251	10,000	227	3,000
					273—285 *	4,760	—	—
(XIII)	CO_2Et	CO_2Et	H	Me	210	12,400	—	—
					243	5,640	229	4,100
					290	10,570	260	3,670
(XIV)	CO_2Et	CO_2Et	Me	Me	213	8,000	—	—
					250	4,500	235	4,100
					293	10,500	263	3,900
(XV)	CO_2Et	CO_2Et	Br	Me	<210	>12,000	252	4,370
					ε varies little between 230 and 255 mμ			
					283	12,250	—	—

Absorption Characteristics of pyrrole derivatives 

	R^1	R^2	R^3	R^4	$\lambda_{max.}$	$\epsilon_{max.}$	$\lambda_{min.}$	$\epsilon_{min.}$
(XVI)	CO_2Et	Me	CO_2Et	Me	221	25,300	238	7,550
					273	16,100	—	—
(XVII)	CO_2Et	Me	Ac	Me	235	22,800	—	—
					255 *	12,000	268	8,800
					283	11,800	—	—
(XVIII)	CO_2Et	Me	$CO{\cdot}CO_2Et$	Me	243·5	25,200	<210	<6,000
					292	8,540	275	6,670
(XIX)	CO_2Et	Br	Me	CO_2Et	220	17,350	239	3,800
					278	20,250		
(XX)	CO_2Et	Me	Et	CO_2Me	221	17,700	235	900
					280	21,900		
(XXI)	CO_2Et	Me	Et	CHO	231	14,200	215	6,500
					303	21,100	250	1,600
(XXII)	Me	CO_2Et	CO_2Et	Me	215	11,200	234	3,500
					267·5	8,450	—	—
(XXIII)			(See text)		~212	14,600	252	3,700
					266	4,550	—	—
			(Methiodide)		<230	high	250	4,800
					262·5	5,500	—	—
(XXIV)			(See text)		~208	17,500	—	—
					228 *	9,150	250	3,820
					266·5	4,880	—	—
			(in 0·05N-HCl in EtOH)		~208	17,500	—	—
					225 *	9,000	244	4,800
					256	5,470	—	—
					Isosbestic points at		244·5	4,800
							and 263·5	4,800
(XXV)			(See text)		~210	13,200	—	—
					227	11,600	218	11,400
					243 *	9,700	280	1,000
					373·5	22,000	—	—
				(+HCl)	212	15,000	229	7,770
					241	9,720	276	700
					348·5	20,800	—	—
					Isosbestic points at		~220	—
							~280	—
							and at 242	9,700
							359	17,000
	Me	CO_2Et	$>C_6H_4$		215	35,500	—	—
(3-Carbethoxy-2-methylindole)					228 *	18,000	243	9,150
					253	10,100	265	8,600
					282	11,300	—	—

* = Shoulder. λ in mμ.

from aqueous methanolic hydrochloric acid (Found: C, 55·9; H, 7·6; N, 9·7; Cl, 12·5%), and its *picrate*, m. p. 205—220° (decomp.), from alcohol (Found: C, 48·6; H, 4·9; N, 15·1%). These analyses are inconsistent with each other. The base had absorption maxima at 215 and 268 mμ, which changed to 215 and 263·5 mμ with acid.

4′-Carbethoxy-1 : 2-dihydro-1 : 5′-dimethylpyrrolo[2′ : 3′-3 : 4]pyridine (XXV).—A solution of the tetrahydro-base (XXIV) (0·24 g.) in acetic acid (1·5 c.c.) and water (3 c.c.) was boiled with mercuric acetate (1·5 g.) for 20 min. The mercurous acetate was removed, and a solution of potassium bromide added to the filtrate. The supernatant liquid was decanted from the gum which was first precipitated and treated with more potassium bromide. The white needles of the *hydrogen mercuric tribromide salt* of (XXV) which then separated were recrystallized from water and had m. p. 168—169° (0·32 g.) (Found: C, 22·0; H, 2·6; N, 4·25. $C_{12}H_{17}O_2N_2Br_3Hg$ requires C, 21·8; H, 2·6; N, 4·2%). The *picrate* could be prepared from this complex salt or, better, by direct addition of picric acid to the reaction mixture. It crystallized from dioxan in yellow prisms, m. p. 201—206° (decomp.) (Found: C, 47·4; H, 4·3; N, 15·0. $C_{18}H_{19}O_9N_5,\frac{1}{2}H_2O$ requires C, 47·2; H, 4·4; N, 15·3%). The free *dihydro*-base (XXV) was regenerated from its picrate with lithium hydroxide and chromatographed on alumina in benzene, from which it was eluted by ethyl acetate containing 4% of methanol; crystallized from ethyl acetate, it formed very pale buff prisms, m. p. 140—149° (decomp.) (Found: C, 65·3; H, 7·1. $C_{12}H_{16}O_2N_2$ requires C, 65·45; H, 7·3%). It could not be sublimed. An earlier fraction from the chromatogram, eluted with benzene–ethyl acetate (1 : 1), provided a small amount of a colourless *substance*, m. p. 220—222°, which sublimed at its m. p. (Found: C, 61·5, 61·0; H, 7·05, 6·85; N, 11·3,

12·6. $C_{22}H_{30}O_5N_4$ requires C, 61·4; H, 7·0; N, 13·0%). Its spectrum, which was unchanged by acid, had maxima at 213, 263, and 276 mμ, $E^{1\%}_{1\,cm.}$ 1200, 515, and 540, respectively.

The author is grateful to Professor C. Rimington for his interest and encouragement, to Miss H. James who measured some of the ultra-violet spectra, and to Dr. L. A. Duncanson, of Imperial Chemical Industries Limited, Butterwick Research Laboratories, for the infra-red data and their interpretation.

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