Reaction of Dimethylvinylidene Carbene with Methylpyrroles

Ian Birtwistle
Chemical Development Laboratories, The Wellcome Foundation Ltd., Temple Hill, Dartford DA1 5AH
Vernon Rogers*
School of Chemistry, Thames Polytechnic, Woolwich, London SE18 6PF

Treatment of a series of methylpyrroles with dimethylvinylidene carbene, generated under phase-transfer catalytic conditions, was found to give 3-vinylpyridines; in three cases allenic-2*H*-pyrroles were also isolated.

Dimethylvinylidene carbene (2) has been generated by the reaction of strong base with 3-chloro-3-methylbut-1-yne (1) or 1-bromo-3-methylbuta-1,2-diene (3), and more recently phase-transfer catalytic methods have been used.[1,2] The addition of

$$Me_2CCl–C{\equiv}CH \xrightarrow{-HCl} Me_2C{=}C{=}C{:} \xleftarrow{-HBr} Me_2C{=}C{=}CHBr$$
$$\text{(1)} \qquad\qquad \text{(2)} \qquad\qquad \text{(3)}$$

allenic carbenes to alkenes to give cyclopropanes is well known, and their reactions with oxygen heterocycles,[3] indoles, and 2,5-dimethylpyrrole (12)[4] have been investigated. In this study pyrrole (4) and a selection of methylated pyrroles were treated with dimethylvinylidene carbene (2), generated from 3-chloro-3-methylbut-1-yne (1) by a phase-transfer catalytic method, and the resulting basic products were isolated chromatographically, and identified spectroscopically as 3-vinylpyridines and 2*H*-pyrroles; products and isolated yields are indicated in Table 1.

Increasing the number of methyl substituents increased the total yield of products to give a maximum of 36.2% in the case of 2,5-dimethylpyrrole (12), after which yields fell, presumably as competing reaction pathways became more important. The low yield in the case of pyrrole (4) itself appears to be a measure of its low reactivity towards dimethylvinylidene carbene (2), and is

Table 2. Ratios of isomeric pyridines

Pyrrole	% Attack on the 2,3-bond	% Attack on the 4,5-bond
2-Me	58	42
3-Me	78	22
2,3,4-Me$_3$	80	20
2,3,5-Me$_3$	89	11

not a result of side-reactions as it was estimated (g.l.c.) that 89% remained at the end of the reaction. The influence of the methyl substituents was also seen in the preferential attack of dimethylvinylidene carbene (2) on the more highly substituted, and hence more electron-rich pyrrole "double bond". Estimations of the ratios of ring-expansion products, shown in Table 2, were made by g.l.c. before separation of the products, and reflect regiospecific preferences more accurately than do isolated yields. Hartzler[5] found steric factors to be of little importance in the addition of dimethylvinylidene carbene (2) to alkenes, describing it as a "nearly naked carbene", so the ratios of the isomeric pyridines shown in Table 2 may be considered to reflect the relative electron densities at the 2,3- and 4,5-bonds.

Table 1.

|	R^1	R^2	R^3	R^4		R^1	R^2	R^3	R^4	R^5	Yield (%)		R^1	R^2	Yield (%)
(4)	H	H	H	H	(5)	H	CH=CMe$_2$	H	H	H	(2.6)				
(6)	Me	H	H	H	(7)	Me	CH=CMe$_2$	H	H	H	(9.6)				
					(8)	Me	H	H	CH=CMe$_2$	H	(6.1)				
(9)	H	Me	H	H	(10)	H	CH=CMe$_2$	Me	H	H	(5.0)				
					(11)	H	Me	H	CH=CMe$_2$	H	(1.6)				
(12)	Me	H	H	Me	(13)	Me	CH=CMe$_2$	H	H	Me	(35.0)				
					(14)	Me	CH=C=CMe$_2$	H	CH=CMe$_2$	Me	(1.2)				
(15)	Me	Me	H	Me	(16)	Me	CH=CMe$_2$	Me	H	Me	(4.6)	(18)	H	Me	(5.8)[a]
					(17)	Me	Me	H	CH=CMe$_2$	Me	(1.6)				
(19)	Me	Me	Me	H	(20)	H	CH=CMe$_2$	Me	Me	Me	(1.8)	(22)	Me	H	(8.6)[a]
					(21)	H	Me	Me	CH=CMe$_2$	Me	(4.1)				
(23)	Me	Me	Me	Me	(24)	Me	CH=CMe$_2$	Me	Me	Me	(2.6)	(25)	Me	Me	(9.0)[a]
(26)	H	Me	Me	H	(27)	H	CH=CMe$_2$	Me	Me	H	(10.6)				

[a] Yield after distillation.

The probable mechanism for the formation of the vinylpyridines involves attack of the carbene on the neutral pyrrole molecule[4], as proposed by Jones and Rees[6] in the reaction of dichlorocarbene with pyrroles, to give the cyclopropane intermediate (28). Rearrangement followed by proton shift then leads to the pyridine. The formation of a bis-addition product (14) in the reaction of 2,5-dimethylpyrrole (12) suggests that the cyclopropane intermediate has a moderate
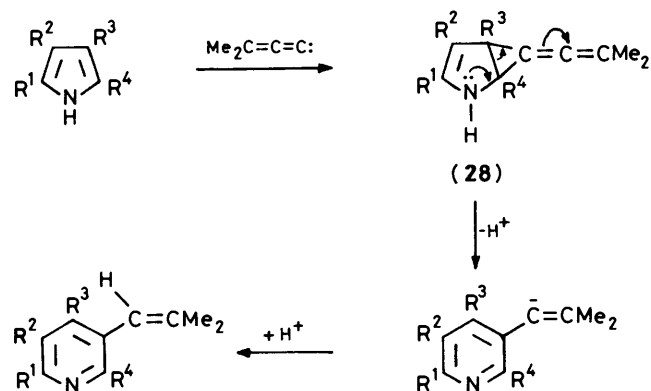

Scheme.

lifetime, as sufficient time elapses for a second carbene moiety to attack it. The bis-addition product (14) may be formed by the mechanism outlined below, in which the intermediate cyclopropane (29) is attacked by a second carbene molecule, giving a dicyclopropane adduct (30). Ring expansion may then occur to give the intermediate (31) which then undergoes

(29) (30)

(14) (31)
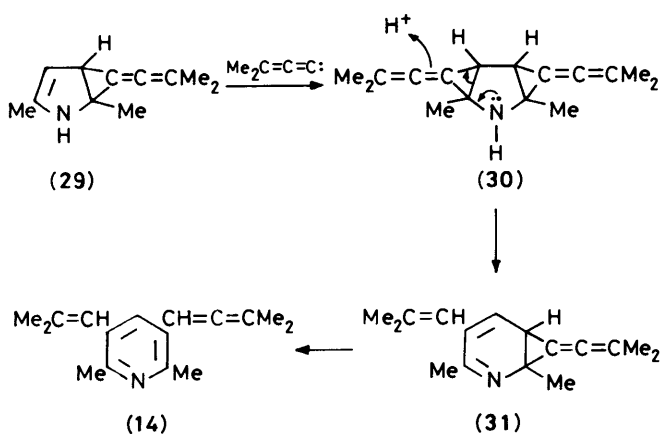
rearrangement to the pyridine (14). An alternative path by which the compound may arise involves the formation of the anion (32) which then undergoes electrophilic attack, by a second carbene molecule, in the β-position. While the first possibility seems more plausible, the second mechanism cannot be ruled out.

(32)
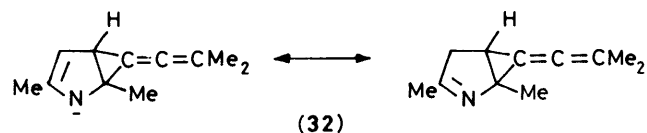
It was impossible to differentiate between the trimethyl-pyridines (20) and (21) on the basis of their [1]H n.m.r. spectra since each spectrum was consistent with either structure. Assignments were made with reasonable confidence by comparing their u.v. spectra with those of the other pyridines produced during the course of this work. Pyridines normally

have two bands in the 200—400 nm range; the first at 250—290 nm, and the second at 200—240 nm.[7] The position of this second band is dependent on the degree of conjugation of the ring with other suitable groups. Of the 12 pyridines obtained, 9 had a maximum in the region of 236 nm, consistent with conjugated pyridines, while 3 had no maximum in the 215—240 nm range, indicating a lack of conjugation of the vinyl group with the pyridine ring. In two of the unconjugated pyridines (16) and (24) the alkenyl side-chain was known to be adjacent to two methyl groups, which could be expected to twist it out of the plane of the pyridine ring. Since it seems reasonable to assume that the isomer in which conjugation is lacking is the one in which there are two methyl groups adjacent to the alkenyl side chain, the major isomer is considered to be (21). Not un-expectedly the major isomer was that formed by attack of the carbene on the more substituted pyrrole 2,3-bond.

The three 2H-pyrroles isolated [(18), (22) and (25)] all contained a distinctive band in their i.r. spectra (ca. 1 970 cm^{-1}, C=C=C) and a septet integrating for 1 H in their [1]H n.m.r. spectra, indicating the presence of a 3-methylbuta-1,2-dienyl group. The methyl groups of the 3-methylbuta-1,2-dienyl entity gave rise to two separate sets of doublets, as a result of their diastereotopic nature. The 2H-pyrroles are believed to arise from electrophilic attack of carbene (2) on the pyrrole ring or its anion, although a reaction pathway via an alternative mode of ring opening of the intermediate (28) cannot be dismissed. I.r. spectra, mass spectra, and [1]H n.m.r. spectra were all consistent with the structures proposed, however, the alternative 3H-pyrrole structures (33)—(35) could not be disregarded. The allenic 2H-pyrrole structures are supported by a comparison of their properties with those of 2,2,3,4,5-pentamethyl-2H-pyrrole

(33) R^1 = H, R^2 = Me
(34) R^1 = Me, R^2 = H
(35) R^1 = Me, R^2 = Me

(36) (37)
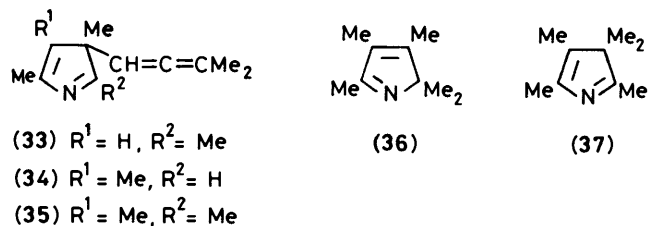
(36) and its isomer 2,3,3,4,5-pentamethyl-3H-pyrrole (37), reported by Wong and Ritchie.[8] The i.r. spectrum of the 2H-pyrrole (36) showed bands at 1 665 and 1 570 cm^{-1}, similar to the bands at 1 664 and 1 565 cm^{-1} found for the allenic pyrrole produced from 2,3,4,5-tetramethylpyrrole (23), while the 3H-pyrrole (37) showed bands at 1 650 and 1 580 cm^{-1}. Additionally the u.v. spectrum of (36) exhibited a maximum at 240 nm (3 940) and that of the 2,3,4,5-tetramethylallenic pyrrole (25) showed an inflection at 234 nm (4 200), while that of the 3H-pyrrole (37) was quite different [$\lambda_{max.}$ 262 nm (2 600)].

Further, the [1]H n.m.r. spectrum of the 2H-pyrrole (36) shows a 6 H singlet at δ 1.82 for the methyl groups at C-3 and C-4 and correlates well with the 6 H singlet at δ 1.75 given by the tetramethyl allenic pyrrole (25). On the above evidence the allenic pyrroles have been assigned the 2H-pyrrole structures (18), (22) and (25).

Allenic pyrroles do not appear to have been described in the literature and it is likely that they represent a new class of compound.

Experimental

Solutions were dried over magnesium sulphate. M.p.s were determined using an Electrothermal apparatus and are uncorrected. I.r. spectra were recorded on fluorocarbon mulls of their hydrochloride salts except for the 2H-pyrroles which were

recorded as liquid films. U.v. spectra were recorded on a Perkin-Elmer 402 instrument in absolute ethanol, the pyridines as hydrochloride salts, the 2H-pyrroles as bases. [1]H N.m.r. spectra were recorded on free bases in deuteriochloroform, unless otherwise stated, using tetramethylsilane as internal standard; the following instruments were used, Varian EM360 (60 MHz), Bruker WP-80 (80 MHz), Bruker HX90(FT) (90 MHz) and Bruker WM360 (360 MHz). Mass spectra were recorded using an AEI/Kratos MS902 instrument. G.l.c. was performed on a 2 m column packed with OV210 (3%) using a Pye-Unicam GCD instrument. T.l.c. was performed on silica gel using 1:1 toluene–ethyl acetate as eluant.

The methylpyrroles used were made by published procedures [9] or obvious variations on them; they were characterised by i.r. and [1]H n.m.r. spectroscopy, and their purities were established by g.l.c. 3-Chloro-3-methylbut-1-yne was prepared by the method of Hennion and Nelson.[10]

Reaction of Pyrroles with 3-Chloro-3-methylbut-1-yne.—The reaction between 2,3,4-trimethylpyrrole and 3-chloro-3-methyl-but-1-yne is described in detail. The remaining reactions between pyrroles and 3-chloro-3-methylbut-1-yne were carried out in essentially the same manner. In all cases the initially nearly colourless benzene phase darkened considerably during the course of the reaction, eventually becoming black. Separation of the basic fraction of the reaction products was achieved by extraction into dilute hydrochloric acid, followed by basification and extraction into ether, as described for 2,3,4-trimethylpyrrole. Pressure chromatography was performed using a grade of silica gel suitable for t.l.c., under a slight pressure (0—8 lb in^{-2}) of nitrogen, and is in essence the technique described by Hunt and Rigby.[11] Hydrochloride salts were prepared by acidifying an ethanolic solution of the base with concentrated hydrochloric acid, and evaporating the resulting solution to dryness, under reduced pressure.

(a) *2,3,4-Trimethylpyrrole* (**19**). A solution of 3-chloro-3-methylbut-1-yne (8.20 g, 80 mmol) in benzene (20 ml) was added over 2 h to a rapidly stirred mixture of 2,3,4-trimethylpyrrole (4.37 g, 40 mmol), tetrabutylammonium bisulphate (1.90 g, 5.6 mmol), benzene (75 ml), and aqueous potassium hydroxide (50% w/w; 30 ml) whilst maintaining the temperature at 5 °C. The mixture was stirred at 5 °C for a further 2 h then at room temperature for 18 h; a nitrogen atmosphere was maintained throughout. The resulting dark emulsion was diluted with water (50 ml) and separated into a colourless aqueous phase and a black benzene phase. The aqueous phase was extracted with benzene (100 ml), and the combined benzene extracts washed with saturated brine (100 ml) and then dried. Evaporation of the benzene under reduced pressure left a dark red oil (13.2 g), which was partitioned between 0.5M-hydrochloric acid (200 ml) and methylene dichloride (100 ml). The acid phase was washed with more methylene dichloride (2 × 100 ml), basified with concentrated ammonia, and then extracted with ether (3 × 100 ml). The combined ether extracts were washed with saturated brine (100 ml) and dried. Evaporation of the ether under reduced pressure left a light brown oil (1.45 g) which contained three components, estimated by g.l.c. to be in the ratio 70:24:6, with retention times of 2.3, 3.7, and 5.4 min. Separation of the components was achieved using a silica gel (150 g) pressure column, and mixtures of hexane–ether of increasing polarity as eluant.

The minor component, isolated as its hydrochloride salt as a brown semisolid (0.15 g, 1.8%), crystallised from ethyl acetate (2 ml) giving *2,3,4-trimethyl-5-(2-methylprop-1-enyl)pyridine hydrochloride* (**20**) as purple crystals (0.07 g), m.p. 132—135 °C (Found: C, 66.3; H, 8.2; Cl, 17.05; N, 6.4. $C_{12}H_{17}N \cdot HCl \cdot \frac{1}{4} H_2O$ requires C, 66.65; H, 8.6; Cl, 16.4; N, 6.5%); $\lambda_{max.}$ 236 (9 500 dm^3 mol^{-1} cm^{-1}) and 267 infl nm (4 700); $\nu_{max.}$ 2 400, 2 115,

2 070, and 1 995 (C=$\overset{+}{N}$H), 1 668 (C=C), 1 652, 1 620, 1 610 and 1 535 (pyridine ring), 1 390 and 1 378 cm^{-1} (Me's); δ (360 MHz) 1.64 (3 H, d, J 1.4 Hz, CH=CMe), 1.90 (3 H, d, J 1.5 Hz, CH=CMe), 2.15 (3 H, s, 3-Me), 2.20 (3 H, s, 4-Me), 2.50 (3 H, s, 2-Me), 6.12 (1 H, m, ArCH=C), and 8.04 (1 H, s, 6-H); g.l.c. (100 °C) R_t 5.4 min. The second component, isolated as its hydrochloride salt as a brown solid (0.35 g, 4.1%), crystallised from ethanol–ether giving 2,4,5-*trimethyl-3-(2-methylprop-1-enyl)pyridine hydrochloride* (**21**) as off-white crystals (0.21 g), sublimed at *ca.* 190 °C (Found: C, 68.4; H, 8.4; Cl, 16.6; N, 6.6. $C_{12}H_{17}N \cdot HCl$ requires C, 68.1; H, 8.6; Cl, 16.75; N, 6.6%); $\lambda_{max.}$ 275 nm (5 300 dm^3 mol^{-1} cm^{-1}); $\nu_{max.}$ 2 440, 2 120, 2 070, 2 040 and 1 978 (C=$\overset{+}{N}$H), 1 672 (C=C), 1 620 and 1 533 (pyridine ring), 1 395 and 1 388 cm^{-1} (Me); δ (360 MHz) 1.39 (3 H, d, J 1.3 Hz, CH=CMe), 1.94 (3 H, d, J 1.5 Hz, CH=CMe), 2.30 (3 H, s, 5-Me), 2.34 (3 H, s, 4-Me), 2.66 (3 H, s, 2-Me), 5.94 (1 H, m, ArCH=C), and 8.19 (1 H, s, 6-H); g.l.c. (100 °C R_t 3.7 min. The major component, obtained as a pale yellow liquid (0.60 g, 8.6%), was distilled under reduced pressure giving 2,3,4-*trimethyl-2-(3-methylbuta-1,2-dienyl)-2H-pyrrole* (**22**) as a colourless liquid (0.23 g), b.p. 103—104 °C at 17 mmHg (Found: C, 81.1; H, 10.0; N, 7.8; $C_{12}H_{17}N$ requires C, 82.2; H, 9.8; N, 8.0%); $\lambda_{max.}$ 241 nm (3 380 dm^3 mol^{-1} cm^{-1}); $\nu_{max.}$(film) 3 065, 1 970 (allene), 1 660, and 1 575 cm^{-1}; δ (360 MHz) 1.18 (3 H, s, 2-Me), 1.68 (3 H, d, J 2.9 Hz, CH=C=CMe), 1.72 (3 H, d, J 2.9 Hz, CH=C=CMe), 1.77 (3 H, q, J 1.1 Hz, 3-Me), 1.81 (3 H, q, J 1.1 Hz, 4-Me), 4.48 (1 H, septet, J 2.9 Hz, CH=C=C), and 7.82 (1 H, s, 5-H); g.l.c. (100 °C) R_t 2.3 min; m/z 176 (17%), 175 (M^+, 37), 174 (46), 160 (100), 145 (68), 122 (93), 121 (7), and 108 (31).

(b) *Pyrrole* (**4**). Pyrrole (6.71 g, 100 mmol), 3-chloro-3-methylbut-1-yne (20.51 g, 200 mmol), and tetrabutylammonium bisulphate (4.41 g, 13 mmol) were allowed to react in benzene (220 ml) as above, and the mixture was worked up in a similar fashion to (a) to give 3-(2-*methylprop-1-enyl)pyridine hydrochloride* (**5**) as purple crystals (0.44 g, 2.6%), m.p. 138—142 °C (Found: C, 63.4; H, 7.2; Cl, 21.15; N, 8.4. $C_9H_{11}N \cdot HCl$ requires C, 63.7; H, 7.1; Cl, 20.9; N, 8.3%); $\lambda_{max.}$ 234 (10 900 dm^3 mol^{-1} cm^{-1}) and 254 nm (9 500); $\nu_{max.}$ 2 420, 2 140 and 2 020 (C=$\overset{+}{N}$H), 1 653 (C=C), 1 622, 1 601, and 1 552 cm^{-1} (pyridine ring); δ (60 MHz) 1.86 (3 H, s, CH=CMe), 1.93 (3 H, s, CH=CMe), 6.15 (1 H, s, ArCH=C), 7.00—7.20 (1 H, m, 5-H), 7.30—7.60 (1 H, m, 4-H), and 8.25—8.50 (2 H, m, overlapping 2-H and 6-H).

(c) *2-Methylpyrrole* (**6**). 2-Methylpyrrole (2.0 g, 24.7 mmol), 3-chloro-3-methylbut-1-yne (5.05 g, 49.3 mmol) and tetrabutyl-ammonium bisulphate (1.36 g, 4 mmol) were allowed to react in benzene (70 ml) as above, and the mixture was worked up in a similar fashion to (a) to give (i) 2-*methyl-5-(2-methylprop-1-enyl)pyridine* (**8**), as a pale red oil (0.22 g, 6.1%) which was converted into its hydrochloride salt and crystallised from ethanol–ether as pale brown plates (0.2 g), m.p. 180—182 °C (Found: C, 65.2; H, 7.5; Cl, 19.7; N, 7.65. $C_{10}H_{13}N \cdot HCl$ requires C, 65.4; H, 7.7; Cl, 19.3; N, 7.6%); $\lambda_{max.}$ 256 (10 200 dm^3 mol^{-1} cm^{-1}) and 293infl nm (3 400); $\nu_{max.}$ 2 335, 2 130, 2 090, 2 065, 1 995 and 1 965 (C=$\overset{+}{N}$H), 1 660 (C=C), 1 633, 1 597 and 1 548 cm^{-1} (pyridine ring); δ (60 MHz) 1.86 (3 H, s, CH=Me), 1.93 (3 H, d, CH=CMe), 2.54 (3 H, s, 2-Me), 6.12 (1 H, m, ArCH=C), 7.01 (1 H, d, $J_{3,4}$ 8.2 Hz, 3-H), 7.35 (1 H, dd, $J_{4,3}$ 8.2 Hz, $J_{4,6}$ 2.3 Hz, 4-H), and 8.36 (1 H, d, $J_{6,4}$ 2.3 Hz, 6-H); g.l.c. (80 °C) R_t 9.5 min; (ii) 2-*methyl-3-(2-methylprop-1-enyl)pyridine* (**7**) obtained as a pale brown oil (0.35 g, 9.6%), which was converted into its hydrochloride salt and sublimed at 120 °C (12 mmHg) to give a white powdery solid, m.p. 161—163 °C (Found: C, 65.2; H, 7.6; Cl, 19.0; N, 7.4. $C_{10}H_{13}N \cdot HCl$ requires C, 65.4; H, 7.7; Cl, 19.3; N, 7.6%); $\lambda_{max.}$ 234.5 (10 100 dm^3 mol^{-1} cm^{-1}) and 257 nm (6 100); $\nu_{max.}$ 2 410, 2 125, 2 085, 2 035, 2 015 and 1 985 (C=$\overset{+}{N}$H), 1 657 (C=C), 1 623, 1 602 and 1 550 cm^{-1} (pyridine ring); δ (60

MHz) 1.67 (3 H, s, CH=CMe), 1.92 (3 H, d, CH=CMe), 2.45 (3 H, s, 2-Me), 6.08 (1 H, m, ArCH=C), 6.93 (1 H, dd, $J_{4,5}$ 7.8 Hz, $J_{5,6}$ 5.0 Hz, 5-H), 7.26 (1 H, dd, $J_{4,5}$ 7.8 Hz, $J_{4,6}$ 1.5 Hz, 4-H), and 8.25 (1 H, dd, $J_{6,5}$ 5.0 Hz, $J_{6,4}$ 1.5 Hz, 6-H); g.l.c. (80 °C) R_t 8.0 min.

(d) 3-*Methylpyrrole* (**9**). 3-Methylpyrrole (6.0 g, 74 mmol), 3-chloro-3-methylbut-1-yne (15.98 g, 148 mmol) and tetrabutyl-ammonium bisulphate (3.40 g, 10 mmol) were allowed to react in benzene (170 ml) as above, and the mixture was worked up in a similar fashion to (a) to give (i) 3-*methyl*-5-(2-*methylprop*-1-*enyl*)*pyridine hydrochloride* (**11**) as a purple solid (0.22 g, 1.6%), which crystallised from ethyl acetate–ethanol as pale pink crystals (0.03 g), m.p. 149—150 °C (Found: C, 65.1; H, 7.6; N, 7.5. $C_{10}H_{13}N\cdot HCl$ requires C, 65.4; H, 7.7; N, 7.6%); $\lambda_{max.}$ 238.5 (11 100 dm^3 mol^{-1} cm^{-1}) and 257infl nm (7 140); $v_{max.}$ 2 425, 2 110 and 1 940 (C=$\overset{+}{N}$H), 1 655 (C=C), 1 640 and 1 560 (pyridine ring), 1 387 and 1 380 cm^{-1} (Me's); δ (90 MHz) 1.85 (3 H, d, J 1.5 Hz, CH=CMe), 1.91 (3 H, d, J 1.5 Hz, CH=CMe), 2.31 (3 H, s, 3-Me), 6.17 (1 H, m, ArCH=C), 7.32 (1 H, m, 4-H) and 8.27 (2 H, m, 2 and 6-H); g.l.c. (100 °C) R_t 12.4 min; m/z (free-base) 147 (M^+, 100%), 132 (62), and 117 (45); (ii) 4-*methyl*-3-(2-*methylprop*-1-*enyl*)*pyridine hydrochloride* (**10**) as a purple solid (0.68 g, 5.0%) which crystallised from ethyl acetate–ethanol as pale pink crystals (0.19 g), m.p. 169—170 °C (Found: C, 65.0; H, 7.6; N, 7.5. $C_{10}H_{13}N\cdot HCl$ requires C, 65.4; H, 7.7; N, 7.6%); $\lambda_{max.}$ 232.5 (8 770 dm^3 mol^{-1} cm^{-1}) and 257 nm (5 900); $v_{max.}$ 2 440, 2 115, 2 005 and 1 890 (C=$\overset{+}{N}$H), 1 658 (C=C), 1 630, 1 592 and 1 522 (pyridine ring), 1 390 and 1 380 cm^{-1} (Me's); δ (90 MHz) 1.71 (3 H, d, J 1.2 Hz, CH=CMe), 1.94 (3 H, d, J 1.6 Hz, CH=CMe), 2.24 (3 H, s, 4-Me), 6.12 (1 H, m, ArCH=C), 7.10 (1 H, d, J 4.9 Hz, 5-H), 8.31 (1 H, d, J 4.9 Hz, 6-H), and 8.31 (1 H, s, 2-H); g.l.c. (100 °C R_t 9.8 min; m/z (free-base) 147 (M^+, 100%), 132 (78), and 117 (67).

(e) 2,5-*Dimethylpyrrole* (**12**). 2,5-Dimethylpyrrole (14.27 g), 150 mmol), 3-chloro-3-methylbut-1-yne (30.77 g, 300 mmol), and tetrabutylammonium bisulphate (6.79 g, 20 mmol) were allowed to react in benzene (200 ml) as above, and the mixture was worked up in a similar manner to (a) to give a golden oil (13.37 g). Part of this oil (1.0 g) was resolved into its components by chromatography on a pressure column to give (i) 2,6-*dimethyl*-5-(3-*methylbuta*-1,2-*dienyl*)-3-(2-*methylprop*-1-*enyl*) *pyridine* (**14**) as a colourless oil (0.03 g, 1.2%), which converted into its hydrochloride salt and crystallised from ethyl acetate as fawn crystals, m.p. 200—203 °C (Found: C, 71.2; H, 8.2; Cl, 13.8; N, 5.15. $C_{16}H_{21}N\cdot HCl\cdot\frac{1}{3}H_2O$ requires C, 71.2; H, 8.4; Cl, 13.1; N, 5.2%); $v_{max.}$ 2 450, 2 120, 2 040 and 1 980 (C=$\overset{+}{N}$H), 1 665 (C=C), 1 640 and 1 560 (pyridine ring), 1 395 and 1 375 cm^{-1} (Me's); $v_{max.}$(film, free base) 1 960 cm^{-1} (allene); δ (80 MHz) 1.60 (3 H, d, J 1.1 Hz, CH=CMe), 1.73 (6 H, d, J 2.9 Hz, CH=C=CMe_2), 1.84 (3 H, d, J 1.1 Hz, CH=CMe), 2.33 (3 H, s, pyridyl Me), 2.45 (3 H, s, pyridyl Me), 6.07 (1 H, septet, J 2.9 Hz, ArCH=C=C), 6.13 (1 H, m, ArCH=CMe$_2$, and 7.23 (1 H, s, 4-H); g.l.c. (150 °C) R_t 3.3 min; m/z (free-base) 227 (M^+, 65%), 212 (100), 196 (26), 182 (28), 174 (100), 160 (86), and 159 (9); (ii) 2,6-dimethyl-3-(2-methylprop-1-enyl)pyridine (**13**)[4] as a colourless oil (0.63 g, 35.0%) which was converted into its hydrochloride salt and crystallised from ethanol–ether as colourless crystals, m.p. 161—162 °C (Found: C, 66.65; H, 8.0; Cl, 18.3; N, 7.0. $C_{11}H_{15}N\cdot HCl$ required C, 66.8; H, 8.2; Cl, 17.9; N, 7.1%); $\lambda_{max.}$ 237 (11 200 dm^3 mol^{-1} cm^{-1}), 256 infl(6 300) and 282 infl nm (4 400); $v_{max.}$ 2 400, 2 120, 2 050 and 1 995 (C=$\overset{+}{N}$H), 1 650 (C=C), 1 640, 1 595 and 1 550 (pyridine ring), and 1 390 cm^{-1} (Me's); δ (60 MHz) 1.67 (3 H, d, CH=CMe), 1.93 (3 H, d, CH=CMe), 2.48 (3 H, s, pyridyl Me), 2.52 (3 H, s, pyridyl Me), 6.17 (1 H, m, ArCH=C), 6.92 (1 H, d, J 8.0 Hz, 5-H), and 7.30 (1 H, d, J 8.0 Hz, 4-H); g.l.c. (150 °C) R_t 0.7 min.

(f) 2,3,5-*Trimethylpyrrole* (**15**). 2,3,5-Trimethylpyrrole (8.73 g, 80 mmol), 3-chloro-3-methylbut-1-yne (16.40 g, 160 mmol), and tetrabutylammonium bisulphate (3.73 g, 11 mmol) were allowed to react in benzene (180 ml) as above, and the mixture was worked up in a similar fashion to (a) to give (i) 2,4,6-*trimethyl*-3-(2-*methylprop*-1-*enyl*)*pyridine* (**16**) as a pale golden oil (0.64 g, 4.6%), which was converted into its hydrochloride salt and crystallised from ethyl acetate as pale purple crystals (0.11 g), m.p. 152—154 °C (Found: C, 67.8; H, 8.4 Cl, 16.9; N, 6.6. $C_{12}H_{17}N\cdot HCl$ requires C, 68.1; H, 8.6; Cl, 16.75; N, 6.6%); $\lambda_{max.}$ 230 infl (6 200 dm^3 mol^{-1} cm^{-1}) and 275 nm (5 400); $v_{max.}$ 2 440, 2 110, 2 030, 1 980 and 1 955 (C=$\overset{+}{N}$H), 1 663 (C=C), 1 642 and 1 601 (pyridine ring), and 1 390 cm^{-1} (Me's); δ (60 MHz), 1.46 (3 H, s, CH=CMe), 1.94 (3 H, d, CH=CMe), 2.14 (3 H, s, 4-Me), 2.41 (3 H, s, 2 or 6-Me), 2.48 (3 H, s, 6 or 2-Me), 6.00 (1 H, m, ArCH=C), and 6.79 (1 H, s, 5-H); g.l.c. (80 °C) R_t 4.2 min; (ii) 2,5,6-*trimethyl*-3-(2-*methylprop*-1-*enyl*)*pyridine* (**17**) as a pale red oil (0.22 g, 1.6%), which was converted into its hydrochloride salt and crystallised from ethanol–ether as pale pink crystals (0.20 g), m.p. 167—168 °C (Found: C, 67.9; H, 8.5; Cl, 16.9; N, 6.5. $C_{12}H_{17}N\cdot HCl$ requires C, 68.1; H, 8.6, Cl, 16.75; N, 6.6%); $\lambda_{max.}$ 236 (9 800 dm^3 mol^{-1} cm^{-1}) and 287 nm (4 900); $v_{max.}$ 2 420, 2 120, 2 045 and 1 990 (C=$\overset{+}{N}$H), 1 655 (C=C), 1 630 and 1 560 (pyridine ring), 1 404 and 1 390 cm^{-1} (Me's); δ (60 MHz) 1.71 (3 H, s, CH=CMe), 1.94 (3 H, d, CH=CMe), 2.24 (3 H, s, 5-Me), 2.43 (3 H, s, 2 or 6-Me), 2.48 (3 H, s, 6 or 2-Me), 6.14 (1 H, m, ArCH=C), and 7.11 (1 H, s, 4-H); g.l.c. (80 °C) R_t 5.4 min; (iii) 2,3,5-*trimethyl*-2-(3-*methylbuta*-1,2-*dienyl*)-2H-*pyrrole* (**18**) as a colourless liquid (0.82 g, 5.8%), b.p. 50—51 °C at 0.15 mmHg (Found: C, 82.15; H, 9.8; N, 8.4. $C_{12}H_{17}N$ requires C, 82.2; H, 9.8; N, 8.0%); $\lambda_{max.}$ 221 (4 380 dm^3 mol^{-1} cm^{-1}) and 234 nm (4 190); $v_{max.}$(film) 3 065, 1 970 (allene), 1 640 and 1 557 cm^{-1}; δ (360 MHz) 1.24 (3 H, s, 2-Me), 1.72 (3 H, d, J 2.9 Hz, CH=C=CMe), 1.77 (3 H, d, J 2.9 Hz, CH=C=CMe), 1.95 (3 H, d, J 1.5 Hz, 3-Me), 2.17 (3 H, s, 5-Me), 4.58 (1 H, septet, J 2.9 Hz, CH=C=C), and 5.87 (1 H, q, J 1.5 Hz, 4-H); g.l.c. (80 °C) R_t 3.4 min; m/z 175 (M^+, 43%), 160 (100), 145 (77), 134 (21), 119 (33), and 108 (57).

(g) 2,3,4,5-*Tetramethylpyrrole* (**23**). 2,3,4,5-Tetramethylpyr-role (4.93 g, 40 mmol), 3-chloro-3-methylbut-1-yne (8.20 g, 80 mmol), and tetrabutylammonium bisulphate (1.70 g, 5 mmol) were allowed to react in benzene (220 ml) as above, and the mixture was worked up in a similar manner to (a) to give (i) 2,4,5,6-*tetramethyl*-3-(2-*methylprop*-1-*enyl*)*pyridine* (**24**) as a pale brown oil (0.20 g, 2.6%), which was converted into its hydrochloride salt and crystallised from ethyl acetate as purple crystals (0.08 g), m.p. 182—184 °C (Found: C, 69.15; H, 8.9; Cl, 16.3; N, 6.1. $C_{13}H_{19}N\cdot HCl$ requires C, 69.2; H, 8.9, Cl, 15.7; N, 6.2%); $\lambda_{max.}$ 280 nm (5 850 dm^3 mol^{-1} cm^{-1}); $v_{max.}$ 2 400, 2 120, 2 040 and 1 985 (C=$\overset{+}{N}$H), 1 670 (C=C), 1 630, 1 595 and 1 538 (pyridine ring), 1 398 and 1 382 cm^{-1} (Me's); δ (60 MHz) 1.45 (3 H, s, CH=CMe), 1.95 (3 H, d, CH=CMe), 2.14 (3 H, s, 5-Me), 2.19 (3 H, s, 4-Me), 2.39 (3 H, s, 2 or 6-Me), 2.53 (3 H, s, 6 or 2-Me), and 6.08 (1 H, m, ArCH=C); (ii) 2,3,4,5-*tetramethyl*-2-(3-*methylbuta*-1,2-*dienyl*)-2H-*pyrrole* (**25**) as a colourless liquid (0.68 g, 9.0%), b.p. 53—54 °C at 0.2 mmHg. (Found: C, 81.75; H, 9.85; N, 8.5. $C_{13}H_{19}N$ requires C, 82.5; H, 10.1; N, 7.4%); $\lambda_{max.}$ 234 infl nm (4 200 dm^3 mol^{-1} cm^{-1}); $v_{max.}$(film) 1 970 (allene), 1 664 and 1 565 cm^{-1}; δ (90 MHz), 1.14 (3 H, s, 2-Me), 1.67 (3 H, d, J 2.7 Hz, CH=C=CMe), 1.71 (3 H, d, J 2.7 Hz, CH=C=CMe), 1.75 (6 H, s, 3 and 4-Me), 2.10 (3 H, s, 5-Me), and 4.43 (1 H, septet, J 2.7 Hz, CH=C=C); m/z 189 (M^+, 29%), 188 (19), 174 (67), 159 (73), and 122 (83).

(h) 3,4-*Dimethylpyrrole* (**26**). 3,4-Dimethylpyrrole (3.14 g, 33 mmol), 3-chloro-3-methylbut-1-yne (6.77 g, 66 mmol) and tetrabutylammonium bisulphate (1.60 g, 4.7 mmol) were allowed to react in benzene (90 ml) as above, and the mixture

was worked up in a similar fashion to (a) to give 4,5-*dimethyl*-3-(2-*methylprop*-1-*enyl*)*pyridine hydrochloride* (**27**) as a dark gum (0.69 g, 10.6%), which was twice crystallised from ethyl acetate to give pale purple crystals (0.39 g), m.p. 130 °C (decomp.) (Found: C, 66.4; H, 8.5; Cl, 18.4; N, 6.9. $C_{11}H_{15}N \cdot HCl$ requires C, 66.8; H, 8.2; Cl, 17.9; N, 7.1%); $\lambda_{max.}$ 235 (9 740 dm^3 mol^{-1} cm^{-1}), 260infl nm (5 170); $\nu_{max.}$ 2 380, 2 100, 2 080 and 1 955 (C=$\overset{+}{N}$H), 1 655 (C=C), 1 625, 1 600 and 1 538 (pyridine ring), 1 395 and 1 385 cm^{-1} (Me's); δ (80 MHz) 1.66 (3 H, d, J 1.1 Hz, CH=C*Me*), 1.93 (3 H, d, J 1.3 Hz, CH=C*Me*), 2.14 (3 H, s, 5-Me), 2.25 (3 H, s, 4-Me), 6.15 (1 H, m, ArC*H*=C), 8.16 (1 H, s, ArH), and 8.20 (1 H, s, ArH).

Acknowledgements

References

1 T. Sasaki, S. Eguchi, and T. Ogawa, *J. Org. Chem.*, 1974, **39**, 1927.
2 T. B. Patrick and D. J. Schmidt, *J. Org. Chem.*, 1977, **42**, 3354.
3 S. R. Landor, V. Rogers, and H. R. Sood, *Tetrahedron*, 1977, **33**, 73.
4 S. R. Landor, V. Rogers, and H. R. Sood, *J. Chem. Soc., Perkin Trans. 1*, 1976, 2103.
5 H. D. Hartzler, *J. Am. Chem. Soc.*, 1961, **83**, 4997.
6 R. L. Jones and C. W. Rees, *J. Chem. Soc. C*, 1969, 2249.
7 E. S. Stern and C. J. Timmons, 'Introduction to Electronic Absorption Spectroscopy in Organic Chemistry,' 3rd edn. Edward Arnold.
8 J. L. Wong and M. H. Ritchie, *J. Chem. Soc., Chem. Commun.*, 1970, 142.
9 R. L. Hinman and S. Theodoropulos, *J. Org. Chem.*, 1963, **28**, 3052.
10 G. F. Hennion and K. W. Nelson, *J. Am. Chem. Soc.*, 1957, **79**, 2142.
11 B. J. Hunt and W. Rigby, *Chem. Ind. (London)*, 1967, 1868.