Reactions of Halogenomethanes in the Vapour Phase. Part 1. Reactions of Chloroform with Pyrrole and Methylpyrroles at 550 °C

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Chloroform reacts with pyrrole and with some methylpyrroles (2)—(9) in the vapour phase at 550 °C using a continuous-flow method to give high yields (71—92%) of chloro- and chloromethyl-pyridines (10)—(33) formed by ring expansion.

SINCE the investigations of Hine [1] into the mechanism of the basic hydrolysis of chloroform, several base-catalysed reactions involving chloroform, trichloroacetic acid, and trichloroacetic esters, have been studied, particularly for their mechanistic interest. Surprisingly few large-scale preparations involving carbenes however, have been reported. The long known, but now little used, Reimer–Tiemann reaction of pyrrole with chloroform and base exemplifies some of the common difficulties experienced with reactions involving chloroform: more than one product is formed with a relatively low total yield. Recently, considerable success has been achieved with the aid of phase transfer catalysts such as quaternary ammonium compounds and crown ethers.[3]

The present work was begun with the intention of using halogenomethanes in reactions of a carbene or carbenoid type which could be developed into large scale preparations. For this purpose it seemed that high temperature gas phase reactions might be suitable since a continuous flow method would be easily possible. The variation of temperature, pressure and flow rate should also be exploitable so as to obtain optimum yields. Furthermore, it was hoped that the inclusion of suitable substrates such as heterocyclic compounds along with the halogenomethane might yield products with reactive halogen atoms which could prove to be useful intermediates for other synthetic work.

Earlier workers [4] have shown that chloroform vapour in a stream of helium at 450—525 °C in a Vycor reaction chamber yields hydrogen chloride and tetrachloroethylene as the major products together with smaller amounts of other chlorinated hydrocarbons. Similar studies were carried out by other workers.[5] The reaction of chloroform at high temperatures with various olefins was reported by three groups of workers at about the same time. Kung and Bissinger [6] found that a mixture of chloroform and cyclohexene vapours in contact with a heated platinum wire gave a mixture of 3-dichloromethylcyclohexene, toluene, and a very small amount of 7,7-dichloronorcarane. Strain and Bartlett [7] passed propylene and chloroform through a glass tube at 529—533 °C and obtained chloroprene as the main product. Engelsma [8] studied the vapour phase decomposition of chloroform at 400—500 °C in the presence of various alkenes and obtained hydrogen chloride and chlorodienes, *e.g.* isobutene yielded 2-chloro-3-methylbuta-1,3-diene (38% based on chloroform converted). However, the present work was undertaken with a view to the use of chloroform and other halogenomethanes with five-membered heterocyclic compounds as substrates. There has been some support for the possibility of ring expansion of five-membered heterocycles in the vapour phase. For instance, Rice and Londergan [9] found that 3- (25—33%) and 2-chloropyridine (2—5%) were produced on heating chloroform with pyrrole at 550 °C. They suggested that either the reaction was base-catalysed by the glass of the reaction tube or that addition of dichlorocarbene to the 2,3-positions of pyrrole followed by ring expansion with elimination of hydrogen chloride might have occurred.

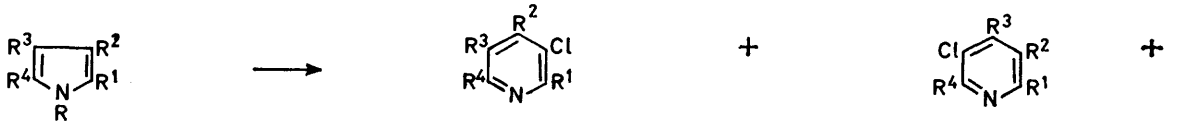
Our work on these reactions has been in progress for some years and we intend to report on the use of chloroform, carbon tetrachloride, and bromoform in a range of previously unknown ring expansion, cyclisation, rearrangement, and ring-opening reactions. We shall also describe investigations of the reaction kinetics and mechanisms for the processes by which chloroform decomposes, and for the reaction of chloroform with another reagent under high temperature, vapour phase conditions in a flow system. In this first paper we are concerned with the experimental features associated with the pyrolysis reaction in a preparative flow system, and the analysis, identification, and distribution of reaction product types as exemplified by a study of the reactions of chloroform with pyrrole and various methylpyrroles.

Experiments were conducted using various ratios of pyrrole to chloroform, a variety of addition rates, and different tray assemblies and packings in the pre-heater in order to determine the effects of these parameters on the yield of products. The latter were separated into basic and neutral fractions, and g.l.c. showed the presence of 3-chloropyridine, 2-chloropyridine, pyridine, hexachloroethane, and tetrachloroethylene. Interestingly, an increased yield of pyridines coincided with a decreased yield of chlorinated hydrocarbons. The major differences between our results with pyrrole and those obtained in earlier work are (*a*) the high yields of ring-expanded products obtained (an optimum yield of 86% based on pyrrole compared with the maximum yield of 38% previously obtained in vapour phase work [10]); (*b*) the much greater proportion (up to 25%) of 2-chloropyridine obtained in our experiments compared to the trace quantities found by Rice and Londergan; and (*c*) the formation of pyridine, albeit in trace quantities.

Investigations of apparatus design, reactant ratios, addition rates, and surface effects on the yield of products gave the following information for the reactor (a vertical assembly). The position and the number of trays used to preheat the reactants were critical and the apparatus was most effective when 5 trays filled with Fenske glass helices and separated by 1.5 cm were situated with the top tray 14.5 cm from the top of the furnace. A molar ratio of pyrrole to chloroform of 1 : 5 was found to give the best results when *ca.* 0.75 mol of chloroform was used and the solution added at a uniform rate during 30 min. A longer time for the addition caused a drop in yield, while a shorter time was not always easily achieved together with maintenance of a constant addition rate. Successive additions of volumes of the reactant mixture as mentioned above followed by analysis of the products from each addition, without removal of the continuous carbon deposit formed on the reaction tube and preheater assembly between each addition, showed that the yield of chloropyridines reached a maximum at about the fifth reactant mixture added and that at the twelfth addition the yield was 77% of the optimum. Thus, surface effects appear to play a significant, though not necessarily dominant, part in the reaction. Despite this finding of increased yield after carbonisation of the reactor tube, the majority of the results have been obtained with initially clean reactor tubes in order to avoid contaminants from preceding reactions, and the yields quoted in this (with the exception of those for pyrrole) and subsequent papers have been obtained in this way.

The results obtained with pyrrole encouraged us to investigate the vapour phase reactions of chloroform with the methylpyrroles (2)—(9) using a similar reaction mixture ratio, addition rate, and tray assembly to those optimum for pyrrole. The products were analysed by g.l.c. and separated by preparative g.l.c. for the purpose of characterisation. In each case a high conversion to the chloromethylpyridines (71—92% based on the methylpyrrole) was obtained, again with a high proportion (12—55%) of the 2-chloromethylpyridines, but with no evidence for the formation of any non-chlorinated pyridines.

In the cases of two of the pyrroles, 2,4-dimethylpyrrole (6) and 2,5-dimethylpyrrole (7), there is evidence to suggest that rearrangement involving the migration of a methyl group has occurred prior to ring expansion. Thus, 2,4-dimethylpyrrole, on reaction with chloroform, gave small amounts of 2-chloro-3,6-lutidine (32) and 3-chloro-2,6-lutidine (15), which are the main products from the reaction of 2,5-dimethylpyrrole with chloroform. Conversely, 2,5-dimethylpyrrole with chloroform also gave small amounts of 2-chloro-4,6-lutidine (33), 3-chloro-2,5-lutidine (21), and 3-chloro-4,6-lutidine (20), the major products from the reaction of 2,4-dimethylpyrrole with chloroform.



(1) R = R^1 = R^2 = R^3 = R^4 = H
(2) R = Me, R^1 = R^2 = R^3 = R^4 = H
(3) R^1 = Me, R = R^2 = R^3 = R^4 = H
(4) R^2 = Me, R = R^1 = R^3 = R^4 = H
(5) R^1 = R^2 = Me, R = R^3 = R^4 = H
(6) R^1 = R^3 = Me, R = R^2 = R^4 = H
(7) R^1 = R^4 = Me, R = R^2 = R^3 = H
(8) R^2 = R^3 = Me, R = R^1 = R^4 = H
(9) R^1 = R^2 = R^3 = R^4 = Me, R = H

(10) R^1 = R^2 = R^3 = R^4 = H
(11) R^1 = Me, R^2 = R^3 = R^4 = H
(12) R^2 = Me, R^1 = R^3 = R^4 = H
(13) R^1 = R^2 = Me, R^3 = R^4 = H
(14) R^2 = R^3 = Me, R^1 = R^4 = H
(15) R^1 = R^4 = Me, R^2 = R^3 = H
(16) R^1 = R^2 = R^3 = R^4 = Me

(17) R^1 = Me, R^2 = R^3 = R^4 = H
(18) R^2 = Me, R^1 = R^3 = R^4 = H
(19) R^1 = R^2 = Me, R^3 = R^4 = H
(20) R^1 = R^3 = Me, R^2 = R^4 = H
(21) R^2 = R^4 = Me, R^1 = R^3 = H

(22) R^1 = R^2 = R^3 = R^4 = H
(23) R^1 = Me, R^2 = R^3 = R^4 = H
(24) R^2 = Me, R^1 = R^3 = R^4 = H
(25) R^1 = R^2 = Me, R^3 = R^4 = H
(26) R^1 = R^3 = Me, R^2 = R^4 = H
(27) R^2 = R^3 = Me, R^1 = R^4 = H
(28) R^1 = R^2 = R^3 = R^4 = Me

(29) R^1 = Me, R^2 = R^3 = R^4 = H
(30) R^2 = Me, R^1 = R^3 = R^4 = H
(31) R^1 = R^2 = Me, R^3 = R^4 = H
(32) R^1 = R^4 = Me, R^2 = R^3 = H
(33) R^1 = R^3 = Me, R^2 = R^4 = H

Although high yields were obtained from the reaction of chloroform with pyrrole and with methylpyrroles, the relative difficulty of separating the products by preparative g.l.c. probably precludes the method from being used for large scale preparations. On the other hand, most of the products are not easily obtained by any other route, and so the method is still of considerable synthetic value.

EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer 225 spectrometer for liquid films between CsI plates. ^{1}H n.m.r. spectra were determined with a HA–100 D spectrometer for solutions in deuteriochloroform except where otherwise stated, with tetramethylsilane as internal standard. Mass spectral data were obtained from an A.E.I. MS 902 instrument at 70 eV, and the g.l.c.–m.s. data was produced by use of a Perkin-Elmer 881 chromatograph linked *via* a jet separator to the mass spectrometer.

The chloroform used for the reactions was obtained by passing AnalaR grade chloroform down a column of basic alumina (activity grade 1, 100 g l^{-1} chloroform). Pyrrole and 1-methylpyrrole were obtained from commercial sources, and 2-methylpyrrole,[10] 3-methylpyrrole,[11] 2,3-dimethylpyrrole,[12] 2,4-dimethylpyrrole,[12,13] 2,5-dimethylpyrrole,[14] 3,4-dimethylpyrrole,[15] and 2,3,4,5-tetramethylpyrrole [16] were prepared by reported methods.

Authentic samples were available for comparison with some of the pyrolysis reaction products: 2- and 3-chloropyridine, 2-chloro-3-picoline, 2-chloro-4-picoline, 2-chloro-5-picoline, and 2-chloro-6-picoline (all from commercial sources); 3-chloro-2,6-lutidine and 3-chloro-2,4,5,6-tetramethylpyridine (both from Dr. R. Nicoletti); 3-chloro-4-picoline,[17] 3-chloro-6-picoline,[18] and 2-chloro-4,6-lutidine [19] (all specially synthesised by reported methods); and 3-chloro-2-picoline and 3-chloro-5-picoline synthesised from 3-amino-2-picoline [20] and 3-amino-5-picoline,[21] respectively, by diazotisation of the amine and decomposition by the Sandmeyer reaction using copper(I) chloride and concentrated hydrochloric acid. The purity of all these compounds was checked by g.l.c. and found to be $\geqslant 99\%$.

Apparatus.—A vertical tube of silica or Pyrex glass (0.69 m × 4.1 cm int. diam.) was supported in the heated zone (0.62 m × 4.5 cm int. diam.) of a Carbolite tube furnace. Measurements showed that there was very little temperature variation over the length of the heated zone of the reaction tube when the furnace temperature was set at 550 °C with a constant flow of nitrogen through the tube. However, during a reaction this constant temperature was maintained over only about a third of the length of the tube with an appreciable temperature gradient (*ca.* 150—550 °C) over the remainder. A preheater was placed at the top of the reactor tube and consisted of a vertical series of glass trays (1.2 × 3 cm diam.) with perforated bases and held 1.5 cm apart between two glass supports. Each tray was filled with Fenske glass helices (*ca.* 235, total weight 3.8 g, total surface area 157 × 10^{-5} m^2). The number of trays employed varied with the substrate. Typically, 5 trays occupied a position 14.5—21.6 cm from the upper end of the reaction tube and offered a hot bed (365—465 °C) to the reactants soon after their entrance to the tube. The presence of this preheater had a marked effect on the yield of the products. Several experiments were performed for each substrate to determine the optimum number and position of the preheater trays.

Above the preheater was mounted the addition assembly for the reactants. This was designed to allow a constant, but variable, flow of reactants into the furnace. Essentially it consisted of two pressure-equalising dropping funnels, one of which acted as reservoir for the other (the constant rate funnel). The rate-controlling part of the constant rate funnel consisted of a capillary tube (9 × 0.1 cm int. diam.) through which a polished tungsten restriction wire, sealed into a glass rod, could just slide. The tungsten wire was of the same length as the capillary. The position of the glass rod holding the tungsten wire could be altered by a screw cap adaptor, and thus a desired flow of reactants into the furnace could be achieved. A constant head of liquid was maintained immediately above the capillary by the periodic addition of solution from the reservoir dropping funnel. In this manner, the flow of reactants into the furnace was maintained at a constant rate. The complete assembly was lagged with heating tape and asbestos string and maintained at 50 °C.

Pyrolysis Procedure.—Typically, a solution of the pyrrole (0.15 mol) in chloroform (0.75 mol) was introduced from the dropping funnel at a constant rate of 2.5 ml min^{-1} into the preheater. Nitrogen at a flow rate of 300 ml min^{-1} was used to sweep the volatilised mixture into the hot zone. The pyrolysate was condensed in a series of 4 receiver traps, one cooled with ice, two with a slurry of solid CO_2–acetone, and a fourth with liquid N_2. Upon completion of the pyrolysis the products from the various traps were combined. The reaction tube and the traps were washed out with chloroform (60 ml) and then with 6% HCl (60 ml), and these washings added to the pyrolysate. The mixture was filtered through a bed of Celite to remove the suspended carbonaceous matter, and the residue washed on the filter bed with 6% HCl (25 ml) and chloroform (20 ml). The washes were combined with the main filtrate, from which, after standing for 1½ h, the organic layer was separated and further extracted with 6% HCl (3 × 40 ml). The combined acidic solutions were neutralised with 30% NaOH solution with cooling to 5—10 °C. The alkaline solution was extracted with dichloromethane (4 × 80 ml), the extract dried ($MgSO_4$; 5.0 g), and the solvent removed on a steam-bath using a Vigreux column. The residue was vacuum distilled and analysed by g.l.c. and g.l.c.–m.s., and the components separated by preparative g.l.c.

The space time, calculated as (reaction time) × (volume of reaction tube) ÷ [total number of moles of reactants and N_2 (expressed as a volume at the temperature and pressure of the pyrolysis)], varied between 15 and 25 sec. These values assume that the length of the reaction zone is the same as the length of the tube, and neglect the volume occupied by the preheater.

Analytical Procedures.—G.l.c. analyses and preparative scale separations were made on a Pye 105 gas chromatograph fitted with a flame ionisation detector, with nitrogen as carrier gas. The following analytical columns were employed (glass, 1.5 m × 0.4 cm int. diam.): A, Carbowax 20 M (10%) on Diatomite C, B, OV 17 (3%) on Chromosorb G, C, Bentone 34–di-isodecylphthalate (1 : 1; 5%) on Chromosorb G (all support materials 100—120 mesh). Preparative columns (glass, 2.2 m × 0.6 cm int. diam.) used were 1, Carbowax 20 M (20%), 2, OV17 (20%), 3, Bentone 34–di-isodecylphthalate (1 : 1; 20%) (all supported on Diatomite C, 60—80 mesh). Quantitative g.l.c. was carried out using triangulation. The detector response for a representative selection of the products encountered was determined and found in each to be linear. The trapping efficiency of materials collected during the preparative g.l.c. separations was generally found to be between 75 and 85%. The purity of materials separated by preparative g.l.c. was invariably checked by re-submitting them to further g.l.c. analysis. The constituents of reaction mixtures were identified by one or more of the following: (*a*) comparison of their retention times on two or more stationary phases with those of authentic samples, (*b*) the use of combined g.l.c.–m.s., and (*c*) the isolation of the compound by preparative g.l.c. followed by the determination of i.r., ^1H n.m.r., and mass spectra. In the last case, the data obtained was either compared with those from authentic samples or in the case of novel compounds, used to establish the structure.

Vapour Phase Reactions.—The results obtained from the vapour phase reaction of chloroform with each pyrrole are described and for each case the following data are given: the name of the pyrrole; in parentheses the structure reference number; the total yield of product based on the recovered

starting material; the reference letter for the analytical g.l.c. column and the temperature used for the separation; the components of the reaction mixture in the order of the retention times. The name of each component is followed by its reference number (in parentheses), its relative retention distance, and its percentage of the total product.

Pyrrole (1): 86%; A, 80°; pyridine, 1.0, trace; 3-chloropyridine (10), 1.38, 75%; 2-chloropyridine (22), 2.96, 25%. The chlorinated products were isolated by preparative g.l.c. on column 1 at 100 °C.

1-Methylpyrrole (2): 71%; B, 120°; pyrrole (1), 1.0, 1%; pyridine, 1.31, trace; 3-chloropyridine (10), 2.34, 77%; 2-chloropyridine (22), 3.0, 22%. The chloropyridines were isolated by preparative g.l.c. on column 2 at 100 °C.

2-Methylpyrrole (3): 82%; A, 175°; four components, 1.00, 27%; 1.00, 41%; 1.62, 30%; and 4.71, 2%. Component 1 was shown to be 3-*chloro*-2-*picoline* (11) (Found: *M*, 127.0186. $C_6H_6N^{35}Cl$ requires *M*, 127.0189), $\nu_{max.}$ 3 060 (Ar), 2 928, 2 850 (Me), 1 587, 1 573 (pyridine ring), and 792 cm^{-1} (2,3-disubstituted pyridine), τ 7.38 (3 H, s, 2-Me), 2.94 (1 H, qu, $J_{5,4}$ 8.0, $J_{5,6}$ 4.7 Hz, 5-H), 2.41 (1 H, qu, $J_{4,5}$ 8.0, $J_{4,6}$ 1.5, $J_{6,5}$ 4.7 Hz, 6-H). Component 2 was 3-chloro-6-picoline (17), $\nu_{max.}$ 3 040 (Ar), 2 925, 2 860 (Me), 1 580, 1 560 (pyridine ring), and 820 cm^{-1} (2,5-disubstituted pyridine), τ 7.50 (3 H, s, 6-Me), 2.95 (1 H, d, $J_{5,4}$ 8.2 Hz, 5-H), 2.51 (1 H, qu, $J_{4,2}$ 2.5, $J_{4,5}$ 8.2 Hz, 4-H), and 1.57 (1 H, d, $J_{2,4}$ 2.5 Hz, 2-H). Component 3 was 2-chloro-6-picoline (29), $\nu_{max.}$ 3 060 (Ar), 2 920, 2 840 (Me), 1 589, 1 565 (pyridine ring), and 780 cm^{-1} (2,6-disubstituted pyridine), τ 7.49 (3 H, s, 6-Me), 2.92 (2 H, qu, $J_{3,4}$ 8.0, $J_{3,5}$ 5.2 Hz, 3- and 5-H), 2.48 (1 H, t, $J_{4,3}$ 8.0 Hz, $J_{4,5}$ 8.0 Hz, 4-H). Component 4 was 2-chloro-3-picoline (23), $\nu_{max.}$ 3 050 (Ar), 2 925, 2 840 (Me), 1 581, 1 565 (pyridine ring), and 790 cm^{-1} (2,3-disubstituted pyridine), τ 7.62 (3 H, s, 3-Me), 2.88 (1 H, qu, $J_{5,4}$ 7.5, $J_{5,6}$ 4.8 Hz, 5-H), 2.47 (1 H, qu, $J_{4,5}$ 7.5, $J_{4,6}$ 2.0 Hz, 4-H), and 1.79 (1 H, qu, $J_{6,4}$ 2.0, $J_{6,5}$ 4.8 Hz, 6-H). The combined 3-chloropicolines and each of the 2-chloropicolines were isolated separately by preparative g.l.c. on column 2 at 105 °C. The composition of the mixture of 3-chloropicolines was then estimated from the ^1H n.m.r. spectrum of the mixture.

3-Methylpyrrole (4): 80%; C, 130°; four components, 1.00, 20%; 1.50, 33%; 2.52, 10%; and 3.72, 37%. Component 1 was shown to be 3-*chloro*-5-*picoline* (18) (Found: *M*, 127.0184. $C_6H_6N^{35}Cl$ requires *M*, 127.0189), $\nu_{max.}$ 3 030 (Ar), 2 920, 2 858 (Me), 1 595, 1 581 (pyridine ring), and 866 cm^{-1} (3,5-disubstituted pyridine), τ 7.66 (3 H, s, 5-Me), 2.52 (1 H, m, 4-H), 1.69 (1 H, d, $J_{6,4}$ 1.0 Hz, 6-H), and 1.63 (1 H, d, $J_{2,4}$ 2.5 Hz, 2-H). Component 2 was 3-chloro-4-picoline (12), $\nu_{max.}$ 3 050 (Ar), 2 920, 2 850 (Me), 1 595, 1 580 (pyridine ring), and 825 cm^{-1} (3,4-disubstituted pyridine), τ 7.60 (3 H, s, 4-Me), 2.85 (1 H, d, $J_{5,6}$ 5.0 Hz, 5-H), 1.65 (1 H, d, $J_{6,5}$ 5.0 Hz, 6-H), and 1.48 (1 H, s, 2-H). Component 3 was 2-chloro-5-picoline (30), $\nu_{max.}$ 3 050 (Ar) 2 930, 2 873 (Me), 1 589, 1 570 (pyridine ring), and 820 cm^{-1} (2,5-disubstituted pyridine), τ 7.67 (3 H, s, 5-Me), 2.78 (1 H, d, $J_{3,4}$ 8.0 Hz, 3-H), 2.54 (1 H, qu, $J_{4,3}$ 8.0, $J_{4,6}$ 2.5 Hz, 4-H), and 1.78 (1 H, d, $J_{6,4}$ 2.5 Hz, 6-H). Component 4 was 2-chloro-4-picoline (24), $\nu_{max.}$ 3 050 (Ar), 2 920, 2 860 (Me), 1 593, 1 550 (pyridine ring), and 820 cm^{-1} (2,4-disubstituted pyridine), τ 7.67 (3 H, s, 4-Me), 2.99 (1 H, d, $J_{5,6}$ 5.0 Hz, 5-H), 2.86 (1 H, s, 3-H), and 1.78 (1 H, d, $J_{6,5}$ 5.0 Hz, 6-H). Column 3 at 125° was used to achieve a preparative separation of each compound.

2,3-Dimethylpyrrole (5): 83%; B, 155°; four components, 1.00, 38%; 1.33, 29%; 1.81, 22%; and 4.29, 11%. The products were separated by preparative g.l.c. on column 3 at 130 °C. Component 1 was shown to be 3-*chloro*-2,4-*lutidine* (13) (Found: *M*, 141.0344. $C_7H_8N^{35}Cl$ requires *M*, 141.0346), $\nu_{max.}$ 3 050 (Ar), 2 920, 2 850 (Me), 1 591 (pyridine ring), and 825 cm^{-1} (2,3,4-trisubstituted pyridine), τ 7.63 (3 H, s, 4-Me), 7.39 (3 H, s, 2-Me), 3.01 (1 H, d, $J_{5,6}$ 5.0 Hz, 5-H), and 1.79 (1 H, d, $J_{6,5}$ 5.0 Hz, 6-H). Component 2 was 3-*chloro*-5,6-*lutidine* (19) (Found: *M*, 141.0348. $C_7H_8N^{35}Cl$ requires *M*, 141.0346), $\nu_{max.}$ 3 040 (Ar), 2 920, 2 855 (Me), 1 579, 1 555 (pyridine ring), and 884 cm^{-1} (2,3,5-trisubstituted pyridine), τ 7.75 (3 H, s, 5-Me), 7.55 (3 H, s, 6-Me), 2.63 (1 H, d, $J_{4,6}$ 2.5 Hz, 4-H), and 1.73 (1 H, d, $J_{6,4}$ 2.5 Hz, 6-H). Component 3 was 2-chloro-5,6-lutidine [22] (31), $\nu_{max.}$ 3 040 (Ar), 2 920, 2 860 (Me), 1 582, 1 564 (pyridine ring), and 814 cm^{-1} (2,3,6-trisubstituted pyridine), τ 7.76 (3 H, s, 5-Me), 7.54 (3 H, s, 6-Me), 2.96 (1 H, d, $J_{3,4}$ 7.7 Hz, 3-H), and 2.66 (1 H, d, $J_{4,3}$ 7.7 Hz, 4-H), and component 4 was 2-*chloro*-3,4-*lutidine* (25) (Found: *M*, 141.0341. $C_7H_8N^{35}Cl$ requires *M*, 141.0346), $\nu_{max.}$ 3 050 (Ar), 2 920, 2 850 (Me), 1 584, 1 546 (pyridine ring), and 825 cm^{-1} (2,3,4-trisubstituted pyridine), τ 7.68 (6 H, s, 3- and 4-Me), 3.02 (1 H, d, $J_{5,6}$ 4.6 Hz, 5-H), and 1.94 (1 H, d, $J_{6,5}$ 4.6 Hz, 6-H), τ (trifluoroacetic acid) 7.39 (3 H, s, 3-Me), 7.28 (3 H, s, 4-Me), 2.20 (1 H, d, $J_{5,6}$ 6.0 Hz, 5-H), and 1.60 (1 H, d, $J_{6,5}$ 6.0 Hz, 6-H).

2,4-Dimethylpyrrole (6): 81%; C, 160°; six components, 1.00, 2%; 1.24, 19%; 1.52, 29%; 2.29, <1%; 2.65, 47%; and 3.93, 2%. A partial preparative separation was achieved on column 2 at 120 °C and the fraction containing both components 2 and 3 was further separated on column 3 at 170 °C; but only component 3 of this binary mixture was obtained pure.

Components 1 and 4 were identified as 3-chloro-2,6-lutidine (15) and 2-chloro-3,6-lutidine (32), respectively, by comparison of their retention distances and mass spectra with those obtained from an authentic sample of (15) and samples of both isolated from the pyrolysis of compound (7). Component 2 was not obtained pure but was clearly established as 3-*chloro*-2,5-*lutidine* (21) by analysis of the ^1H n.m.r. spectrum of the mixture of components 2 and 3. 3-Chloro-2,5-lutidine has τ 7.72 (3 H, s, 5-Me), 7.43 (3 H, s, 2-Me), 2.58 (1 H, d, $J_{4,6}$ 1.9 Hz, 4-H), and 1.81 (1 H, d, $J_{6,4}$ 1.9 Hz, 6-H). Component 3 was 3-*chloro*-4,6-*lutidine* (20) (Found: *M*, 141.0341. $C_7H_8N^{35}Cl$ requires *M*, 141.0346), $\nu_{max.}$ 3 010 (Ar), 2 920, 2 850 (Me), 1 593 (pyridine ring), and 865 cm^{-1} (2,4,5-trisubstituted pyridine), τ 7.68 (3 H, s, 4-Me), 7.54 (3 H, s, 6-Me), 3.00 (1 H, s, 5-H), and 1.64 (1 H, s, 2-H). Component 5 was 2-chloro-4,6-lutidine (33), $\nu_{max.}$ 3 042 (Ar), 2 920, 2 850 (Me), 1 602, 1 550 (pyridine ring), and 861 cm^{-1} (2,4,6-trisubstituted pyridine), τ 7.73 (3 H, s, 4-Me), 7.54 (3 H, s, 6-Me), 3.14 (1 H, d, $J_{5,3}$ 0.7 Hz, 5-H), and 3.07 (1 H, d, $J_{3,5}$ 0.7 Hz, 3-H), and component 6 was 2-*chloro*-3,5-*lutidine* (26) (Found: *M*, 141.0346. $C_7H_8N^{35}Cl$ requires *M*, 141.0346), τ 7.74 (3 H, s, 5-Me), 7.68 (3 H, s, 3-Me), 2.66 (1 H, d, $J_{4,6}$ 2.0 Hz, 4-H), and 1.96 (1 H, d, $J_{6,4}$ 2.0 Hz, 6-H).

2,5-Dimethylpyrrole (7): 91%; C, 170°; five components, 1.00, 85%; 1.68, 1%; 2.08, 2%; 2.64, 10%; and 3.32, 2%. A preparative separation was carried out on column 3 at 170°. No attempt was made to separate the very small amounts of components 2, 3, and 5, which were identified as 3-chloro-2,5-lutidine (21), 3-chloro-4,6-lutidine (20), and 2-chloro-4,6-lutidine (33), respectively, by comparison of their retention distances and mass spectra with those ob-

tained from an authentic sample of (33) and of samples of all three isolated from the pyrolysis of compound (6). Component 1 was shown to be 3-chloro-2,6-lutidine (15), $\nu_{max.}$ 3 050 (Ar), 2 920, 2 850 (Me), 1 573 (pyridine ring), and 815 cm^{-1} (2,3,6-trisubstituted pyridine), τ 7.54 (3 H, s, 6-Me), 7.44 (3 H, s, 2-Me), 3.13 (1 H, d, $J_{5,4}$ 8.0 Hz, 5-H), and 2.58 (1 H, d, $J_{4,5}$ 8.0 Hz, 4-H). Component 4 was 2-*chloro*-3,6-*lutidine* (32) (Found: *M*, 141.0340. $C_7H_8N^{35}Cl$ requires *M*, 141.0346), $\nu_{max.}$ 3 020 (Ar) 2 920, 2 852 (Me), 1 596, 1 565 (pyridine ring), and 820 cm^{-1} (2,3,6-trisubstituted pyridine), τ 7.68 (3 H, s, 3-Me), 7.52 (3 H, s, 6-Me), 3.03 (1 H, d, $J_{5,4}$ 7.7 Hz, 5-H), and 2.59 (1 H, d, $J_{4,5}$ 7.7 Hz, 4-H).

3,4-Dimethylpyrrole (8): 83%; A, 185°; component 1, 1.00, 45%; component 2, 1.65, 55%. A preparative g.l.c. separation was achieved on column 1 at 150 °C. Component 1 was found to be 3-*chloro*-4,5-*lutidine* (14) (Found: *M*, 141.0344. $C_7H_8N^{35}Cl$ requires *M*, 141.0346), $\nu_{max.}$ 3 040 (Ar), 2 920, 2 860 (Me), 1 580, 1 545 (pyridine ring), and 880 cm^{-1} (3,4,5-trisubstituted pyridine), τ 7.74 (3 H, s, 5-Me), 7.71 (3 H, s, 4-Me), 1.81 (1 H, s, 6-H), and 1.66 (1 H, s, 2-H). Component 2 was 2-*chloro*-4,5-*lutidine* (27) (Found: *M*, 141.0341. $C_7H_8N^{35}Cl$ requires *M*, 141.0346), $\nu_{max.}$ 3 045 (Ar), 2 920, 2 860 (Me), 1 590, 1 555 (pyridine ring), and 862 cm^{-1} (2,4,5-trisubstituted pyridine), τ 7.81 (3 H, s, 5-Me), 7.77 (3 H, s, 4-Me), 2.94 (1 H, s, 3-H), and 1.94 (1 H, s, 6-H).

2,3,4,5-Tetramethylpyrrole (9): 92%; B, 165°; 3-chloro-2,4,5,6-tetramethylpyridine [23] (16), 1.00, 74%; 2-chloro-3,4,5,6-tetramethylpyridine [23] (28), 2.03, 26%. The mixture was separated on column 2 at 175 °C.

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