Reaction of Ketone Alkylhydrazones with Phosphorus Trichloride: a General Mild Route to Substituted Pyrroles

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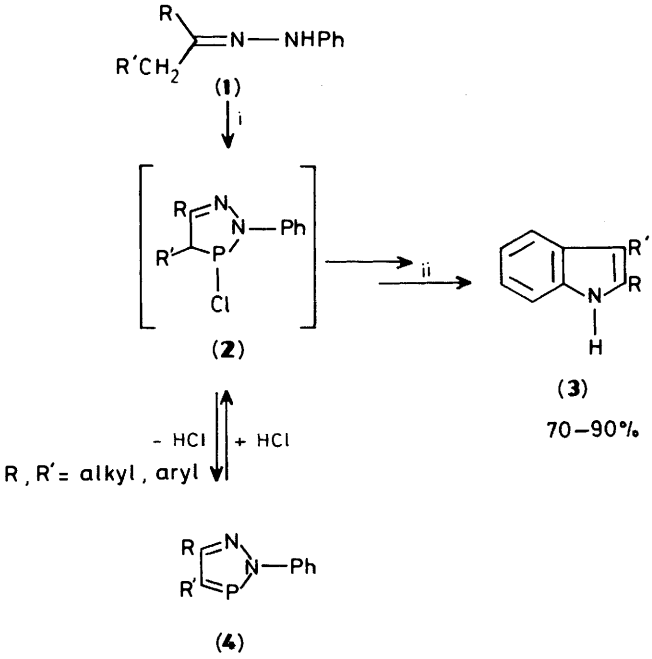
A new convenient and mild procedure for the synthesis of symmetrically and unsymmetrically substituted pyrroles is described. This one-pot synthesis consists of two different stages. The first stage, addition of PCl_3 to an alkylhydrazone, is always carried out at room temperature. The second stage, addition of an enolizable ketone to the previous reaction mixture, is performed at room temperature, or at 80 °C under reduced pressure. The results provide clear evidence that diazaphosphole derivatives being formed in the first stage are intermediates in this pyrrole synthesis.

The pyrrole ring constitutes the characteristic core of a great number of natural and biochemical products.[1] Thus a new method of constructing the pyrrole ring may well be of advantage in the synthesis of these compounds.

Symmetrically substituted pyrroles are usually prepared through Piloty–Robinson[2] synthesis using ketazines. However, this reaction requires drastic conditions, the yields are often very poor, and the synthesis of unsymmetrical pyrroles by this method has never been achieved. In addition, *C*-alkylpyrroles usually have to be synthesized *via* transformation of methoxycarbonyl- or acyl-pyrroles prepared by other methods.[3]

In a recent communication[4] we have reported the first results of a new synthesis of symmetrical pyrroles by reaction of ketone alkylhydrazones, PCl_3, and subsequent addition of the same ketone in a one-pot operation. The purpose of this paper is to describe the details of this synthesis and to study the possibility of obtaining unsymmetrical pyrroles using the same procedure.



Scheme 1. *Reagents and conditions:* i, PCl_3, room temperature; ii, room temperature

Results and Discussion

As we reported,[5] the reaction between an arylhydrazone (**1**) and PCl_3 gives indoles (**3**) in good yields after a few minutes at room temperature. In addition it was reported[6] that the same reaction gave diazaphosphole derivatives (**4**) (Scheme 1). Recently[7] we have demonstrated that diazaphospholes and indoles can arise from a common intermediate which should be the chlorodihydrodiazaphosphole (**2**). The mechanism suggested for indolization involves an acid-promoted cleavage of the P–N bond of intermediate (**2**) to give intermediates similar to those of the accepted Fischer indolization mechanism,[8] where the dichlorophosphino group, substituting an hydrogen atom, should promote the loss of Cl_2PNH_2 with consequent aromatization to the indole in a Wittig-like elimination.

In a medium which dissolves all the possible phosphorus adducts, indoles (**3**) are formed at room temperature in an irreversible manner and are the almost exclusive reaction products.

In connection with these results we wished to study the fate of the alkylhydrazone or its diazaphosphole derivative when the reaction with PCl_3 was carried out under the same solvent conditions and in the presence of an excess of starting ketone.

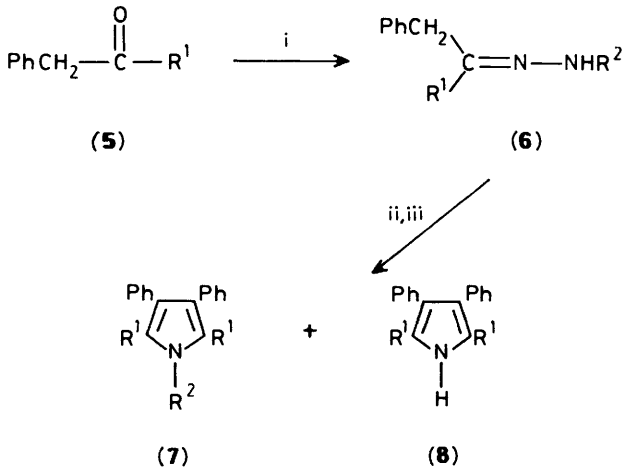
From the beginning of this research we soon discovered the possibility of obtaining pyrroles even if it was difficult to find the best reaction conditions. This is due to the fact that the pyrrolization of an alkylhydrazones such as (**6**) is a two-stage one-pot procedure. For this reason the course of some reactions was followed by g.l.c.–mass spectroscopy. In the case of symmetrical pyrroles the best yields were obtained as follows. A dry dichloromethane solution of the hydrazone (**6**) was treated at room temperature with an equimolar amount of PCl_3. After *ca.* 3 h the original ketone (**5**) (0.7 mol equiv.) and PCl_3 were added to the mixture. The reaction mixture was kept for some days at room temperature or for a few (15—40) minutes under reduced pressure at 80 °C. The reaction mixture was then quenched with aqueous sodium hydrogen carbonate and extracted by dichloromethane. Symmetric pyrroles (**7**) and (**8**) were isolated by column chromatography. The ratios between *N*-substituted (**7**) and *N*-unsubstituted pyrroles (**8**) were highly dependent on the reactants and on the reactions conditions. However, when the reaction was carried out at room temperature almost exclusive or predominant formation of *N*-substituted pyrroles (**7**) was observed. Clearly the time necessary for the first stage of the reaction can be different in the various cases and this fact makes this reaction more complex than the corresponding indolization of arylhydrazones. However, when using the same ketone in the first and second stage it is not necessary to define the appropriate reaction time. In fact, pyrroles were also obtained when the reaction was carried out at room temperature directly on a mixture of ketone (**5**) (1.7 mol equiv.) the required hydrazine (1 mol equiv.), and PCl_3 (2.7 mol equiv.). In this case, however, the yields were

lower and the reaction time was longer. Another difficulty which is not encountered in the indole synthesis is the very easy hydrolysis of alkylhydrazones, and then it is very important to eliminate any traces of water in the reactants to obtain the best yields.

When in the second stage the ketone was used in equimolar amounts it was recovered in 20—30% yield at the end of the reaction. In contrast, when using 0.7 mol equiv. of the ketone (**5**) we obtained almost the same yields and the advantage of an easier separation of pyrrole products.

It should be noted that PCl_3 was being used here not only as an activator of pyrrole formation but also as a water scavenger in the second stage and then for protection of the hydrazone against premature hydrolysis. During this study we were surprised to find that PCl_3 or its derivatives also have the important function of protecting pyrroles from their readily ocurring decomposition. In fact if we kept our reaction mixture for several days or months before quenching with aqueous hydrogen carbonate we did not observe decomposition of the pyrroles. When, after column separation, the same pyrroles were kept under the same conditions we observed a gradual decomposition (development of a dark violet or red colour in the solution). In contrast, after the addition of PCl_3 to the same pyrroles we did not note any decomposition. From this mixture pyrroles can be recovered by simple treatment with aqueous work-up and extraction with dichloromethane.

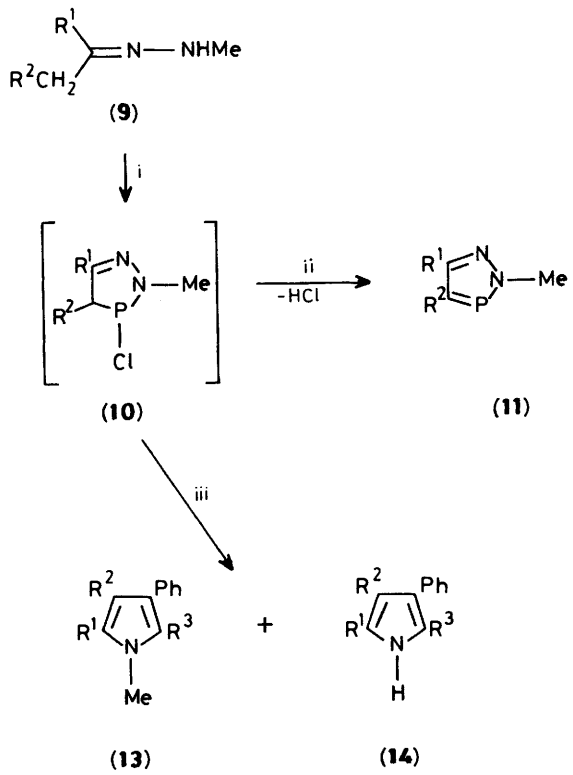
Scheme 2 shows the symmetrical pyrroles obtained in this manner.



	Ratio (7):(8)	Overall yield (%)
a; $R^1 = R^2 = Me$	5:1	40
b; $R^1 = Me$, $R^2 = PhCH_2$	3:1	35
c; $R^1 = PhCH_2$, $R^2 = Me$	3:1	30
d; $R^1 = Ph$, $R^2 = Me$	6:1	30

Scheme 2. *Reagents and conditions:* i, NH_2NHR^2; ii, PCl_3, room temperature; iii, PCl_3 + (**5**), room temperature

As a first comment on these results we note that symmetrical pyrroles were formed only when easily enolizable ketones such as benzyl ketones were used. In fact when we utilized dialkyl ketones no appreciable amounts of symmetrical pyrroles were obtained. However, we know that in the indolization with PCl_3 indoles (**3**) are synthesized from dialkyl ketones (see Scheme 1). For this reason we think that if in our pyrrolization the key intermediate is a diazaphosphole derivative such as (**2**) this can be formed in the first stage with every α-methylene ketone and consequently only in the second stage is it necessary to use an easily enolizable ketone. Then, an extension of this method to



	Ratio (13):(14)	Overall yield (%)
a; $R^1 = R^2 = R^3 = Me$	5:1	38
b; $R^1 = PhCH_2$, $R^2 = Ph$, $R^3 = Me$	1:2	55
c; R^1 = n-octal, R^2 = n-heptyl, $R^3 = Me$	3:1	47
d; $R^1 = R^2 = Me$, $R^3 = Ph$	3:1	35
e; $R^1 = R^3 = Me$, $R^2 = Et$	4:1	52
f; $R^1 = Et$, $R^2 = R^3 = Me$	3:1	50

Scheme 3. *Reagents and conditions:* i, PCl_3, room temperature, 12—20 h; ii, heat; iii, $PhCH_2COR^3$ (**12**) (0.7 mol equiv.), PCl_3, room temperature, 2—3 h or 70—80 °C, a few min

unsymmetrically substituted pyrroles should always require the addition of a benzyl ketone (**5**) to any other easily enolizable ketone in the second stage of our one-pot procedure.

Experimental data have confirmed this hypothesis. Unsymmetrical pyrroles (**13**) and (**14**) were obtained from addition of the benzyl ketones (**12**) in the second stage. It should be noted that the same unsymmetrical pyrroles were not obtained when we used benzyl ketones in the first stage and the corresponding dialkyl ketones in the second stage. Obviously, in the case of the pyrrole (**13b**) in which we used two different benzyl ketones the two procedures can be used with identical results.

Scheme 3 summarizes the unsymmetrical pyrroles obtained by this procedure.

In the case of unsymmetrical pyrroles it is useful to determine the time necessary for the completion of the first stage. Monitoring (g.l.c.–m.s.) of the reaction mixture showed that complete disappearance of the hydrazone (**9**) and the concomitant formation of the diazaphosphole (**11**) occurred after *ca.* 12—20 h. Presumably diazaphospholes (**11**) arise from the precursor hydrochlorides (**10**) by heating in the injector chamber. If the addition of the second ketone occurred before the total formation of the intermediate (**10**), it was possible to obtain symmetrical pyrroles derived from the possible exchange of the ketone in the starting hydrazone. The *in situ* generation of an intermediate such as (**10**) does not permit this exchange, a feature present in the Piloty synthesis.

Table 1. Spectral data of symmetrical pyrroles (**7**) and (**8**)

Compd.	$\delta_H(CDCl_3)$	Exact mass Found (Calc.)
(**7a**)	2.30 (s, 6 H), 3.57 (s, 3 H), 7.1—7.5 (m, 10 H, ArH)	261.1519 (261.1517)
(**8a**)	2.35 (s, 6 H), 7.1—7.8 (m, 11 H, ArH + NH)	247.1363 (247.1361)
(**7b**)	2.18 (s, 6 H), 5.10 (s, 2 H), 6.70—7.5 (m, 15 H, ArH)	337.1828 (337.1830)
(**7c**)	3.09 (s, 3 H) 4.07 (s, 4 H), 6.90—7.50 (m, 20 H, ArH)	413.2151 (413.2143)
(**8c**)	3.99 (s, 4 H), 7.1—7.35 (m, 21 H, ArH + NH)	399.1991 (399.1987)
(**7d**)	3.40 (s, 3 H), 7.06 (s, 10 H, ArH), 7.40 (s, 10 H, ArH)	385.1831 (385.1830)

Table 2. Spectral data of unsymmetrical pyrroles (**13**) and (**14**)

Compd.	$\delta_H(CDCl_3)$	Exact mass Found (Calc.)
(**13a**)	2.00 (s, 3 H, 3-Me), 2.17 (br s, 6 H, 2-, 5-Me), 3.37 (s, 3 H, 1-Me), 6.82—7.4 (m, 5 H, ArH)	199.1362 (199.1360)
(**14a**)	2.00 (s, 3 H, 3-Me), 2.17 (br s, 6 H, 2-, 5-Me), 6.85—7.40 (m, 6 H, ArH + NH)	185.1205 (185.1204)
(**13b**)	2.16 (s, 3 H, 5-Me), 3.23 (s, 3 H, 1-Me), 4.0 (s, 2 H, CH_2), 7.0—7.44 (m, 15 H, ArH)	337.1832 (337.1820)
(**14b**)	2.16 (s, 3 H, 5-Me), 3.97 (s, 2 H, CH_2), 6.97—7.70 (m, 16 H, ArH + NH)	323.1671 (323.1673)
(**13c**)	0.6—3.0 (m, 32 H, C_8H_{17} and C_7H_{15}), 2.10 (s, 3 H, 5-Me), 3.4 (s, 3 H, 1-Me), 7.0—7.43 (m, 5 H, ArH)	381.3397 (381.3395)
(**14c**)	0.6—3.0 (m, 32 H, C_8H_{17} and C_7H_{15}), 2.19 (s, 3 H, 5-Me), 7.0—7.66 (m, 6 H, ArH + NH)	367.3237 (367.3238)
(**13d**)	2.10 (s, 3 H, 3-Me), 2.30 (s, 3 H, 2-Me), 3.40 (s, 3 H, 1-Me), 7.0—7.35 (m, 10 H, ArH)	361.1515 (261.1517)
(**14d**)	2.0 (s, 3 H, 3-Me), 2.26 (s, 3 H, 2-Me), 7.0—7.55 (m, 11 H, ArH + NH)	247.1362 (247.1361)
(**13e**)	1.00 (t, *J* 8 Hz, 3 H, CH_2Me), 2.20 (br s, 6 H, 2-, 5-Me), 2.46 (q, *J* 8 Hz, 2 H, CH_2Me), 3.36 (s, 3 H, 1-Me), 7.10—7.60 (m, 5 H, ArH)	213.1520 (213.1517)
(**13f**)	1.12 (t, *J* 8 Hz, 3 H, CH_2Me), 2.00 (s, 3 H, 3-Me), 2.20 (s, 3 H, 5-Me), 2.56 (q, *J* 8 Hz, 2 H, CH_2Me), 3.36 (s, 3 H, 1-Me), 7.10—7.60 (m, 5 H, ArH)	213.1519 (213.1517)

The second stage was carried out by addition of benzyl ketone (**12**) (0.7 mol equiv.) and PCl_3 to the reaction mixture. After 2—4 h at room temperature the mixture was evaporated and kept at 70—80 °C under reduced pressure for *ca.* 30—40 min. Only in the case of the hydrazone (**9b**) was the first stage of 3 h, and the second stage could be performed only at room temperature.

The prevalence or almost exclusive formation of *N*-substituted pyrroles (**13**) was observed in all cases with the exception of hydrazone (**9b**) in which the prevalence of *N*-unsubstituted product (**14b**) over (**13b**) was noted.

All unsymmetric pyrroles described in this paper are new compounds and were identified essentially by ^1H n.m.r. and mass spectroscopy. Apparently, our method can easily prepare several differently substituted pyrroles hitherto rather inaccessible, and is a useful alternative to known synthetic methods for substituted pyrroles because of the easy availability of starting materials and reagents and the simple and mild conditions. In addition, PCl_3 also has the important function of protecting *N*-substituted and *N*-unsubstituted pyrroles against their ready decomposition and it can be removed by simple quenching with aqueous hydrogen carbonate. Finally our results provide further evidence that diazaphosphole derivatives, generated *in situ*, can be intermediates in the synthesis of aza-heterocycles.

Experimental

^1H N.m.r. spectra were recorded at 60 MHz with a Varian EM 360 instrument. Chemical shifts were given in p.p.m. from tetramethylsilane as internal standard. G.l.c.–m.s. analyses were carried out with a HP59970 workstation formed by an HP 5890 gas-chromatograph equipped with a methyl silicone capillary column and by an HP-5970 mass detector. Mass spectra were recorded with a VG 7070 spectrometer. M.p.s are uncorrected and were determined with a Buchi apparatus. The analytical samples of oily pyrroles were obtained by bulb-to-bulb distillation and b.p.s given are the oven temperatures. Commercial PCl_3 was used without further purification. Yields are based on the starting quantities of ketones used for the formation of alkylhydrazones. Light petroleum refers to that fraction boiling in the range 40—60 °C.

Alkylhydrazones.—These were obtained by heating the respective alkylhydrazine and ketone together in equivalent amounts in benzene solution at reflux for *ca.* 2 h under Dean–Stark conditions. After removal of the solvent the crude products were used immediately.

General Procedure for Symmetric Pyrroles.—Phosphorus trichloride (11 mmol) was added at room temperature to a stirred dichloromethane solution (50 ml) of a hydrazone (**6**) (10 mmol). The mixture was allowed to react at room temperature, with further addition (if necessary) of CH_2Cl_2 to ensure homogeneity. After *ca.* 3 h a ketone (**5**) (7 mmol) and further PCl_3 (7 mmol) were added to the mixture which was kept at room temperature for some days or at 80 °C for *ca.* 40 min under reduced pressure using a Rotavapor. The course of the reaction was followed by g.l.c.–m.s. analysis and t.l.c. It should be noted that several pyrroles gave, after some minutes or some hours, characteristic coloured spots on t.l.c. on silica gel and this feature permitted their recognition. At the end of the reaction the mixture was poured into saturated aqueous $NaHCO_3$. The organic layer was separated, washed with water, and the pyrroles were separated by column chromatography (rapid elution). Some decomposition on the column was noted by the column becoming coloured. The pyrroles were characterized essentially by ^1H n.m.r. and mass spectroscopy (see Table 1) and their structures confirmed by comparison with authentic samples.

1,2,5-*Trimethyl*-3,4-*diphenylpyrrole* (**7a**). The second stage of the reaction went to completion in 3 days at room temperature or after 30 min at 80 °C under reduced pressure. The pyrroles (**7a**) and (**8a**) in the ratio ~5:1 or 3:1 were obtained in 40% yield and were separated by passage through a short silica gel column (light petroleum–diethyl ether, 5:1); (**7a**) (R_F 0.43) as white crystals, m.p. 144—145 °C (lit.,[9] 145—146 °C); and (**8a**) (R_F 0.20) as white crystals, m.p. 150—151 °C (lit.,[10] 150 °C). The spots on the t.l.c. became violet-green after a few min.

1-*Benzyl*-2,5-*dimethyl*-3,4-*diphenylpyrrole* (**7b**). After 6 days at room temperature or after 30 min at 80 °C under reduced pressure the pyrroles (**7b**) and (**8b**) in the ratio 3:1 (at room temperature) and 2:1 (at 80 °C) were obtained in 35 or 40% yield. Chromatographic separation on a short silica gel column (light petroleum–diethyl ether, 5:1) gave pure compound (**7b**) as white crystals, m.p. 143—145 °C (lit.,[11] 147—149 °C) (R_F

0.46); and pure (**8b**), m.p. 150—151 °C, identical with the previous compound (**8a**). The spot for (**7b**) on t.l.c. became violet after some hours.

2,5-*Dibenzyl*-1-*methyl*-3,4-*diphenylpyrrole* (**7c**). The second stage of the reaction went to completion in 8 days at room temperature to give pyrroles (**7c**) and (**8c**) (in the ratio ~3:1) in 30% yield. The same reaction mixture after 40 min at 80 °C under reduced pressure gave pyrroles (**7c**) and (**8c**) in the ratio ~1:1 in 31% yield. Chromatographic separation on a short silica gel column (light petroleum–diethyl ether, 5:1) gave pure compound (**7c**) (R_F 0.44) as white crystals, m.p. 161—162 °C (lit.,[9] 160 °C); and pure *compound* (**8c**) (R_F (0.21) as white crystals, m.p. 160—161 °C (Found: C, 89.9; H, 6.2; N, 3.3. $C_{30}N_{25}N$ requires C, 90.31; N, 3.51%).

1-*Methyl*-2,3,4,5-*tetraphenylpyrrole* (**7d**). The second stage of the reaction went to completion after 40 min at 80 °C under reduced pressure, to give almost exclusive formation of the pyrrole (**7d**) in 30% yield after chromatographic separation on silica gel (light petroleum–diethyl ether, 5:1) m.p. 209—210 °C (lit.,[12] 210 °C). Small amounts of compound (**8d**) were also observed.

General Procedure for Unsymmetrical Pyrroles.—A mixture of phosphorus trichloride (11 mmol) and the hydrazone (**9**) (10 mmol) in dichloromethane (50 ml) was stirred at room temperature for *ca.* 12—20 h. The reaction mixture was submitted to g.l.c.–m.s. analysis and the chromatogram showed at the end of the first stage of reaction the corresponding diazaphosphole (**11**) and small amounts of the corresponding hydrazone. In the second stage ketone (**12**) (7 mmol) and further PCl_3 (7 mmol) were added to the mixture which was kept at room temperature for *ca.* 2—3 h, and then at 70—80 °C under reduced pressure for *ca.* 30—40 min. G.l.c. monitoring showed the decrease of diazaphosphole and the increase of the corresponding unsymmetrical pyrroles: after the reaction was complete the mixture was quenched with saturated aqueous $NaHCO_3$ and submitted to separation by column chromatography on silica gel (rapid elution). The products were characterized by microanalysis, ^1H n.m.r. spectroscopy, and mass spectrometry (see Scheme 3 and Table 2).

1,2,3,5-*Tetramethyl*-4-*phenylpyrrole* (**13a**). The first stage of the reaction went to completion in 12 h at room temperature, the second stage in 3 h at room temperature and in 40 min at 70—80 °C under reduced pressure. Pyrroles (**13a**) and (**14a**) in the ratio ~5:1 were obtained in 38% yield. Chromatographic separation on a short silica gel column (light petroleum–diethyl ether, 5:1) gave pure *compound* (**13a**) as a yellow glassy oil, b.p. 130—135 °C at 0.4 mmHg, (R_F 0.58) (Found: C, 84.3; H, 8.5; N, 6.9. $C_{14}H_{17}N$ requires C, 84.37; H, 8.60; N, 7.03%); and pure *compound* (**14a**) as a violet solid, m.p. 108—109 °C (R_F 0.30) (Found: C, 84.2; H, 8.1; N, 7.5. $C_{13}H_{15}N$ requires C, 84.28; H, 8.16; N, 7.56%).

2-*Benzyl*-1,5-*dimethyl*-3,4-*diphenylpyrrole* (**13b**). The first stage went to completion in 3 h and the second stage in 48 h at room temperature or at 70—80 °C in 30 min under reduced pressure. Pyrroles (**13b**) and (**14b**) in the ratio 1:2 were obtained in 55% yield. Chromatographic separation on a short silica gel column (light petroleum–diethyl ether, 5:1) gave pure *compound* (**13b**) as a yellow glassy oil, b.p. 170—180 °C at 0.1 mmHg (R_F 0.60) (Found: C, 88.9; H, 6.8; N, 4.1. $C_{25}H_{23}N$ requires C, 88.98; H, 6.87; N, 4.13%); and pure *compound* (**14b**) as a white-pink solid, m.p. 165—166 °C (R_F 0.38) (Found: C, 88.9; H, 6.5; N, 4.3. $C_{24}H_{21}N$ requires C, 89.12; H, 6.55; N, 4.33%).

3-*Heptyl*-1,5-*dimethyl*-2-*octyl*-4-*phenylpyrrole* (**13c**). The first stage went to completion in 20 h and the second stage in 4 h at room temperature and in 40 min at 70—80 °C under reduced pressure. Pyrroles (**13c**) and (**14c**) in the ratio ~8:1 were obtained in 47% yield. Chromatographic separation on a short silica gel column (light petroleum–diethyl ether, 10:1) gave pure *compound* (**13c**) as a pale yellow oil, b.p. 155—160 °C at 0.1 mmHg (R_F 0.62) (Found: C, 84.9; H, 11.3; N, 3.6. $C_{27}H_{43}N$ requires C, 84.97; H, 11.36, N, 3.67%); and pure *compound* (**14c**) as a pale pink oil (R_F 0.42) (Found: C, 84.9; H, 11.2; N, 3.7. $C_{26}H_{41}N$ requires C, 84.24; N, 3.81%).

1,2,3-*Trimethyl*-4,5-*diphenylpyrrole* (**13d**). The first stage of the reaction went to completion in *ca.* 12 h and the second stage in 4 h at room temperature and in 40 min at 70—80 °C. Pyrroles (**13d**) and (**14d**) in the ratio ~3:1 were obtained in 35% yield. Separation on a short silica gel column (light petroleum–diethyl ether, 5:1) gave pure *compound* (**13d**) as a white solid, m.p. 180—182 °C (R_F 0.60) (Found: C, 87.2; H, 7.3; N, 5.3. $C_{19}H_{19}N$ requires C, 87.31; H, 7.33; N, 5.36%); and pure *compound* (**14d**) as a violet greasy solid (Found: C, 87.3; H, 6.8; N, 5.6. $C_{18}H_{17}N$ requires C, 87.41; H, 6.93; N, 5.66%).

3-*Ethyl*-1,2,5-*trimethyl*-4-*phenylpyrrole* (**13e**). The first stage went to completion in *ca.* 15 h and the second stage in 3 h at room temperature and in 30 min at 70—80 °C under reduced pressure. Pyrroles (**13e**) and (**14e**) in the ratio ~4:1 were obtained in 52% yield. Flash separation on a short silica gel column (light petroleum–diethyl ether, 15:1) gave pure *compound* (**13e**) (R_F 0.6) as a pale yellow oil, b.p. 180—190 °C at 0.1 mmHg (Found: C, 84.4; H, 8.9; N, 6.5. $C_{15}H_{19}N$ requires C, 84.45; H, 8.98; N, 6.57%); and impure compound (**14e**) as an unstable yellow oil (R_F 0.2).

2-*Ethyl*-1,3,5-*trimethyl*-4-*phenylpyrrole* (**13f**). The first stage went to completion in *ca.* 20 h and the second stage in 3 h at room temperature and in 30 min at 70—80 °C. Pyrroles (**13f**) and (**14f**) in the ratio 3:1 were obtained in 50% yield. Flash separation on a short silica gel column (light petroleum–diethyl ether, 15:1) gave pure *compound* (**13f**) as a pale yellow oil, b.p. 170—180 °C at 0.05 mmHg (R_F 0.5) (Found: C, 84.3; H, 8.8; N, 6.5. $C_{15}H_{19}N$ requires C, 84.45; H, 8.98; N, 6.57%); and impure compound (**14f**) as an unstable violet oil.

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