

THE REACTION BETWEEN 2,5-DIALKYLPIRROLES AND DICHLOROCARBENE^{a,b}

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Abstract—An intermediate in the reaction between pyrrole 1 and dichlorocarbene-PhHg⁺, has been isolated, and its structure determined by X-ray diffraction. This compound can be converted into 3-chloropyridine and 2H-pyrrole under the action of acids and/or bases.

2,5-Dialkyl pyrroles react with dichlorocarbene under several experimental conditions giving addition (2,5-dialkyl-2H-pyrroles or Plancher's pyrrolenines) and ring expansion products (2,6-dialkyl-3-chloropyridines).²

The original³ hypothesis that 2H-pyrroles were intermediates in the ring expansion reaction was ruled out.⁴ The observation that strongly basic conditions increased the yield of 2H-pyrroles, as compared to 3-chloropyridines, suggested⁵ that the latter arose from cycloaddition of the dichlorocarbene on the pyrrole ring, while 2H-pyrroles were formed through an electrophilic attack of the reagent on the conjugate base of the substrate. In this way two different intermediates have been supposed and this hypothesis is commonly accepted at present.⁶

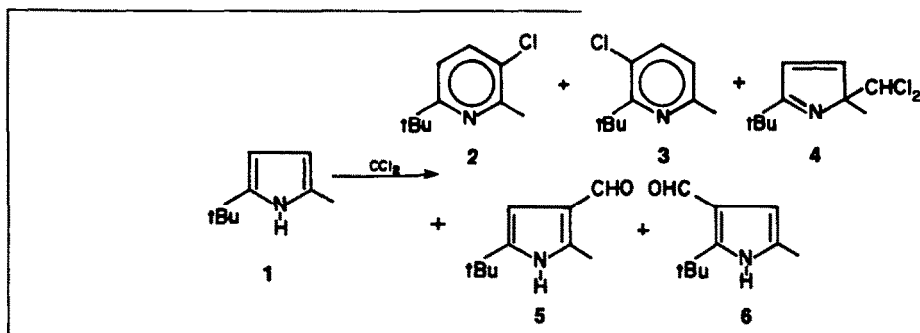
Other data are nevertheless in contrast with the mechanism outlined above, and they agree with the existence of a single intermediate.⁷ The same idea was put forth several years ago.⁸

Thus, in order to collect new data, we studied the reaction of a pyrrole with dichlorocarbene generated by decomposition of phenyltrichloromethylmercury. Dichlorocarbene can be obtained either by thermolysis¹⁰ or NaI catalyzed decomposition¹¹ of this reagent in aprotic solvents. Trial experiments showed that the first method gave tarry reaction mixtures with very poor yields. Better results were obtained by decomposing the PhHgCCl₃ with NaI.

The present paper deals with a study of the products obtained in this reaction and the results strongly support a mechanism involving a single intermediate.

RESULTS

2-Methyl-5-*t*-butyl pyrrole 1 was chosen as substrate because several of the reactions products of this compound with dichlorocarbene (2-6) have already been characterized.^{7,12}



Reactions of pyrroles with dichlorocarbene have been generally studied by generating the reagent in protic and basic media, and sometimes with dichlorocarbene generated by thermolysis of sodium trichloroacetate. In this case, the behaviour of pyrroles⁵ differed from that observed for indoles;⁹ the latter gave ring expansion and addition products (i.e. 3-chloroquinolines and 3H-indoles), while pyrroles afforded only ring expansion products.

Chromatographic separation of the reaction mixture enabled us to isolate, beside 2, 3 and 4, a crystalline product 7 in 5% yield, which contained mercury (from its mass spectrum); and IR and NMR spectra were consistent with the presence of a phenyl and a pyrrolenine nucleus.

Figure 1 shows the molecular structure of 7 obtained by X-ray structure determination. Table 1 lists atomic fractional coordinates for all nonhydrogen atoms, corresponding to an R value of 0.062. Bond distances and angles are reported in Table 2. The value of bond lengths in the 5-membered ring together with coplanarity of N, C(2), C(3), C(4), C(5) and C(7) atoms allowed to assign the double bonds between C(3)-C(4) and C(5)-N.

^aA previous short communication has been published (Ref. 1).

^bDedicated to Prof. L. Panizzi on the occasion of his 70th birthday.

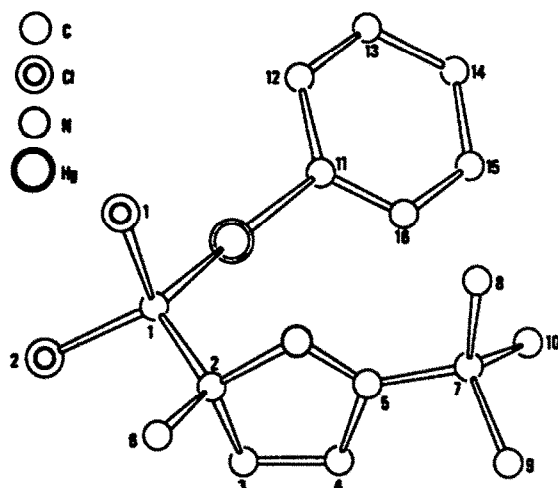


Fig. 1. Molecular structure of [1,1-dichloro-1-(2-methyl-5-t-butyl-2H-2-pyrryl)] phenylmercury 7.

Table 1. Fractional atomic coordinates of [1,1-dichloro-1-(2-methyl-5-t-butyl-2H-2-pyrryl)] phenylmercury 7. Standard deviations are given in parentheses.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Hg	.2468(1)	.0697(0)	.1180(0)
Cl(1)	.2301(8)	-.1290(3)	.1602(2)
Cl(2)	-.1603(8)	-.0585(3)	.0838(2)
N	.1667(18)	.0005(7)	.2873(7)
C(1)	.0634(24)	-.0321(9)	.1532(8)
C(2)	-.0189(23)	-.0154(9)	.2314(8)
C(3)	-.1454(24)	.0677(10)	.2257(8)
C(4)	-.0446(26)	.1243(10)	.2758(9)
C(5)	.1498(22)	.0784(9)	.3124(7)
C(6)	-.1485(29)	-.0909(11)	.2612(10)
C(7)	.2959(23)	.1153(9)	.3781(8)
C(8)	.4865(29)	.0573(11)	.3998(10)
C(9)	.1627(38)	.1324(15)	.4453(13)
C(10)	.3838(38)	.2034(16)	.3541(13)
C(11)	.4502(24)	.1694(9)	.0953(8)
C(12)	.6051(28)	.1572(12)	.0421(10)
C(13)	.7627(28)	.2200(11)	.0367(10)
C(14)	.7643(31)	.2965(13)	.0813(11)
C(15)	.6040(27)	.3064(11)	.1305(9)
C(16)	.4526(27)	.2430(11)	.1368(9)

The Hg atom is bonded almost linearly with C(1) and C(11) and the distances are in the range of values most frequently found for Hg-C covalent bonds.¹³⁻¹⁵ Hence the structure of 7 was established as [1,1-dichloro-1-(2-methyl-5-t-butyl-2H-2-pyrryl)] phenylmercury.

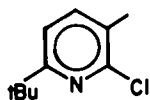
The substituents on C(1) and C(2) assume a staggered conformation, with methyl group facing between the two chlorine atoms (Fig. 1), while one methyl group in the t-butyl group is eclipsed with the nitrogen atom. There are no particularly short intermolecular contacts and the molecules are held together by van der Waals' forces only.

It appeared reasonable that 7 arose from the trapping of an intermediate of the reaction between the pyrrole 1 and dichlorocarbene. Therefore, the behaviour of 7

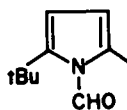
towards acid and bases in different (protic and aprotic) media was studied carefully. Compound 7 proved to be sufficiently stable in ethanol 95° when warmed at 80°C (only a trace of pyrrole 1 was detected after 18 h) and was completely stable in dimethoxyethane (DME) under the same conditions. Experiments were therefore carried out at this temperature in these solvents.

In addition to products already known, two different compounds (8 and 9) were present in the reaction mixtures. An independent synthesis of 8 and the conversion of 9 into pyrrole 1 by basic hydrolysis,¹⁶ coupled with its mass spectrum, enabled us to identify these two products as 2-chloro-3-methyl-6-t-butyl pyridine 8, and 1-formyl-2-methyl-5-t-butyl pyrrole 9, respectively.

Results of these experiments are reported in Table 3.



8



9

The behaviour of 7 in presence on an excess of p-toluensulfonic acid was also investigated. In these conditions, along with some tars, a new crystalline product 10, containing mercury, was isolated.

Spectra were similar with those of 7, but the phenyl group was not present.

Figure 2 shows the molecular structure of 10 for the two independent molecules of the asymmetric unit, as

Table 2. Bond distances (Å) and angles (°) for 7. Standard deviations are given in parentheses.

Hg-C(1)	2.08(1) Å	C(5)-C(7)	1.50(2) Å
Hg-C(11)	2.06(2)	C(7)-C(8)	1.51(2)
C1(1)-C(1)	1.82(2)	C(7)-C(9)	1.54(3)
C1(2)-C(1)	1.80(2)	C(7)-C(10)	1.54(3)
N-C(2)	1.46(2)	C(11)-C(12)	1.43(2)
N-C(5)	1.29(2)	C(11)-C(16)	1.35(2)
C(1)-C(2)	1.53(2)	C(12)-C(13)	1.39(2)
C(2)-C(3)	1.50(2)	C(13)-C(14)	1.41(3)
C(2)-C(6)	1.54(2)	C(14)-C(15)	1.40(2)
C(3)-C(4)	1.35(2)	C(15)-C(16)	1.37(2)
C(4)-C(5)	1.49(2)		
C(1)-Hg-C(11)	173.3(6)°	N-C(5)-C(7)	123.3(13)°
C(2)-N-C(5)	107.3(11)	C(4)-C(5)-C(7)	123.5(12)
Hg-C(1)-C1(1)	108.0(7)	C(5)-C(7)-C(8)	111.7(12)
Hg-C(1)-C1(2)	112.7(7)	C(5)-C(7)-C(9)	108.4(14)
Hg-C(1)-C(2)	112.7(9)	C(5)-C(7)-C(10)	109.4(14)
C1(1)-C(1)-C1(2)	105.1(8)	C(8)-C(7)-C(9)	112.8(15)
C1(1)-C(1)-C(2)	108.8(10)	C(8)-C(7)-C(10)	107.2(14)
C1(2)-C(1)-C(2)	109.2(10)	C(9)-C(7)-C(10)	107.3(15)
N-C(2)-C(1)	107.9(11)	Hg-C(11)-C(12)	120.3(11)
N-C(2)-C(3)	106.2(11)	Hg-C(11)-C(16)	119.7(11)
N-C(2)-C(6)	108.1(12)	C(12)-C(11)-C(16)	119.6(14)
C(1)-C(2)-C(3)	108.0(11)	C(11)-C(12)-C(13)	119.2(15)
C(1)-C(2)-C(6)	114.4(12)	C(12)-C(13)-C(14)	120.4(16)
C(3)-C(2)-C(6)	111.9(12)	C(13)-C(14)-C(15)	117.9(17)
C(2)-C(3)-C(4)	107.5(14)	C(14)-C(15)-C(16)	121.2(15)
C(3)-C(4)-C(5)	106.2(13)	C(15)-C(16)-C(11)	121.7(15)
N-C(5)-C(4)	112.9(13)		

Table 3. Action of acids and bases on 7 at 80°C for 18 h

Run	Solvent	Reagent (molar ratio)	Products (relative GC%)					Yield (by GLC)
			1	2	4	8	9	
1	EtOH	-	100	-	-	-	-	Trace
2	DME	-	Unreacted substrate					-
3	EtOH	KOH (10:1) ^a	10	-	90	-	-	70
4	DME	MeONa (10:1) ^{a,b}	Unreacted substrate					-
5	DME	MeONa/MeOH (10:1:1) ^{a,b}	Trace	-	100	-	-	50
6	EtOH	TsOH (1:1)	8	30	50	5	7	45
7	EtOH	TsOH (1:1)	Trace	40	40	20	Trace	50
8	DME	TsOH (1:1)	15	66	-	Trace	19	40
9	DME	TsOH (1:1)	10	70	-	Trace	20	45

a) With a molar ratio (1:1) the reaction was too slow.

b) The reaction time was prolonged for 3 days.

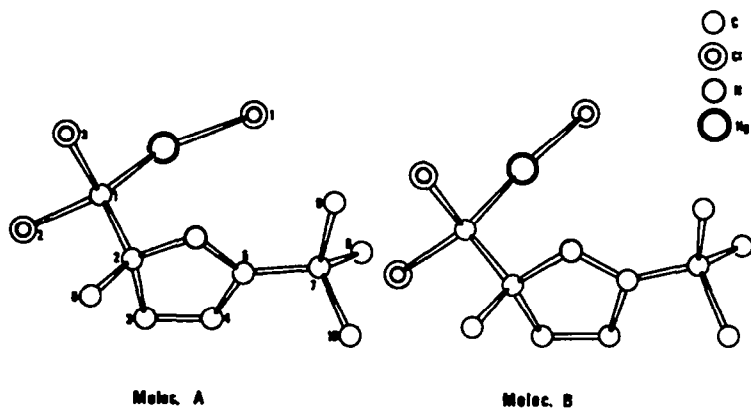


Fig. 2. Molecular structures of the two independent molecules of (1,1-dichloro-1-(2-methyl-5-t-butyl-2H-pyrryl)] chloromercury 10. They are represented in a common orientation.

derived from X-ray structure determination. For comparison they are drawn in a similar orientation. Table 4 lists the atomic fractional coordinates of all non-hydrogen atoms, and they correspond to an R value of 0.069. Table 5 shows a list of bond lengths and bond angles. They, together with stereochemical features, are consistent with the structure of [1,1-dichloro-1-(2-methyl-5-t-butyl-2H-pyrryl-2-)] chloro-mercury for the compound 10.

In the limits of experimental errors the two molecules of the asymmetric unit assume the same conformation around of both C(1)–C(2) and C(5)–C(7) bonds, corresponding to that observed in the crystal for the compound 7. The Cl–Hg–C bonds deviate significantly from linearity, and similar departure is observed in most of the two-coordinate mercury compounds.^{13,14,17}

Assuming the van der Waals' radii $r_{\text{Hg}} = 1.50 \text{ \AA}$,¹³ $r_{\text{Cl}} = 1.80 \text{ \AA}$ and $r_{\text{N}} = 1.50 \text{ \AA}$,¹⁸ short contacts result between mercury, chlorine and nitrogen atoms of adjacent molecules. The coordination geometry is irregular for both the mercury atoms, and it is shown in Fig. 3, with a projection of the crystal structure along the *b* axis of the crystal.

Two Cl (1A), related by a centre of symmetry, lie at 3.10 and 3.17 Å from Hg(B) with Cl (1A)–Hg(B)–Cl (1A') angle of 78° and the plane containing these three atoms is almost perpendicular to the Hg(B)–Cl (1B) bond. Hg(A) is engaged in other two short contacts of 3.08 and 2.76 Å

with Cl (3B') and N(B') of a molecule B' related to molecule B by a centre of symmetry, and these weak interactions also involve atoms lying on a plane nearly perpendicular to Hg(A)–Cl(1A) bond, with Cl(3B')–Hg(A)–N(B') angle of 66°. These two planes are almost parallel to each other.

Compound 10 proved to be thermally stable, but, unlike 7, was stable to acids, while under the action of ethanolic KOH it was converted into 4.

DISCUSSION AND CONCLUSIONS

The origin of mercurial 7 and its chemical behaviour must be both related to the well-known property of halomethyl mercurials to undergo easy nucleophilic substitution.^{11,19} Thus, an intermediate of the reaction between pyrrole 1 and dichlorocarbene, even though a weak nucleophile, can be trapped by the excess of PhHgCCl₃.

The reaction of 7 to give 2 is formally similar to the conversion 2H-pyrrole-3-chloropyridine: this latter is already known,⁴ but a carbenoid species is involved as a consequence of severe conditions for basicity (BuLi) or temperature (MeONa, 240°C). Thermal stability of 7 (runs 1 and 2, Table 3) excludes a carbenoid route affording pyridine 2.

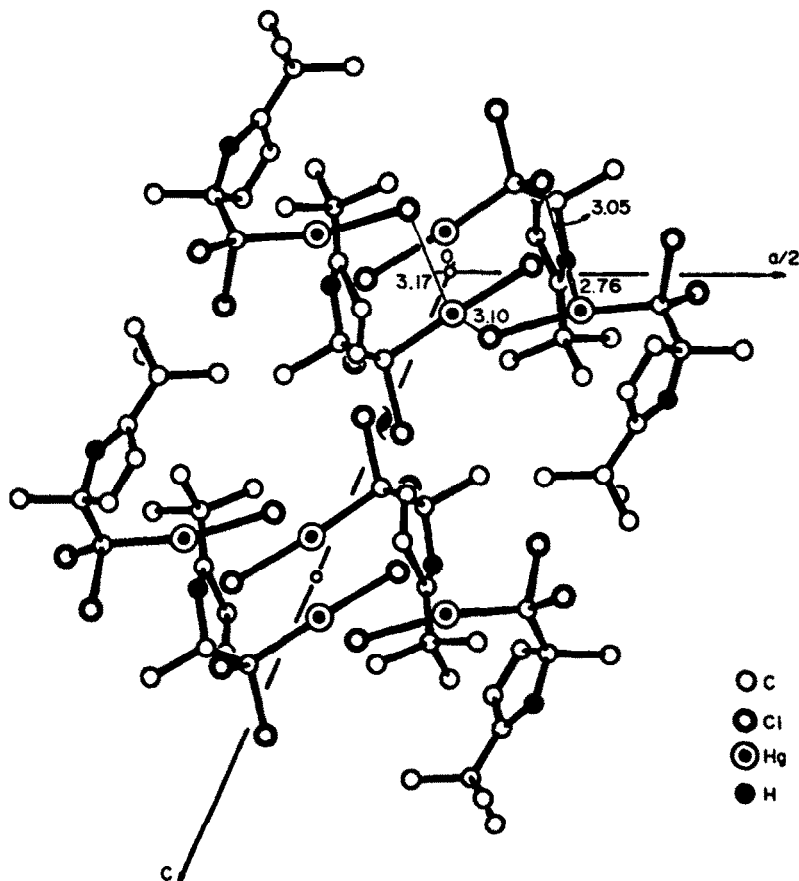
Bases convert 7 into 2H-pyrrole 4, but a protic solvent, as expected,⁷ is required (runs 3–5). 7 under the action of acids (in molar ratio 1:1) is mainly converted into the

Table 4. Fractional atomic coordinates of [1,1-dichloro-1-(2-methyl-5-t-butyl-2H-pyrryl)] chloromercury 10. Standard deviations are given in parentheses.

	Molecule A			Molecule B		
	x/a	y/b	z/c	x/a	y/b	z/c
Hg	.2221(1)	-.0494(1)	.0597(1)	.0326(1)	.1936(1)	.0661(1)
Cl(1)	.1042(6)	-.0595(7)	.1040(6)	.1204(7)	.2295(8)	-.0108(7)
Cl(2)	.3142(12)	.0673(19)	-.0573(12)	.0332(9)	.1969(10)	.2615(6)
Cl(3)	.3871(12)	-.1479(15)	.0294(16)	-.0825(7)	.0344(7)	.1358(6)
N	.412(4)	.006(5)	.202(4)	-.168(2)	.263(2)	.022(2)
C(1)	.340(3)	-.019(3)	.049(3)	-.040(3)	.177(3)	.145(2)
C(2)	.401(3)	.057(5)	.121(3)	-.116(2)	.268(3)	.117(2)
C(3)	.357(5)	.183(7)	.116(5)	-.080(3)	.390(4)	.133(3)
C(4)	.346(5)	.180(7)	.191(5)	-.108(3)	.452(5)	.060(3)
C(5)	.381(3)	.077(4)	.244(3)	-.172(2)	.365(2)	-.014(2)
C(6)	.493(4)	.079(6)	.122(4)	-.180(4)	.251(5)	.168(4)
C(7)	.367(6)	.065(8)	.328(6)	-.215(3)	.404(4)	-.105(3)
C(8)	.279(5)	.079(7)	.332(5)	-.287(3)	.500(4)	-.104(3)
C(9)	.434(6)	.145(8)	.404(6)	-.150(4)	.459(6)	-.142(4)
C(10)	.400(7)	-.070(10)	.362(7)	-.269(3)	.307(4)	-.165(2)

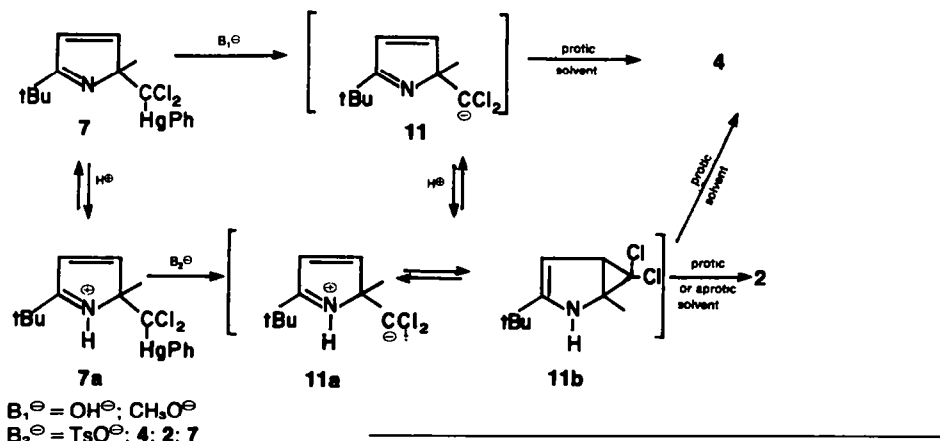
Table 5. Bond lengths (Å) and angles (°) for 10. Standard deviations range between 0.4 and 0.10 (Å), and between 2 and 7° respectively

	Molec. A	Molec. B		Molec. A	Molec. B
Hg-C1(1)	2.34 Å	2.30 Å	C1(1)-Hg-C(1)	166°	173°
Hg-C(1)	2.05	2.09	C(2)-N-C(5)	107	110
C1(2)-C(1)	1.89	1.81	Hg-C(1)-C1(2)	107	109
C1(3)-C(1)	1.76	1.77	Hg-C(1)-C1(3)	104	110
N-C(2)	1.38	1.44	Hg-C(1)-C(2)	114	110
N-C(5)	1.30	1.30	C1(2)-C(1)-C1(3)	103	106
C(1)-C(2)	1.49	1.55	C1(2)-C(1)-C(2)	104	110
C(2)-C(3)	1.60	1.50	C1(3)-C(1)-C(2)	115	111
C(2)-C(6)	1.54	1.60	N-C(2)-C(1)	106	110
C(3)-C(4)	1.30	1.30	N-C(2)-C(3)	109	104
C(4)-C(5)	1.44	1.59	N-C(2)-C(6)	109	108
C(5)-C(7)	1.47	1.43	C(1)-C(2)-C(3)	110	111
C(7)-C(8)	1.50	1.62	C(1)-C(2)-C(6)	117	114
C(7)-C(9)	1.59	1.58	C(3)-C(2)-C(6)	106	109
C(7)-C(10)	1.67	1.51	C(2)-C(3)-C(4)	100	113
			C(3)-C(4)-C(5)	114	103
			N-C(5)-C(4)	110	109
			N-C(5)-C(7)	132	131
			C(4)-C(5)-C(7)	117	119
			C(5)-C(7)-C(8)	124	106
			C(5)-C(7)-C(9)	110	113
			C(5)-C(7)-C(10)	104	111
			C(8)-C(7)-C(9)	107	110
			C(8)-C(7)-C(10)	106	106
			C(9)-C(7)-C(10)	104	111

Fig. 3. Crystal packing of (1,1-dichloro-1-(2-methyl-5-t-butyl-2H-2-pyrrolyl)] chloromercury 10, viewed down the *b* axis.

pyridine **2** in aprotic solvent, while in EtOH, the route to pyrrolenine **4** becomes important (runs 6–9).

The data presented in Table 3 can be rationalized on the basis of the following scheme:

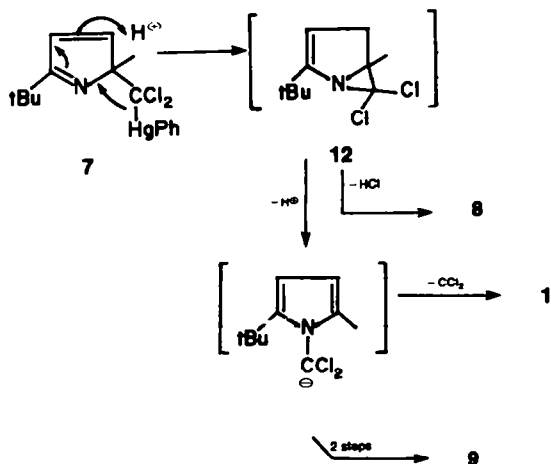


In basic conditions only a nucleophilic displacement of pyrrolenine anion **11** is possible in presence of a protic solvent which acts as proton donor.

In acidic conditions (TsOH in molar ratio 1:1), the protonated species **7a** can release easily the neutral species **11a**. Weak nucleophiles which are present (tosyl anion, **4**, **2** or **7**) can favour this route. In this respect, the tendency of halomethylmercurials to give coordination complexes with Lewis bases has been already observed.²⁰

The fate of **11a** depends on the medium of reaction. In protic solvents the proton transfer competes with the ring expansion, whereas the latter route becomes predominant in aprotic media. Incidentally, the species **11a** in equilibrium with the bicyclic valence tautomer **11b**, can be the intermediate in the reaction of dichlorocarbene with pyrroles in several experimental conditions. This aspect will be considered later.

The presence of compounds **1**, **8** and **9** in the reaction mixtures is less clear. A possible rationalization can be related to an alternative proton attack to C_3 in **7**.



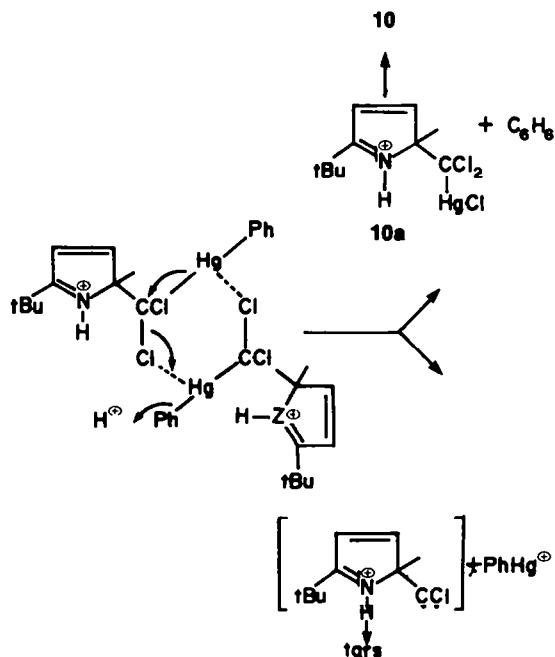
In this way, the formation of the aziridine **12** (structurally similar to an already known reaction product of **4**

with sodium ethoxide¹²) can be justified. Subsequent C_2 - C_3 cleavage of the aziridine ring²¹ affords to the product in which the carbon originally provided by the reagent is transferred to nitrogen giving rise to **1** and **9**.

An alternative ring expansion gives rise to 2-chloropyrrole **8**.

The small amount of pyrrole **1** present in runs 3 and 5 (Table 3), can be attributed to the solvolysis of substrate, as shown in run 1.

The behaviour of **7** in presence of a large excess of acid seems to be related to the absence, in this case, of Lewis bases. The displacement of **11a** is no more possible the only possible path being an electrophilic attack of the proton on the aromatic ring.²² Coordination bonds between mercury and chlorine (which are evident in the crystals of **10**) can favour a concerted reaction in which **10** is formed, as depicted below:

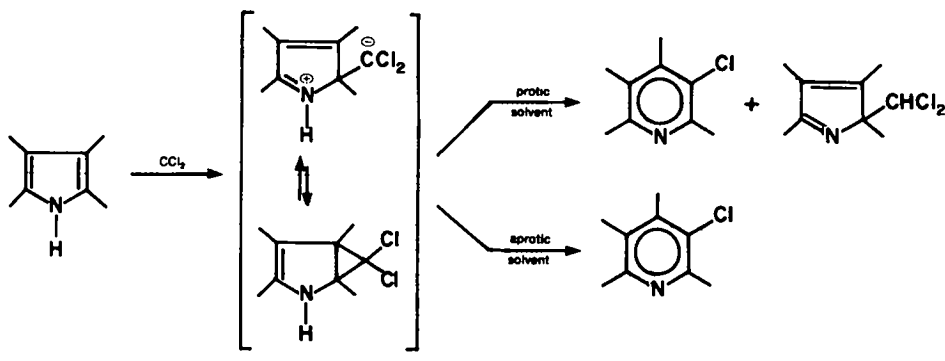


The stability of **10** in acidic conditions must be related to the well-known low reactivity of organomercury compounds in which organic residues are substituted by halogenes.²³

The data presented so far show that an intermediate in the reaction of dichlorocarbene with pyrrole 1, trapped by the phenylmercury cation, can be converted into both ring expansion and addition products, the relative importance of these pathways being regulated only by the proticity of the medium, and depending on the presence of an N-protonated substrate (like 7a).

This behaviour parallels in any respect that of parent reactions (pyrroles and indoles with dichlorocarbene),^{5,9} all these data being strictly coherent with our previous observations on pyrroles and indoles.^{7,24}

Therefore we feel that when these reactions are carried out in neutral (aprotic) or in moderate basic (protic) media, in which the concentration of indissociate substrate is very high, a single intermediate like 11a in equilibrium with 11b (both formed by electrophilic attack and/or cycloaddition of reagent) can give rise to both expansion and addition products. Thus we suppose that, in moderate alkaline or in neutral conditions, the mechanism can be depicted as follows:



On the other hand, in neutral aprotic media, an alternative mechanism, depending on the presence of a high amount of indissociate substrate which can act as proton donor, can be followed, leading to 3H-indoles. The absence of 2H-pyrroles under these conditions is consistent with the proposed mechanism, or can be accounted for by the known instability of these compounds in the reaction conditions.²⁴

EXPERIMENTAL

M.p.s are uncorrected. IR spectra were recorded on Perkin Elmer 257 while for NMR spectra a Perkin Elmer R-32 was used. Mass spectra were carried out with an AEI MS-12 at 70 eV. Glc analyses were carried out on a Carlo Erba GV, using a 2 m long column (2% OV-17 on Chromosorb G) and N₂ as carrier gas. Tlc analyses were carried out using hexane-ethyl-acetate (9:1) as eluent and I₂ as developer.

For the crystalline products 7 and 10, the lattice type and space groups were determined from Weissenberg photographs, using Cu-K_α radiation. The unit cell dimensions and their standard deviations were calculated from least-squares refinement based on 2 θ values of 15 selected reflections measured on a four-circle diffractometer SYNTEX P2.

The intensity data were recorded on the same automatic diffractometer, using monochromatized Mo-K_α radiation, and were corrected for Lorentz and polarization effects, but not for absorption.

Lists of observed and calculated structure factors and of atomic thermal parameters of 7 and 10 may be obtained from the authors on request.

Action of dichlorocarbene from PhHgCCl₂ on pyrrole 1

(a) Under thermolytic conditions. 2-Methyl-5-t-butyl pyrrole 1²²

(0.1 g) and PhHgCCl₂²⁵ (0.56 g) were refluxed overnight in dry C₆H₆ (5 ml) under N₂. The resulting tarry mixture was filtered, the solvent was evaporated and the crude residue dissolved in light petroleum (40–70°). After filtration and solvent removal a glc analysis of the residue (0.03 g) showed the presence of compounds 1–4 in small amount among other unidentified substances. A similar experiment was carried out using DME as solvent and similar results were obtained.

(b) By NaI catalysis. Pyrrole 1 (3.85 g, 28 mmoles) and PhHgCCl₂ (22.1 g, 56 mmoles) were dissolved in dry DME (350 ml) in a two-necked flask with magnetic stirring and under N₂. NaI (8.4 g, 56 mmoles) in 40 ml of dry DME was added during 2 h and the mixture was left stirring overnight. After filtration and DME removal under reduced pressure, the residue (7.95 g) was dissolved in light petroleum (40–70°) and filtered. Solvent removal gave a crude mixture (4.95 g). Chromatographic elution on SiO₂ (1:100) with hexane-ethyl acetate (95:5) led to, (in elution order) 3-chloropyridines 2 and 3 (mixture; 0.77 g, 15%), unreacted substrate 1 (2.7 g) and a crystalline compound identified as [1,1-dichloro-1-(2-methyl-5-t-butyl-2H-2-pyrrolyl)] phenylmercury 7 (0.69 g, 5%), mp 108–109°C from CH₃CN. IR(KBr): ν_{max} at 3070, 3050, 2980, 2940, 1610, 1525, 1485, 1435, 1370.

1110, 1030, 1005, 750 and 700 cm⁻¹. NMR(CCl₄): 7.17 δ, 5H(Ph); 7.38 and 6.49 δ, 2H, AB system (J = 5Hz), (C₃-H and C₄-H); 1.58 δ, 3H, singlet (CH₃); 1.22, δ, 9H, singlet (t-butyl). MS: peaks from *m/e* 499 to 493; 484–478; 464–458; 442–436; 281–275; 218; 204–198; 183; 182; 168; 141; 132. Subsequent elution with hexane-ethyl acetate (9:1) gave 2-methyl-5-t-butyl-2-dichloromethyl-2H-pyrrole 4 (0.18 g, 3%). Glc examination of column tails showed the presence in traces of 2-methyl-5-t-butyl-3-formyl pyrrole 5 and 2-methyl-5-t-butyl-4-formyl pyrrole 6.

Crystal structure determination of [1,1-dichloro-1-(2-methyl-5-t-butyl-2H-2-pyrrolyl)] phenylmercury 7

Well-shaped colourless crystals of 7 were obtained at room temp. by slow evaporation from acetonitrile solution.

Crystal data are: C₁₆H₁₉NCl₂Hg, M = 496.83, monoclinic, space group P2₁/c, a = 6.261(2), b = 15.400(4), c = 17.594(6) Å, β = 96.08(2)°, U = 1687 Å³, z = 4, D_c = 1.79 g cm⁻³, F(000) = 944, μ(Mo-K_α) = 96.7 cm⁻¹.

The intensity data of 2514 non-zero (I > 3σ(I)) independent reflections with θ < 30° were measured using θ – 2θ scan technique with crystal of 0.25 × 0.30 × 0.30 mm. The crystal structure was determined by means of Patterson and Fourier methods.

The atomic parameters of non-hydrogen atoms were refined by block-diagonal least-squares calculations, assuming anisotropic thermal motion only for Hg and Cl atoms. The final R and R_w were 0.062 and 0.084 respectively, the weight function being W = (a + Fo + b Fo²)⁻¹, with a = 30.0 and b = 0.008. The final positional parameters are listed in Table 1.

Action of acids (molar ratio 1:1) and bases on 7. Mercurial 7 (15 mg) was placed in a tube, dissolved into the appropriate solvent (see Table 3) and a equimolecular amount of n-hexadecane was added as internal GC standard. After the appropriate base or p-toluenesulfonic acid was added, the tube was sealed and warmed at 80°C for the time reported in Table 3. The

resulting basic mixtures were poured into water and extracted with ether, while acidic ones were washed with NaHCO_3 and H_2O . Tlc analyses showed the absence of substrate **7** and glc analyses gave results reported in Table 3.

Synthesis of 2-chloro-3-methyl-6-t-butyl pyridine 8. Compound **8** was prepared by Minisci method.²⁸ 2-Chloro-3-picolone²⁹ (0.64 g), AgNO_3 (0.08 g), pivalic acid (2.5 g) and conc H_2SO_4 (0.8 ml) were dissolved into 15 ml H_2O and warmed at 70°C. A soln of 1.14 g of ammonium peroxydisulfate in 2 ml H_2O was added dropwise under stirring during 10 min and then for a further 30 min. The resulting soln was poured onto ice, made basic with NH_4OH and extracted with CHCl_3 . Solvent removal gave a residue (0.55 g) which, by GC-MS coupling, showed to be a mixture of unreacted substrate and a new compound (GC ratio 2:1). Gas chromatographic and mass spectral properties of the latter were superimposable with those of **8**. MS (*m/e*): 183(22); 182(22); 168(100); 141(45); 117(35); 92(15); 91(22). Mass spectra of chloropyridines **2**, **3** show the same fragments.

Identification of 1-formyl-2-methyl-5-t-butyl pyrrole 9. Identification was carried out following the conversion of **9** into pyrrole **1** under the action of KOH/EtOH .¹⁶ The reaction mixture of run **8** (Table 3) was dissolved into 10% ethanolic KOH and refluxed for 2h. Glc analysis showed that **9** was disappeared and pyrrole **1** was formed in similar amounts as compared with the internal standard (*n*-esadecane). Mass spectrum of **9** (Peaks at *m/e* 165(25); 150(62); 122(100); 107(30); 106(20); 94(20); was very similar to that of formylpyrrole **6** but showed dramatic differences in relative abundances with that of formylpyrrole **5**. This must be related to the relative positions of formyl and *t*-butyl groups.

Action of acids (in molar ratio 10:1) on 7. Mercurial **7** (100 mg) was dissolved in EtOH (7 ml) and 330 mg of *p*-toluenesulfonic acid were added. The soln was warmed at 80°C overnight. The usual workup gave a mixture (75 mg) in which compounds **1-9** were absent (by tlc and glc). Pic of the mixture (hexane-ethyl acetate 9:1) gave 25 mg of a crystalline compound identified as [1,1-dichloro-1-(2-methyl-5-t-butyl-2H-pyrryl-2-)] chloromercury **10**, mp 131–132°C from CH_3CN . IR(CCl_4): ν_{max} at 2970; 2930; 1610; 1475; 1445; 1380; 1370; 1120; 1100 cm^{-1} . NMR(CDCl_3): 7.12 and 6.22 δ , 2H, AB system ($J = 5 \text{ Hz}$), ($\text{C}_2\text{-H}$ and $\text{C}_4\text{-H}$); 1.56 δ , 3H, singlet (CH_3); 1.26 δ , 9H, singlet (*t*-butyl). A similar result was obtained using DME as solvent. **10** was stable when warmed (80°C) in EtOH or DME in presence of TsOH in several molar ratios.

Crystal structure determination of [1,1-dichloro-1-(2-methyl-5-t-butyl-2H-2-pyrryl)] chloromercury 10.

Colourless and poor quality crystals of **10** were obtained from CH_3CN solution at room temp. Crystal data are: $\text{C}_{10}\text{H}_{14}\text{NCl}_2\text{Hg}$, $M = 455.18$, monoclinic, space group $\text{P2}_1/\text{c}$, $a = 16.549(4)$, $b = 11.484(4)$, $c = 16.242(3)$ Å, $\beta = 113.9(2)$, $U = 2821.6$ Å³, $Z = 8$, $D_c = 2.14 \text{ g cm}^{-3}$, $F(000) = 1696$, $\mu(\text{Mo-K}) = 116.6 \text{ cm}^{-1}$. A total of 6151 independent reflections with $\theta < 27^\circ$ were measured in ω -scan mode, with a irregularly-shaped crystal of dimensions ranging between 0.2 and 0.4 mm.

During the data collection four monitoring reflections revealed a significant crystal damage and the intensities were corrected for the appropriate decay factor. 2454 Reflections ($I > 2.5 \sigma(I)$) were considered as observed structure factors. The crystal structure was determined by means of Patterson and Fourier methods.

The atomic parameters of the non-hydrogen atoms were refined by block-diagonal least-squares calculations, assuming anisotropic thermal motion only for Hg and Cl atoms.

The final R and R_w were 0.069 and 0.103 respectively, the weight function being $W = ((\sin \theta)/\lambda)^2$.

The final positional parameters are listed in Table 4 for the two molecules of the asymmetric unit.

The atomic scattering factors and the anomalous scattering corrections were from Ref. 26. All the calculations were performed on a H.P. 21 MX Minicomputer using the crystallographic software (described in Ref. 27).

Action of bases on 10. 5 mg of **10** in a tube were added with an equimolecular amount of *n*-hexadecane and dissolved with 0.3 ml EtOH containing 6 mg of KOH . The tube was sealed and warmed overnight. After the usual work-up, tlc and glc analyses showed the presence of 2H-pyrrole **4** alone, in 85% yield (glc).

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