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Thermal Rearrangement of *N*-Alkyl-, and *N*-Aryl-(2,2-dihalo-1-phenylcyclopropyl)methyleneamines to 1-Alkyl-, and 1-Aryl-2 (or 3)-halo-4-phenylpyrroles

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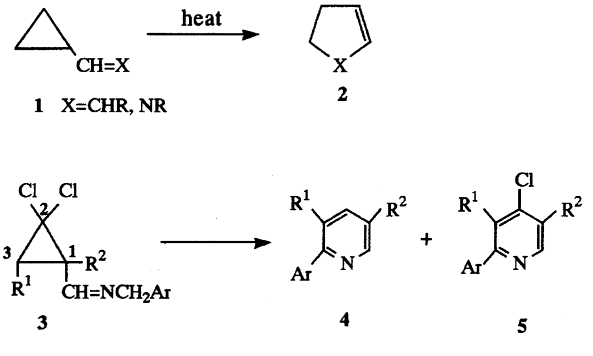
The thermolysis of *N*-*t*-alkyl-, and *N*-aryl-(2,2-dichlorocyclopropyl)methyleneamines yielded directly 1-*t*-alkyl, and 1-aryl-3-chloropyrroles as the major products along with a slight amount of the 2-chloro isomers. The transformation to the 3-chloropyrroles was enhanced in polar solvents. But basic additives directed the thermal rearrangement into the 1,2-bond cleavage of the cyclopropane ring, leading to the 2-chloropyrroles. On the other hand, (difluorocyclopropyl)methyleneamines were pyrolyzed exclusively to 3-fluoropyrroles under 1,3-bond cleavage. The ionic mechanism involving a heterolytic dissociation of chlorine atom under 1,3-bond scission of the cyclopropane ring is proposed for the rearrangement to 3-chloropyrroles, while a homolytic cleavage pathway is proposed for 3-fluoropyrroles. The present thermolysis supplies a unique preparative tool for 2-, and 3-halo-4-phenylpyrrole derivatives.

Since the first practical use of acid-catalyzed thermal rearrangements of cyclopropylmethyleneamine for the pyrrolidine alkaloid synthesis by Stevens in 1967, the scope of this process has been broadened and the application examples have accumulated. The reaction mode has often been discussed in the category of the well-documented vinylcyclopropane to cyclopentene rearrangement because of the similar five-membered ring product (**1**→**2** in Scheme 1).1) On the other hand, we showed recently that *N*-benzyl-(2,2-dichlorocyclopropyl)methyleneamines (**3**) are transformed not to dihydropyrroles but to 2-phenylpyridines (**4**/**5** in Scheme 1). This was the first example of a six-membered ring formation in the area of "vinylcyclopropane" rearrangement.2) A key step to the unique transformation is the hydrogen shift from the benzylic site.

Now our interest has turned to the behavior of (dichloroclopropyl)methyleneamines if the α-carbon of the imino nitrogene bears no hydrogen atoms, and the thermal fate of the bromo- or fluorocyclopropane analogues. We are expecting to develop this new type of heterocyclic transformation as a preparative tool for halogenated pyrroles of pharmacological interest. This paper presents an extensive study of the thermal behavior of *N*-*t*-alkyl- and *N*-aryl-(2,2-dihalocyclopropyl)methyleneamines.3) (Scheme 2)

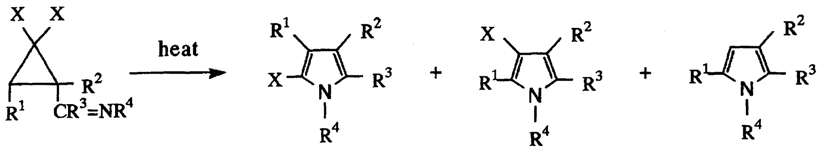


Scheme 1. Thermal rearrangement of vinyl- and iminomethylcyclopropane.

Results and Discussion

Cyclopropylmethyleneamines **6** were prepared by condensation of 2,2-dihalocyclopropane-1-carbaldehydes or 1-acyl-2,2-dihalocyclopropanes with the appropriate amine, and the thermolysis was carried out in a solution in an open vessel or in a sealed tube. The NMR data of the produced pyrroles were summarized in Table 3 (Fig. 1) and 4. The positions of the substituents of the pyrrole ring were assigned with reference to our previous work.2,3)

Thermolysis of *N*-(1-methyl-1-phenylethyl)-(2,2-dichloro-1-phenyl-1-cyclopropyl)methyleneamine **6a** in benzene (in a sealed tube) was carried out at 220 °C and afforded 2-chloro-, and 3-chloro-1-(1-methyl-1-phenylethyl)-4-phenylpyrrole **7a**/**8a** in 1 and 63% yields respectively after 12 h. We could not find any amount of 2-pyrroline intermediates. 3-Chloropyrrole **8a** was also directly obtained along with a trace amount of **7a** by heating **6a** in phenetole at 210 °C in an open vessel. At lower temperatures the formation rate for 2-chloropyrrole was not improved, either (Table 2). The thermolysis did not practically occur at temperatures lower



6 **7** **8** **9**

Scheme 2. Thermal rearrangement of (2,2-dihalocyclopropyl)methyleneamine.

than 150 °C. In pyrolysis of the 1-methyl- and 1-methyl-3-phenyl, and 3-methyl-1-phenyl analogues **6b**/**6c**/**6d** in benzene at 220 °C, the corresponding 3-chloro-1-(1-methyl-1-phenylethyl)pyrroles **8b**/**8c**/**8d** were obtained in 45, 31, and 39% yields, respectively and the formation of the 2-chloro isomers was not observed. Similarly, the Schiff bases of *t*-butylamine **6e**/**6f** were pyrolyzed only to the 3-chloro derivatives **8e** and **8f** in 28 and 33% yields, respectively. (1-Iminoethyl)cyclopropane **6i** was recovered unchanged at 220 °C for as long as 130 h; this thermal stability of **6i** parallels to the cases of (1-alkylvinyl)cyclopropanes.[1] The thermolysis of the imine prepared from aniline **6g** gave 3-chloro-1,4-diphenylpyrrole **8g** only in 1.4% yield. In all these cases, the cyclopropane ring cleavage at the 1,2-bond leading to the 2-chloropyrroles was observed to just a trace degree or not at all.

These reactions were thought to proceed via the ionic ring opening of the cyclopropyl cation generated by the chloride ion dissociation.[2] If the thermolysis evoked in a homolytic fashion, 1,2-bond fission should be favorable, owing to the radical stabilization being greater by CCl_2 than by CH_2. The rearrangement of **6a** in fact was not affected by the presence of a radical scavenger, 2,5-*t*-butylhydroquinone (DBP) (Table 2).

The carbonium ion participation in the rearrangement was supported by enhancement of the pyrrole formation in a polar solvent such as 1-methyl-2-pyrrolidone (NMP). In NMP, the thermolysis of **6a**, **6b**, and **6e** in an open vessel at 200 °C produced selectively **8a**, **8b**, and **8e** in improved yields of 90, 72, and 75%, respectively; a drastic yield increase to as high as 81% was realized in the case of **8g**. In no case using NMP were the 2-chloro isomers found. The condensation of 2,2-dichloro-1-phenylcyclopropanecarbaldehyde and 1-adamantylamine proceeded quite slowly owing to the steric hindrance, but by direct heating of a mixture of the two reactants in high polar solvent, 1,3-dimethyl-2-imidazolidinone at 200 °C for 12 h, 1-adamantyl-3-chloro-4-phenylpyrrole **8h** was isolated in 63% yield, where 1-adamantyl-3-phenylpyrrole **9h** was concomitantly obtained in 10% yield. The formation of the dechlorinated pyrrole arose probably from the disproportionation of once formed **8h**. Such intermolecular crossings take place occasionally in halogen-substituted pyrroles.[5] Use of a polar solvent like ethanol or triglyme showed no appreciable effect for the transformation into the pyrroles. Nonpolar hydrocarbons, hexane and cyclohexane, subdued the rearrangement itself excessively, though the relative rate enhancement for the homolytic 1,2-bond cleavage would be expected. Heating **6a** in DMSO or sulfolane resulted in a spontaneous formation of an intractable dark brown tar.

The original cyclopropylmethyleneamine to dihydropyrrole rearrangement is not strictly a purely thermal process unlike the vinylcyclopropane prototype—an acid catalyst is required.[6] The rearrangement is driven by C=N π -bond abstraction by Lewis acid, followed by either the counter ion or internal trapping of the cation. However, in the case of the (dichlorocyclopropyl)methyleneamine, the leaving chloride ion is responsible for triggering the cyclopropane ring cleavage with the 1,3-bond fission (and the subsequent pathway to the 3-chloropyrrole **8** is predicted as depicted in Scheme 3). It is self-evident that ammonium chloride and Lewis acids did not promote the rearrangement of the (dichlorocyclopropyl)methyleneamine. However, it is here worth mentioning that a strong halide acceptor silver trifluoroacetate, did not function as a rearrangement promo-

Table 1. Thermolysis of **6**[a)]

						Yield/%[b)]		
6	X	R^1	R^2	R^3	R^4	**7**	**8**	**9**
a	Cl	H	Ph	H	$PhCMe_2$	0.8	61	
b	Cl	H	Me	H	$PhCMe_2$	—	45	
c	Cl	Ph	Me	H	$PhCMe_2$	—	31	
d	Cl	Me	Ph	H	$PhCMe_2$	—	39	
e	Cl	H	Ph	H	*t*-Bu	—	28	
f	Cl	Ph	Me	H	*t*-Bu	—	33	
g	Cl	H	Ph	H	Ph	—	1.4	
h[c)]	Cl	H	Ph	H	1-Adamantyl	—	63	10
i[d)]	Cl	H	Ph	Me	$PhCMe_2$	—	—	
j[e)]	Br	H	Ph	H	$PhCMe_2$	—	—	18
k[e)]	Br	H	Ph	H	Ph	—	—	13
l[f)]	F	H	Ph	H	$PhCMe_2$	—	65	
m[f)]	F	H	Ph	H	*t*-Bu	—	41	
n[f)]	F	H	Ph	H	Cyclohexyl	—	35	
o[f)]	F	H	Ph	H	*p*-$MeOC_6H_4CH_2$	—	50	11[g)]
p[f)]	F	H	Ph	H	Ph	—	62	
q[f)]	F	H	Ph	H	1-Naphthyl	—	70	
r[f)]	F	H	Ph	H	*n*-Bu	—	31	

a) Thermolysis in benzene at 220 °C for 12 h (autoclave), unless otherwise stated. b) Isolated yields; the absence of a figure shows that the compound was not observed. c) In 1,3-dimethyl-2-imidazolidinone at 200 °C for 10 h (open). d) 130 h. e) In xylene at 140 °C for 12 h (open). f) 180 °C/20 h. g) 2-(*p*-Methoxyphenyl)-5-phenylpyridine.

Table 2. Effects by Additives and Solvents on the Thermolysis of Imines **6**

Substrate	Additive$^{\text{a)}}$/Solvent		Conditions	Products/Yields/%$^{\text{b)}}$	
6			Temp (°C)/Time (h)	**7**	**8**
a		/Benzene	220/12	1	64
a		/Benzene	180/18	2	56
a		/Benzene	150/20	<1	<1
a		/Phenetole	220/10	3	69
a		/Phenetole	170/18	3	51
a		/Hexane	220/12	1	3
a		/Cyclohexane	220/12	3	5
a		/CCl_4	220/10	4	58
a		/Ethanol	220/10	6	40
a		/Triglyme	220/10	4	68
a		/NMP	200/10	—	(90)
b		/NMP	200/10	—	(72)
e		/NMP	200/10	—	(75)
g		/NMP	200/10	—	(81)
a		/DMSO	180/ 1	—	—
a		/Sulfolane	180/ 1	—	—
a	$(NH_4)_2SO_4$	/Phenetole	170/21	11	9
a	NH_4Cl	/Phenetole	170/11	3	17
a	$ZnCl_2$	/Phenetole	170/11	—	—
a	AcOAg	/Phenetole	170/15	—	—
a	WO_3	/Phenetole	170/11	1	54
a	Al_2O_3	/Phenetole	170/21	69	14
a	CaO	/Phenetole	170/21	76	1
a	MgO	/Phenetole	170/ 8	32	5
a	K_2CO_3	/Phenetole	170/17	71	—
a	NaOH	/Phenetole	170/14	79	—
a	i-Pr_2NH	/Phenetole	170/14	(87)	8
g	i-Pr_2NH	/Phenetole	170/14	(73)	
a	DBU$^{\text{c)}}$	/Phenetole	170/14	78	—
a	DBP$^{\text{d)}}$	/Benzene	220/12	2	60
l	Hydroquinone	/Benzene	220/12	—	21
l	i-Pr_2NH	/Benzene	220/12	—	58

a) Six molar amounts of additive to the substrate were employed, except 3% of DBP were used. b) Yields on GLC and the figures in parentheses are isolated ones; the absence of a figure shows that the compound was not observed. c) 1,8-Diazabicyclo[5.4.0]undec-7-ene. d) 2,5-Di-*t*-butyl-*p*-hydroquinone.

tor either, but merely led to the total decomposition to an unidentified mixture.

From the reaction mechanism, Lewis bases would be expected to affect the rearrangement involving the HCl elimination. Calcium oxide directed the ring opening toward the 1,2-bond cleavege in the thermolysis of **6a** (its optimal molar ratio to the substrate was six). Other Lewis bases proved to exert similar effects. Among the bases studied, diisopropylamine guided this reaction path most effectively, as seen in the selective formation of **7a** in 87.5% yield. 2-Chloro-1,3-diphenylpyrrole **7g** was obtained also in high yield of 73% from **6g**. We assume for the base-guided rearrangement that the nitrogen atom of the imino group, electron-donated by the catalytic base, attacks the most electron-deficient dichloromethylium carbon of **10** with 1,2-bond scission of the cyclopropane ring (Scheme 3).

The rearrangement triggered by the halide ion dissociation was facilitated for (dibromocyclopropyl)methyleneamines. The decay of **6j**/**6k** set out at far lower temperature than the dichloro analogues, and disappeared in refluxing xylene (ca. 140 °C) within 8 h. But in these cases we could find neither 3-bromo-4-phenylpyrrole derivatives **8j**/**8k** nor the 2-bromo isomers **7j**/**7k**, merely isolated debrominated pyrroles **9j**/**9k** in very low yields. Certainly **9j**/**9k** are the disproportionation products of once formed **8j**/**8k**. The thermolysis of **6j**/**6k** proceeded faster in polar solvents, but the pyrrole production was not improved. Also, addition of diisopropylamine afforded a mass of tarry substances.

Thermolysis of *N*-(1-methyl-1-phenylethyl)-(2,2-difluoro-1-phenylcyclopropyl)methyleneamine **6l** took place at lower temperatures (a benzene solution in an ampoule at 180 °C) than that for dichloro analogue **6a**, and afforded specifically the formation of 3-fluoropyrrole derivative **8l** in 65% yield. Thermolysis of the Schiff bases with *N*-*t*-butyl-, and *N*-aryl group **6m**, **6p**, **6q** also proceeded smoothly, and the corresponding *N*-*t*-butyl-, and *N*-aryl-3-fluoro-4-phenylpyrroles (**8m**, **8p**, **8q**) were isolated in good to modest yields. In no case was the

Table 3. ^{1}H NMR Data of the Pyrroles[a]

Compd	δ (ppm) $J_{\mathrm{H-H}}/J_{\mathrm{H-F}}$ (Hz)				
	H-2	H-3[b] or H-4[c]	H-5	Others	
7a		6.42 (d,2.2)	7.29 (d,2.2)	1.98	(6H,s)
				7.0—7.4	(8H,m)
				7.5	(2H,m)
7f		6.51 (d,1.3)	7.05 (d,1.3)	7.1—7.6	(10H,m)
8a	6.76 (d,2.7)		6.84 (d,2.7)	1.85	(6H,s)
				7.1—7.4	(8H,m)
				7.6	(2H,m)
8b	6.65 (d,2.9)		6.32 (d,2.9)	1.82	(6H,s)
				2.03	(3H,s)
				7.0—7.1	(2H,m)
				7.2—7.4	(3H,m)
8c			6.86 (s)	1.66	(6H,s)
				2.14	(3H,s)
				6.6—6.7	(2H,m)
				6.9—7.3	(8H,m)
8d			7.11 (s)	1.76	(3H,s)
				1.90	(6H,s)
				7.1—7.5	(8H,m)
				7.6—7.7	(2H,m)
8e	6.90 (d,2.9)		6.84 (d,2.9)	1.53	(9H,s)
				7.2—7.4	(3H,m)
				7.6	(2H,m)
8f			6.65 (s)	1.36	(9H,s)
				2.07	(3H,s)
				7.2—7.5	(5H,m)
8g	7.12 (d,2.6)		7.15 (d,2.6)	7.1—7.6	(10H,m)
8h	6.94 (d,3.0)		6.87 (d,3.0)	1.75	(6H,m)
				2.0	(6H,m)
				2.2	(3H,m)
8l	6.82 (dd,3.0/$J_{\mathrm{H-F}}$ 4.5)		6.5 (dd,3.0/$J_{\mathrm{H-F}}$ 3.5)	1.85	(6H,s)
				7.08	(2H,dd,8.1/1.5)
				7.2—7.4	(6H,m)
				7.56	(2H,d,7.2)
8m	6.82 (dd,2.9/$J_{\mathrm{H-F}}$ 4.4)		6.63 (dd,2.9/$J_{\mathrm{H-F}}$ 3.0)	1.51	(9H,s)
				7.17	(1H,tt,7.3/1.2)
				7.33	(2H,m)
				7.56	(2H,d,7.8)
8n	6.73 (dd,2.8/$J_{\mathrm{H-F}}$ 4.4)		6.52 (dd,2.8/$J_{\mathrm{H-F}}$ 2.9)	1.0—2.5	(10H,m)
				3.67	(1H,m)
				7.16	(1H,tt,7.3/1.1)
				7.33	(2H,m)
				7.54	(2H,m)

formation of 2-fluoropyrroles found.

The simple reaction initiation of (difluorocyclopropyl)methyleneamines, despite the fact that the heterolysis barrier of C–F (1070 $\mathrm{kJ\,mol^{-1}}$) is greater than that of C–Cl (949 $\mathrm{kJ\,mol^{-1}}$),[7] and the selective 1,3-bond cleavage of the cyclopropane ring, indicate that the rearrangement proceeds differently from the ionic mechanism for the other dihalocyclopropyl analogues. The reaction is provoked by a homolytic cleavage of the 1,3-bond weakened, owing to the 2,2-geminal fluorine atoms.[8,9] The resultant biradical **13** cyclizes to the 2-pyrroline, then is aromatized to the pyrrole by HF elimination (Scheme 3). A marked decrease in the yield of **8l** in the presence of hydrochinone agrees with the radical mechanism (Table 2). The facile rupture of the 1,3-bond of the cyclopropane ring accounts well for the smooth production of *N*-cyclohexyl- and *N*-butylpyrroles **8n**/**8r** from **6n**/**6r**, which should be contrasted with the formation of a complex product mixture in the pyrolysis of dichlorocyclopropylmethyleneamines of mono- or dialkylamines.[2] The specific bond wekening of difluorocyclopropane ring also accords with this argument that *N*-(*p*-methoxybenzyl)-(2,2-difluoro-1-phenylcyclopropyl)methyleneamine **6o** decayed preferably to 1-(*p*-methoxybenzyl)-3-fluoropyrrole **8o** to the competing path to 2-(*p*-methoxyphenyl)-5-phenylpyridine. In the case of *N*-benzyl-(2,2-dichloro-1-phenylcyclopropyl)methyleneamine, the formation of 2,5-diphenylpyridine via

Table 3. (Continued)

Compd	δ (ppm) $J_{\mathrm{H-H}}/J_{\mathrm{H-F}}$ (Hz)				
	H-2	H-3[b)] or H-4[c)]	H-5	Others	
8o	6.68 (dd,2.9/$J_{\mathrm{H-F}}$ 4.4)		6.46 (dd,2.9/$J_{\mathrm{H-F}}$ 2.9)	3.79	(3H,s)
				4.89	(2H,s)
				6.86	(2H,d,8.8)
				7.12	(2H,d,8.8)
				7.15—7.4	(3H,m)
				7.53	(2H,d,7.7)
8p	7.12 (dd,3.0/$J_{\mathrm{H-F}}$ 4.8)		6.94 (dd,3.0/$J_{\mathrm{H-F}}$ 3.0)	7.2—7.5	(8H,m)
				7.62	(2H,d,7.8)
8q	7.02 (dd,2.9/$J_{\mathrm{H-F}}$ 4.5)		6.87 (dd,2.9/$J_{\mathrm{H-F}}$ 2.9)	7.2—7.6	(7H,m)
				7.66	(2H,d,7.7)
				7.8—8.0	(3H,m)
8r	6.66 (dd,2.9/$J_{\mathrm{H-F}}$ 4.3)		6.47 (dd,2.9/$J_{\mathrm{H-F}}$ 3.0)	0.94	(3H,t,7.3)
				1.30	(2H,qt,7.5/7.3)
				1.73	(2H,tt,7.5/7.1)
				3.78	(2H,t,7.1)
				7.17	(1H,tt,7.4/1.1)
				7.33	(2H,m)
				7.53	(2H,d,7.6)
9h	7.17 (dd,2.6/1.7)	6.46 (dd,2.6/1.7)	6.89 (dd,2.6/2.6)	1.76	(6H,m)
				2.12	(6H,m)
				2.22	(3H,m)
9j	7.1 (overlaid)	6.45 (dd,2.9/1.8)	6.80 (dd,2.9/2.0)	1.89	(6H,s)
				7.1—7.2	(4H,m)
				7.2—7.4	(5H,m)
				7.51	(2H,m)
9k	7.4 (overlaid)	6.65 (dd,2.9/1.8)	7.11 (dd,2.9/2.2)	7.15—7.65	(10H,m)

a) In CDCl$_3$, TMS as the internal reference; the numbering of the pyrrole ring for the NMR data, see below.
b) Compounds **7**. c) Compounds **9**.

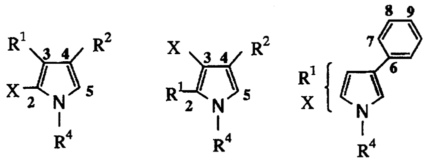


Fig. 1

the benzylic hydrogen shift was exclusively observed.[2)] The selective ring cleavage of **6l** was not diminished by added Lewis bases, either.

This work showed that the rearrangement mode of (dihalocyclopropyl)methyleneamines depends on the nature of the halogen atoms on the cyclopropane ring and the reaction medium as well as on the additives. The titled rearragement may furnish a unique method for direct preparation of 2- or 3-halo-4-phenylpyrrole derivatives, especially in connection with the current medicinal and pesticidal interest in antibiotic pyrrolnitrin and its analogues.[10)] The present thermolysis route will be a reliable choice for 3-fluoropyrroles which could not be efficiently prepared so far.[11)]

Experimental

All melting points are uncorrected. The infrared spectra were recorded on a JASCO A-100 spectrometer. The ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a JEOL JNM-GX270 spectrometer. Mass spectra and high-resolution millimass spectra were obtained at 70 eV using a Shimadzu GCMS 9020-DF.

The starting 2,2-dihalocyclopropane-1-carbaldehydes or the ketones were prepared as described previously,[2)] except for the following two. 1 mmHg=133.322 Pa.

2,2-Dichloro-3-methyl-1-phenylcyclopropane-1-carbaldehyde: To an ice-cooled stirred solution of 2,2-dichloro-3-methyl-1-phenylcyclopropane-1-carbonitrile (7.50 g, 33 mmol) in dry benzene (70 ml) was added dropwise diisobutylaluminium hydride (825 ml of 25% toluene solution) in a gentle stream of nitrogen gas. The mixture was stirred for 24 h at this temperature, and then for 5 h at 35 °C. The cooled mixture, treated with methanol (20 ml), was poured into a saturated ammonium chloride solution (150 ml) and stirred for 20 min. Cold sulfuric acid (10%, 40ml) was added and the separated aqueous layer was extracted with ether (3×30 ml). The combined organic layer was washed with saturated sodium hydrogencarbonate (15 ml), brine, dried (Na$_2$SO$_4$), and concentrated. The residual liquid was distilled at 118—119 °C/0.1 mmHg to afford 4.5 g (60% yield) of the aldehyde as a pale yellow oil. A few center-cut drops in the distillation were used for analysis. IR (neat) 1720 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.68 (3H, d, J=7.0

Table 4. ^{13}C NMR and ^{19}F NMR Data of the Pyrroles[a)]

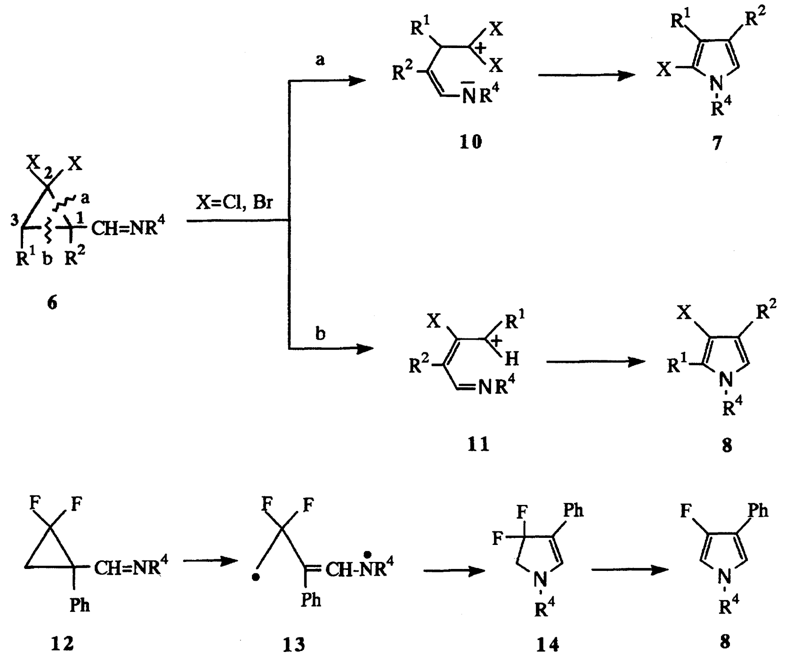
Compds	δ_C (J_{C-F}) and δ_F								
	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	Others
7a	117.3	107.6	122.8	115.2	135.1	124.9	128.7	125.8	30.7, 62.0, 124.8 126.8, 128.5, 146.7
7f	117.2	106.6	125.1	118.2	134.5	124.9	128.3	126.1	126.0, 128.7, 129.1, 138.4
8a	118.0	109.7	121.9	117.3	134.1	127.3	128.6	126.1	30.3, 61.1, 125.1 127.4, 128.3, 146.7
8b	116.9	112.0	116.6	116.2					9.7, 30.3, 60.7, 125.1, 127.2, 128.6, 147.4
8c	130.0	114.3	116.2	116.3	133.1	127.4	132.1	126.9	10.0, 31.3, 61.6, 125.1, 127.6, 128.3, 148.4
8d	126.7	113.2	119.9	115.2	134.2	127.4	128.4	127.1	12.1, 30.8, 61.5, 125.0, 125.9, 128.7, 147.0
8e	116.5	109.5	121.7	115.7	134.2	127.4	128.3	126.0	30.4, 55.6
8f	115.5	114.5	116.3	129.5	134.8	127.9	132.5	128.2	9.8, 31.7, 57.7
8g	118.0	113.1	121.7	117.1	133.5	127.8	129.8	126.7	120.3, 126.4, 128.5, 140.1
8h	115.5	109.1	121.3	114.6	134.4	128.3	128.3	125.9	30.0, 36.1, 43.6 55.9
8l	104.4 (20.3)	147.2 (295.6)	111.4 (10.3)	113.5 (4.4)	133.2 (3.2)	125.7 (3.4)	128.5	125.6	30.1, 60.9, 125.0 127.2, 128.6, 151.3
8m	102.7 (28.5)	149.3 (242.1)	111.0 (10.3)	111.8 (3.9)	133.4 (3.3)	125.7 (3.3)	128.6 (1.3)	125.9	30.3, 55.3
8n	103.3 (28.4)	149.1 (242.7)	111.0 (10.3)	112.9 (4.2)	133.4 (3.3)	125.7 (3.3)	128.6	125.4	25.4, 25.6, 34.4 59.4
8o	105.7 (28.1)	149.6 (243.2)	112.0 (10.2)	115.4 (4.4)	133.1 (3.3)	125.0 (2.6)	128.6	125.8	53.7, 55.3, 114.3 128.8, 129.0, 159.4
8p	104.3 (29.4)	150.1 (245.6)	114.6 (10.7)	113.3 (3.4)	132.4 (3.3)	126.1 (3.3)	126.2	126.0	119.9, 128.7, 129.7, 140.2
8q	108.2 (28.5)	150.3 (244.6)	113.4 (11.0)	117.4 (3.3)	132.6 (3.3)	126.0 (3.3)	128.7	125.3	122.9, 123.4, 126.7, 127.2, 128.2, 128.3, 129.5, 134.3, 137.6, 157.5
8r	105.1 (28.1)	149.3 (242.5)	111.3 (10.0)	115.0 (4.3)	133.2 (3.3)	125.7 (3.5)	128.5	125.5	13.6, 19.8, 33.2, 50.2
9h	117.6	105.4	123.8	113.6	136.3	124.9	128.5	125.0	29.7, 36.2, 43.9, 55.2
9j	120.4	106.0	124.4	116.2	136.1	125.1	128.6	125.2	30.5, 60.6, 124.4, 125.0, 125.2, 147.8
9k	108.9	108.8	127.8	115.9	135.5	125.3	129.7	125.8	120.5, 128.7, 129.8, 140.2

δ_F: **8k** (−170.0), **8l** (−167.8), **8m**(−149.1) **8n** (−166.9), **8o** (−165.4), **8p** (−167.3), and **8q** (−167.4).

a) δ (ppm); J_{C-F} (Hz); in $CDCl_3$; TMS (0.0 ppm) and *p*-bromofluorobenzene (−115.5 ppm) as the internal references for ^{13}C NMR and ^{19}F NMR, respectively; the numbering of the pyrrole ring is the same as in Table 1.

Hz), 2.48 (1H, qd, J=7.0 and 0.7 Hz), 7.4—7.5 (5H, m), 9.68 (1H, d, J=0.7 Hz); MS m/z: 228 (M^+, 3%), 163 (29%), 128 (34%), 105 (100%). HRMS: Calcd for $C_{11}H_{10}OCl_2$: M^+, 228.010. Found: m/z 228.011.

2, 2-Dichloro-3-methyl-1-phenylcyclopropane-1-carbonitrile: To and ice-cooled solution of (E)-2-phenyl-



Scheme 3. Isomerization pathways of compounds **6** and **12**.

2-butenenitrile[12] (20.0 g, 0.14 mol) and benzyltriethylammonium chloride (ca. 2g) in chloroform (130 ml) was added dropwise 50% aqueous solution of sodium hydroxide (100 g). The mixture was stirred at ambient temperature for 15 h, poured into ice-water (300 ml), and then extracted with hexane (2×150 ml). The organic phase was washed with water, dried (Na_2SO_4), and concentrated. The residual liquid was distilled: 10.4 g (33%) of the nitrile as a pale yellow oil; bp 118—120 °C/0.1 mmHg; IR (film) 2210 cm^{-1}; ^1HNMR ($CDCl_3$) δ=1.63 (3H, d, J=6.4 Hz), 2.48 (1H, q, J=6.4 Hz), 7.4 (5H, br. s); MS m/z 225 (M^+, 7%), 190 (30%), 154 (100%). Found: C, 58.70; H, 4.28; N, 6.30%. Calcd for $C_{11}H_9NCl_2$: C, 58.43; H, 4.01; N, 6.20%.

1-Acetyl-2,2-dichloro-1-phenylcyclopropane: A solution of methylmagnesium bromide (40 ml of 1 M solution in THF 1 M=1 mol dm^{-3}) was added dropwise in a course of 1 h to a solution of 2,2-dichloro-1-phenylcyclopropane-1-carbonyl chloride (7.44 g, 30 mmol) in ether (40 ml), while keeping the reaction temperature below −10 °C. After being stirred for an additional 30 min, the resultant solution was gradually warmed to 0 °C and then hydrolyzed by adding dilute hydrochloric acid (100 ml). The organic layer was separated and the aqueous layer was extracted with ether (2×50 ml). The organic portions were combined, washed with a saturated sodium carbonate solution (80 ml), then with water, and dried (Na_2SO_4). The solvent was evaporated and the residue was distilled at 148—149 °C/18 mmHg, yielding 2.30 g (33%) as a viscous liquid. IR (neat) 1715 cm^{-1}; ^1HNMR ($CDCl_3$) δ=2.24 (3H, s), 2.67 (1H, d, J=6.7 Hz), 2.84 (1H, d, J=6.7 Hz), 7.3—7.6 (5H, m); MS m/z 229 (M^+, 2%), 129 (23%), 115 (21%), 45 (100%). HRMS: Calcd for $C_{11}H_{10}Cl_2O$: M^+, 228.010. Found: m/z 228.010.

2,2-Dichloro-1-phenylcyclopropane-1-carbonyl Chloride: A suspension of 2,2-dichlorocyclopropane-1-phenyl-1-carboxylic acid (23.0 g, 0.1 mol) in toluene (200 ml) was treated with thionyl chloride (40 ml). After being stirred for 2 h at room temperature the mixture was heated under reflux until the evolution of gas ceased (ca. 6h). The solvent was evaporated and the residue was distilled at 140—150 °C at 20 mmHg. This yielded 18.3 g (79%) of a colorless liquid, which was used for the reactions. IR (neat) 1765 cm^{-1}; ^1HNMR ($CDCl_3$) δ=1.47 (1H, d, J=2.9 Hz), 1.93 (1H, d, J=2.9 Hz), 7.33 (5H, br. s).

General Preparation Procedure for Schiff Bases. A mixture of aldehyde (10 mmol) and amine (11 mmol) in dry benzene (30 ml) in the presence of anhydrous sodium sulfate (3 g) was stirred at room temperature until the carbonyl absorption of the aldehyde disappeared from the IR spectrum (ca. 12 h). After filtration, followed by evaporation of benzene at 40—50 °C (bath temp), fresh benzene (15 ml) was added to the residue and the benzene was then evaporated off. The procedure for this azeotropic dehydration was repeated twice more. The residue was diluted with dry benzene. Anhydrous calcium chloride (3 g) was added and the mixture was stirred at room temperature for 10 h. After filtration, the solvent was evaporated off and the residure was used for the thermolysis without further purification.

Typical Procedures for Thermolysis: (A) Argon was introduced to a solution of Schiff base (4 mmol) in an appropriate solvent (See Tables 1 and 2, 70 ml) in an ampoule. The sealed ampoule was heated to the given temperature in a silicone bath. The cooled reaction mixture was diluted with benzene and filtered through Celite with suction. The filtrate was washed successively with 5% aq sodium hydroxide, 5% hydrochloric acid and brine, and was dried over anhydrous sodium sulfate. The benzene solution was eluated on a short column containing silica gel (10 g) with benzene to remove tarry materials. The product ratio was determined on GLC (OV-1, 5%; 2 m glass column). The yields in Table 2 were calculated by calibration. Isolation of the products was carried out using a 1 m column [ϕ (15 mm; silica gel (80 g)] by elution first with hexane and then with mixtures of hexane–benzene (the ratio of benzene to hexane was increased gradually). The eluated product was washed with chilled hexane. The isolated yields in Tables 1 and 2 were determined when practically no other peaks were seen on GLC. An analytical sample was prepared by sublimation, distillation or recrystallization.

(B) Thermolysis with an Additive: A stirred solution of the Schiff base in phenetole was heated together with the additive at the reflux temperature under a gentle stream of argon for the period given in Table 1. The reaction mixture was diluted with benzene and filtered through Celite with suction. The filtrate was worked up as described in Typical Procedure (**A**) above.

(C) Thermolysis in NMP: After the thermolysis as described in Typical Procedure (**B**), most of the NMP was distilled off under reduced pressure through a Vigreux column. The residue was dissolved in benzene and was then worked up according to the procedure in Procedure (**A**).

(D) Thermolysis of 6h: A solution of 2,2-dichloro-1-phenylcyclopropane-1-carbaldehyde (2.14 g, 10 mmol) and 1-aminoadamantane (1.51 g, 10 mmol) in 1,3-dimethylimidazolidinone (40 ml) was warmed gradually to 100 °C (ca. 30 min). It was maintained at this temperature for an additional one hour, then heated at 200 °C for 12 h. The isolation work-up followed the procedures in Procedure (**C**). The NMR data of the products are listed in Tables 3 and 4.

2-Chloro-1-(1-methyl-1-phenylethyl)-4-phenylpyrrole (7a): Mp 102—103 °C. MS *m*/*z* 295 (M^+, 11%), 179 (33%), 177 (100%), 119 (92%). Found: C, 77.01; H, 6.05; N, 4.90%. Calcd for $C_{19}H_{18}ClN$: C, 77.15; H, 6.13; N, 4.74%.

2-Chloro-1,4-diphenylpyrrole (7g): Mp 73—75 °C (Lit,[13] 77—78 °C); decomposed gradually to black tarry material on standing in the atmosphere. MS (20 eV) *m*/*z* 253 (M^+, 100%), 217 (24%). HRMS: Calcd for $C_{16}H_{12}ClN$: M^+, 253.066. Found: *m*/*z* 253.066.

3-Chloro-1-(1-methyl-1-phenylethyl)-4-phenylpyrrole (8a): Bp 98—100 °C/0.01 mmHg. MS *m*/*z* 295 (M^+, 2%), 177 (71%), 119 (100%). Found: C, 77.45; H, 6.29; N, 4.60%. Calcd for $C_{19}H_{18}ClN$: C, 77.15; H, 6.13; N, 4.74%.

3-Chloro-1-(1-methyl-1-phenylethyl)-4-methylpyrrole (8b): Bp 78—80 °C/0.02 mmHg. MS *m*/*z* 233 (M^+, 66%), 119 (100%). HRMS: Calcd for $C_{14}H_{16}ClN$: M^+, 233.097. Found: *m*/*z* 233.099.

3-Chloro-1-(1-methyl-1-phenylethyl)-4-methyl-2-phenylpyrrole (8c): Mp 141—142 °C. MS *m*/*z* 309 (M^+, 8%), 191 (100%), 119 (98%). Found: C, 77.58; H, 6.48; N, 4.53%. Calcd for $C_{20}H_{20}ClN$: C, 77.53; H, 6.51; N, 4.52%.

3-Chloro-1-(1-methyl-1-phenylethyl)-2-methyl-4-phenylpyrrole (8d): Mp 106—107 °C. MS *m*/*z* 309 (M^+, 13%), 191 (74%), 177 (28%), 131 (35%), 119 (97%), 91 (100%). Found: C, 77.70; H, 6.80; N, 4.38%. Calcd for $C_{20}H_{20}ClN$: C, 77.53; H, 6.51; N, 4.52%.

1-*t*-Butyl-3-chloro-4-phenylpyrrole (8e): Bp 85—88 °C/0.02 mmHg. MS *m*/*z* 233 (M^+, 34%), 177 (100%), 115 (43%). HRMS: Calcd for $C_{14}H_{16}ClN$: M^+. 233.097. Found: *m*/*z* 233.097.

1-*t*-Butyl-3-chloro-4-methyl-2-phenylpyrrole (8f): Bp 115—118 °C/0.01 mmHg. MS *m*/*z* 247 (M^+, 32%), 191 (100%). HRMS: Calcd for $C_{15}H_{18}ClN$: M^+, 247.113. Found: *m*/*z* 247.114.

3-Chloro-1,4-diphenylpyrrole (8g): Mp 81—82 °C. MS *m*/*z* 253 (M^+, 100%), 219 (42%). Found: C, 75.79; H, 4.63; N, 5.54%. Calcd for $C_{16}H_{12}ClN$: C, 77.74; H, 4.77; N, 5.52%.

1-(1-Adamantyl)-3-chloro-4-phenylpyrrole (8h): Mp 100°C. MS *m*/*z* 311 (M^+, 40%), 135 (100%). Found: C, 77.13; H, 7.40; N, 4.51%. Calcd for $C_{20}H_{22}ClN$: C, 77.03 H, 7.11; N, 4.49%.

1-(1-Methyl-1-phenylethyl)-3-fluoro-4-phenylpyrrole (8l): Mp 87 °C. MS *m*/*z* 279 (M^+, 42%), 161 (100%), 133 (20%), 119 (74%). Found: C, 81.68; H, 6.52; N, 5.00%. Calcd for $C_{19}H_{18}$ FN: C, 81.69; H, 6.49; N, 5.02%.

1-*t*-Butyl-3-fluoro-4-phenylpyrrole (8m): Bp 100—110 °C/1.4 mmHg. MS *m*/*z* 217 (M^+, 35%), 177 (21%), 161 (100%), 133 (28%). HRMS: Calcd for $C_{14}H_{16}FN$: M^+, 217.127. Found: *m*/*z* 217.127.

1-Cyclohexyl-3-fluoro-4-phenylpyrrole (8n): Bp 105—108 °C/0.9 mmHg. MS *m*/*z* 243 (M^+, 87%), 161 (100%), 133 (41%). HRMS: Calcd for $C_{16}H_{18}FN$: M^+, 243.142. Found: *m*/*z* 243.142.

3-Fluoro-1-(4-methoxybenzyl)-4-phenylpyrrole (8o): Mp 60 °C MS *m*/*z* 281 (M^+, 16%), 135 (10%), 121 (100%). Found: C, 76.59; H, 5.74; N, 5.70%. Calcd for $C_{18}H_{16}FNO$: C, 76.84; H, 5.73; N, 5.69%.

3-Fluoro-1,4-diphenylpyrrole (8p): Mp 111 °C. MS *m*/*z* 237 (M^+, 100%), 209 (12%), 133 (46%). Found: C, 80.91; H, 5.05; N, 6.01%. Calcd for $C_{16}H_{12}FN$: C, 80.99; H, 5.10; N, 5.90%.

3-Fluoro-1-(1-naphthyl)-3-phenylpyrrole (8q): Mp 79 °C. MS *m*/*z* 287 (M^+, 100%), 266 (9%), 133 (24%). Found: C, 83.58; H, 4.96; N, 4.90%. Calcd for $C_{20}H_{14}FN$: C, 83.60; H, 4.91; N, 4.88%.

1-Butyl-3-fluoro-4-phenylpyrrole (8r): Bp 97—100 °C/1.5 mmHg. MS *m*/*z* 217 (M^+, 74%), 175 (100%), 174 (98%), 161 (14%), 147 (15%), 146 (15%), 133 (36%). HRMS: Calcd for $C_{14}H_{16}FN$: M^+, 217.127. Found: *m*/*z* 216.126.

1-(1-Adamantyl)-3-phenylpyrrole (9h): Mp 128—130 °C. MS *m*/*z* 277 (M^+, 65%), 143 (11%), 142 (10%), 135 (100%), 115 (31%). HRMS: Calcd for $C_{20}H_{23}N$: M^+, 276.175. Found: *m*/*z* 276.173.

1-(1-methyl-1-phenylethyl)-3-phenylpyrrole (9j): Mp 104 °C. MS *m*/*z* 261 (M^+, 22%), 143 (100%). Found: C, 87.56; H, 7.25; N, 5.33%. Calcd for $C_{19}H_{19}N$: C, 87.36; H, 7.28; N, 5.36%.

1,3-Diphenylpyrrole (9k): Mp 118—119 °C. MS *m*/*z* 219 (M^+, 100%), 191 (11%), 115 (46%). Found: C, 87.56: H, 5.80; N, 6.50%. Calcd for $C_{16}H_{13}N$: C, 87.63; H, 5.98; N, 6.39%.

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