Journal of Organometallic Chemistry, 423 (1992) 173–182
Elsevier Sequoia S.A., Lausanne
JOM 22183

Pyrrolyl compounds of main group elements. Synthesis of group 14 5-metallated pyrrole-2-carbaldehydes

Franck Denat, Hafida Gaspard-Iloughmane and Jacques Dubac *

Laboratoire des Organométalliques (U.R.A.–C.N.R.S. 477), Université Paul-Sabatier, 118 route de Narbonne, 31062 Toulouse Cédex (France)

(Received March 22, 1991)

Abstract

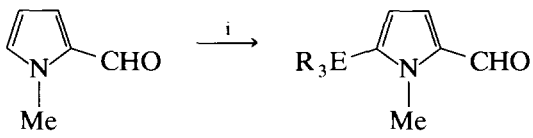
New group 14 5-metallated pyrrole-2-carbaldehydes 5-$R_3E(C_4H_2NR')CHO$ (E = Si, Ge, Sn; R = Me, Et, ^nBu; R′ = H, Me) have been regiospecifically prepared from corresponding pyrrole-2-carbaldehydes by either (i) 5-lithiation after protection of the aldehyde function by treatment with lithium *N*-methylpiperazide or by formation of an azafulvene dimer or (ii) metallation by R_3EX (X = Cl, Br). The 5-silylated compound (E = Si, R = R′ = Me) has been also obtained from 1-methyl-2,5-bis(trimethylsilyl)pyrrole.

Introduction

Pyrrole derivatives C-metallated by a group 14 element are known for silicon [1–10] and tin [4,11,12]. They show metallotropy [2,5,6,8,9] and the carbon–heteroatom bond is readily cleaved by electrophilic reagents [4,12], especially acids [9]. Some *N*-silylated pyrrolyl compounds have been used as intermediates in the synthesis of 3-substituted pyrrole derivatives [13].

Among the pyrrole derivatives, the importance of 5-substituted pyrrole-2-carbaldehydes as synthetic intermediates, in particular in the field of biomolecules, has been emphasized [14]. In the light of earlier studies of the synthesis of 5-silicon substituted furfurals [15] and thiophenecarbaldehydes [16], we thought it likely that the aldehyde function in pyrrolecarbaldehydes might be protected as an acetal [17] or imidazolidine derivative [18]. Moreover these species are less readily lithiated than the corresponding furans or thiophenes [18], and the regeneration of the aldehyde function in the case of acetals requires an acidic medium, which would be inappropriate for the synthesis of the group 14 metallated pyrrole carbaldehydes.

We decided to try lithiation of aromatic or heterocyclic aldehydes directed by α-amino alkoxides [19] for the synthesis of the group 14 metallated *N*-alkylated pyrrole carbaldehydes, for example the *N*-methylated compound (**1**). We chose lithium *N*-methylpiperazide (LNMP) to convert the aldehyde function into the



(1)

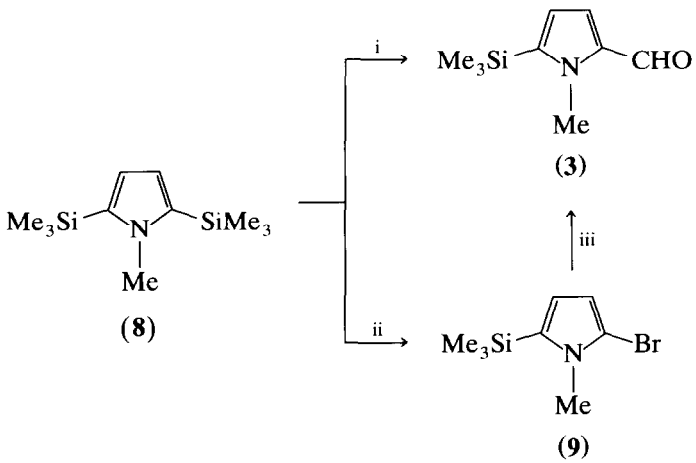
E = Si, R = Me (**3**)
E = Ge, R = Me (**4**), Et (**5**)
E = Sn, R = Me (**6**), ^{n}Bu (**7**)

Scheme 1. i: 1) LNMP; 2) ^{n}BuLi/TMEDA; 3) R_3EX *; 4) H_2O; *: $R_3EX = Me_3SiCl$, Me_3GeCl, Et_3GeBr, Me_3SnCl or $^nBu_3SnCl$.

protected α-amino alkoxide (Pyr-CH(NMP)OLi) [19]; the lithiation was carried out with the n-butyllithium in the presence of TMEDA in hexane at room temperature. Treatment of the relevant halo-silane, -germane, or -stannane R_3EX followed by hydrolysis, gave derivatives **3–7** in good yields (Method A, depicted in Scheme 1). The mild conditions required for the hydrolysis allow regeneration of the aldehyde group without loss of the ER_3H group from the 5 position of the pyrrolyl ring. The thermally stable 5-metallated 1-methylpyrrole-2-carbaldehydes obtained were isolated by distillation under reduced pressure and purified by column chromatography on silica gel.

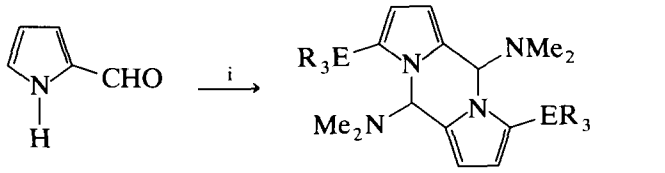
It was shown previously, that the silylation of benzaldehyde carried out under the same conditions [19] gave *ortho*-trimethylsilylbenzaldehyde, and so the heterocyclic aldehyde **1** appeared to undergo lithiation at the 5-position of the pyrrolyl ring [19], we thought it appropriate to confirm this by independent synthesis of the silylated derivative **3**.

Two routes starting from 1-methyl-2,5-bis(trimethylsilyl)pyrrole (**8**) were used (Scheme 2): (a) the Vilsmeier-Haack reaction on **8**, and (b) formylation by dimethylformamide of the 2-bromo-1-methyl-5-trimethylsilylpyrrole (**9**). Yields were



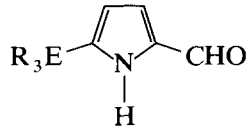
(8) (3) (9)

Scheme 2. i: 1) $POCl_3$/DMF; 2) Na_2CO_3/H_2O; ii: NBS/THF (−70 °C to 0 °C); iii: 1) ^{n}BuLi; 2) DMF.



(2)

E = Si, R = Me (**10**)
E = Ge, R = Me (**11**), Et (**12**)
E = Sn, R = Me (**13**), ^{n}Bu (**14**)



E = Si, R = Me (**15**)
E = Ge, R = Me (**16**), Et (**17**)
E = Sn, R = ^{n}Bu (**18**)

Scheme 3. i: 1) Me_2NH/H_2O; 2) ^{n}BuLi/THF–hexane; 3) Me_3SiCl, Me_3GeCl, Et_3GeBr, Me_3SnCl or $^{n}Bu_3SnCl$; ii: THF/AcONa, H_2O (reflux).

68 and 70% respectively; the 1-methyl-5-trimethylsilylpyrrole-2-carbaldehyde obtained had NMR and IR spectra identical to those of **3** made from **1**.

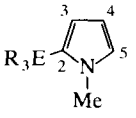
A synthetic equivalent of 2-lithio-5-formylpyrrole has been recently obtained by Muchowski and Hess [14] by the simultaneous blocking of the aldehyde and amine functions of the pyrrole-2-carbaldehyde (**2**); they used the unusual electrophile $^{i}Pr_3SiOSO_2CF_3$, but we found trimethylchlorosilane and other germanium and tin halides satisfactory. We obtained (Method B, depicted in Scheme 3) the C-metallated derivatives **10–14** in excellent yield, but the regeneration of the aldehyde group is more difficult than in method A. The hydrolysis of the C-metallated 6-amino-1-azafulvene dimers **10–14**, which involves actual dissociation into monomers [14], is more difficult than in the case of non-metallated derivatives [14], especially in the case of the tin derivatives **13** and **14**. For these derivatives, the usual conditions used for the hydrolysis (THF/AcONa, H_2O) led, after 5 days of reflux, to a very slight decomposition in the case of **13**, and to 50% decomposition in the case of **14**. In the latter case the resulting aldehyde **18** was isolated.

These C-metallated dimers, as the *cis* or *trans* isomers according to the relative position of dimethylamino substituents, are probably stabilized by a double intramolecular nitrogen–heteroatom ($Me_2N \rightarrow E$) interaction, stronger for tin derivatives **13** and **14** than for silicon or germanium ones (**10–12**). This interaction would reduce the ease of the monomerisation and consequently the hydrolysis.

Addition of potential complexing agent (KF; Et_3N; pyridine; TMEDA; DABCO) to the reaction medium does not change the rate of the hydrolysis of the derivatives **10** and **14**.

Table 1

R_3E substituent chemical shift effects on pyrrole ring hydrogens and ring carbons in 2-trialkylsilyl (germyl or stannyl)-1-methylpyrroles **20–23** [a]



(2, 3, 4, 5 = α, β, β', α')

R_3E = Me_3Si (**20**), Me_3Ge (**21**), Et_3Ge (**22**), Me_3Sn (**23**)

Compound	H(β)	H(β')	H(α')	C(α)	C(β)	C(β')	C(α')
20	0.31	0.10	0.28	11.5	11.5	0.3	5.9
21	0.28	0.17	0.33	12.4	8.9	0.3	4.8
22	0.23	0.15	0.30	9.9	10.2	0.3	4.8
23	0.28	0.20	0.38	11.6	11.1	0.9	4.9

[a] Solvent $CDCl_3$; SCS in ppm (a positive sign denoting a downfield shift). Reference: 1-methylpyrrole (solvent $CDCl_3$): δ H(α) = 6.51, δ H(β) = 6.06 [23], δ C(α) = 121.1, δ C(β) = 107.8 ppm [24].

NMR data

Pentacoordination of silicon [20] and tin [21] can give rise to an upfield shift of the ^{29}Si or ^{119}Sn resonance, relative to that for the corresponding species in which the heteroatom is tetracoordinated. It was shown previously in the case of the nitrogen–silicon interaction [20] that the strength of such interaction, and consequently extent of the upfield shift of the ^{29}Si resonance, depended on the substituents on silicon, and was relatively weak in the case of the trimethyl derivatives. We could not compare the compounds **10**, **13** and **14** with the corresponding species containing tetracoordinated silicon or tin bearing the same groups, we observed an upfield shift of ^{29}Si resonance on going from compound **3** ($\delta = -10.9$ ppm) to **10** ($\delta = -13.5$ ppm), and a larger upfield shift of the ^{119}Sn resonance on going from **6** ($\delta = -48.0$ ppm) to **13** ($\delta = -61.6$ ppm).

Since the ^{29}Si and ^{119}Sn data do not give conclusive evidence for the presence or absence of pentacoordination of silicon and tin in the compounds, an X-ray diffraction study is now being undertaken.

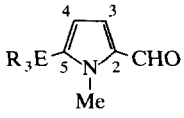
For the assignment of ^1H and ^{13}C resonances of the compounds described, we used the substituent chemical shift (SCS) parameters derived from spectra of 2-trialkyl-silyl, -germyl, and -stannyl derivatives of -1-methylpyrroles (**20–23**) (Table 1). It can be seen from Table 2 that there is a good correlation between the calculated and observed chemical shifts. The largest differences are observed for the carbon $^{13}C(\alpha)$. Examination of the ^1H and ^{13}C 2D spectra of silylated derivative **3** gave the following correlations: 6.87 (^1H)/123.9 (^{13}C) and 6.34 (^1H)/118.9 (^{13}C) (δ in ppm).

Conclusion

Group 14 C-metallated pyrrole-2-carbaldehydes can be readily made from 2-formylpyrroles. In the case of *N*-unsubstituted derivatives carbon–nitrogen metallotropy does not occur, and the C-metallated intermediate azafulvene dimers are probably stabilized by intramolecular nitrogen–heteroatom coordination.

Table 2

Comparison of the observed [a] and calculated [b] ^1H and ^{13}C chemical shifts for ring hydrogens and ring carbons in C-metallated pyrrole-2-carbaldehydes **3–6**



$(2, 3, 4, 5 = \alpha', \beta', \beta, \alpha)$

$R_3E = Me_3Si$ **(3)**, Me_3Ge **(4)**, Et_3Ge **(5)**, Me_3Sn **(6)**

Compound	H(β)	H(β′)	C(α)	C(β)	C(β′)	C(α′)
3	6.34	6.87	145.4	118.9	123.9	135.9
	(6.45)	(6.94)	(142.9)	(120.5)	(123.8)	(137.3)
4	6.26	6.88	147.4	117.1	124.2	135.4
	(6.42)	(7.01)	(143.8)	(117.9)	(123.8)	(136.2)
5	6.27	6.90	145.5	118.4	124.4	135.5
	(6.37)	(6.99)	(141.3)	(119.2)	(123.8)	(136.2)
6	6.27	6.91	148.1	119.2	124.5	135.6
	(6.42)	(7.04)	(143.0)	(120.1)	(124.4)	(136.3)

[a] δ in ppm downfield from TMS; solvent $CDCl_3$. [b] In brackets; chemical shifts are calculated from NMR spectra of 1-methylpyrrolecarboxaldehyde (δ H(β) = 6.14, δ H(β′) = 6.84 [23], δ C(α) = 131.4, δ C(β) = 109.0, δ C(β′) = 123.5, δ C(α′) = 131.4 [24]), and SCS parameters (Table 1).

Experimental section

Reactions involving n-butyllithium were performed by standard syringe/cannula techniques under argon. Tetrahydrofuran was distilled from sodium/benzophenone ketyl before use. Dimethylformamide (DMF), *N,N,N′,N′*-tetramethylenediamine (TMEDA), and *N*-methylpiperazine were dried over CaH_2, distilled prior to use, and stored over 3 Å molecular sieves under nitrogen. 1-Methylpyrrole-2-carbaldehyde and n-butyllithium (1.6 *M* in hexane) were commercially available and used as received, but the concentration of ^{n}BuLi was checked by titration. Pyrrole-2-carbaldehyde was prepared by formylation of pyrrole [22].

^1H and ^{13}C NMR spectra were recorded with solutions in $CDCl_3$ at 80.131 MHz (Bruker AC 80) and 50.323 MHz (Bruker AC 200) respectively.

Melting and boiling points are uncorrected. Column chromatography was carried out on Merck silica gel 60 (230–400 mesh).

Typical procedure for metallation of 1-methylpyrrole-2-carbaldehyde (1). 1-methyl-5-trimethylsilylpyrrole-2-carbaldehyde (3) (Method A)

To a suspension of 20 mmol of lithium *N*-methylpiperazide (LNMP) [19b] in hexane (40 mL), prepared by stirring a mixture of 2 g (20 mmol) of *N*-methylpiperazine and 20 mmol of ^{n}Buli (1.6 *M* in hexane) for 15 min at 0 °C, were added 2 g (18.3 mmol) of 1-methylpyrrole-2-carbaldehyde (**1**). The mixture was stirred for a further 15 min and tetramethylethylenediamine (TMEDA) (4.64 g; 40 mmol) and 40 mmol of ^{n}BuLi (1.6 *M* in hexane) were added (yellow solution). The mixture was stirred for 12 h at room temperature (during which an off-white precipitate separated). 40 mL of anhydrous THF was then added at 0 °C, to give a homogeneous solution, to which a solution of 4.35 g (40 mmol) of trimethylchlorosilane in 20 mL of THF was added dropwise at −40 °C. The mixture was stirred at room

temperature for 4 h and then hydrolysed. After extraction with Et_2O, the extract was dried with Na_2SO_4 and concentrated, and the 1-methyl-5-trimethylsilylpyrrole-2-carbaldehyde (**3**) was separated from volatile products by distillation under reduced pressure (2.3 g; 82% yield based on **1**; yellow liquid, b.p. 78–80 °C/0.4 mmHg) and chromatographed with a 100:5:1 mixture of hexane:Et_2O:Et_3N as eluent. ^{1}H NMR ($CDCl_3$): δ 0.33 (s, SiMe), 4.01 (s, NMe), 6.34 (d, J = 3.9 Hz, H(4)), 6.87 (d, J = 3.9 Hz, H(3)), 9.56 (s, CHO) ^{13}C NMR ($CDCl_3$): δ −0.8 (SiMe), 36.3 (NMe), 118.9 (C(4)), 123.9 (C(3)), 135.9 (C(2)), 145.4 (C(5)), 179.5 (CHO). ^{1}H/^{13}C 2D correlations: 6.87 (^{1}H)/123.9 (^{13}C) and 6.34(^{1}H)/118.9(^{13}C). IR (pure liquid): ν(C=O): 1664 cm^{-1}. Anal. Found: C, 59.7; H, 8.3. $C_9H_{15}NOSi$ calc.: C, 59.62; H, 8.34%. Semi-carbazone, m.p. 204–205 °C.

*1-Methyl-5-trimethylgermylpyrrole-2-carbaldehyde (**4**)*

A similar procedure starting from 1 g (9.15 mmol) of **1** and 3.06 g (20 mmol) of trimethylchlorogermane gave 1.6 g (77%) of **4** as a yellow liquid, b.p. 76–78 °C/0.02 mmHg. ^{1}H NMR ($CDCl_3$): δ 0.45 (s, GeMe), 3.97 (s, NMe), 6.26 (d, J = 3.9 Hz, H(4)), 6.88 (d, J = 3.9 Hz, H(3)), 9.52 (s, CHO). ^{13}C NMR ($CDCl_3$): δ −1.1 (GeMe), 36.3 (NMe), 117.1 (C(4)), 124.2 (C(3)), 135.4 (C(2)), 147.5 (C(5)), 179.1 (CHO). IR (pure liquid): ν(C=O): 1664 cm^{-1}. Anal. Found: C, 47.8; H, 6.8. $C_9H_{15}NOGe$ calc.: C, 47.87; H, 6.70%.

*1-Methyl-5-triethylgermylpyrrole-2-carbaldehyde (**5**)*

A similar procedure starting from 2 g (18.3 mmol) of **1** and 9.38 g (40 mmol) of triethylbromogermane gave 4.0 g (80%) of **5** as a yellow liquid, b.p. 127–129 °C/0.4 mmHg. ^{1}H NMR ($CDCl_3$): δ 1.05 (m, GeEt), 3.96 (s, NMe), 6.27 (d, J = 3.9 Hz, H(4)), 6.90 (d, J = 3.9 Hz, H(3)), 9.51 (s, CHO). ^{13}C NMR ($CDCl_3$): δ 4.9 ($GeCH_2$), 8.9 (Ge–(C)–Me), 36.4 (NMe), 118.4 (C(4)), 124.3 (C(3)), 135.5 (C(2)), 145.5 (C(5)), 178.9 (CHO). IR (pure liquid): ν(C=O): 1664 cm^{-1}. Anal. Found: C, 53.9; H, 7.8. $C_{12}H_{21}NOGe$ calc.: C, 53.20; H, 7.90%. Semi-carbazone: m.p. 184 °C.

*1-Methyl-5-trimethylstannylpyrrole-2-carbaldehyde (**6**)*

A similar procedure starting from 1 g (9.15 mmol) of **1** and 4 g (20 mmol) of trimethyltin chloride gave 1.7 g (68%) of **6** as a yellow liquid, b.p. 111–113 °C/0.3 mmHg. ^{1}H NMR ($CDCl_3$): δ 0.37 (s, SnMe), 3.98 (s, NMe), 6.27 (d, J = 3.9 Hz, H(4)), 6.91 (d, J = 3.9 Hz, H(3)), 9.52 (s, CHO). ^{13}C NMR ($CDCl_3$): δ −8.7 (SnMe), 37.6 (NMe), 119.2 (C(4)), 124.5 (C(3)), 135.6 (C(2)), 148.1 (C(5)), 178.6 (CHO). IR (pure liquid): ν(C=O): 1661 cm^{-1}. Anal. Found: C, 39.9; H, 5.5. $C_9H_{15}NOSn$ calc.: C, 39.75; H, 5.56%.

*1-Methyl-5-tri-n-butylstannylpyrrole-2-carbaldehyde (**7**)*

A similar procedure starting from 2 g (18.3 mmol) of **1** and 13 g (40 mmol) of tri-n-butyltin chloride gave 5.24 g (72%) of **7** as a yellow liquid, b.p. 174–176 °C/0.2 mmHg. ^{1}H NMR ($CDCl_3$): δ 0.88 −1.50 (m, SnBu), 3.96 (s, NMe), 6.26 (d, J = 3.9 Hz, H(4)), 6.92 (d, J = 3.9 Hz), 9.51 (s, CHO). ^{13}C NMR ($CDCl_3$): δ 10.3 ($SnCH_2$), 13.6 (Me), 26.8 and 27.2 ((C)–CH_2–(C)), 37.6 (NMe), 119.7 (C(4)), 124.7 (C(3)), 135.6 (C(2)), 148.6 (C(5)), 178.4 (CHO). Anal. Found: C, 54.4; H, 8.3. $C_{18}H_{33}NOSn$ calc.: C, 54.30; H, 8.35%.

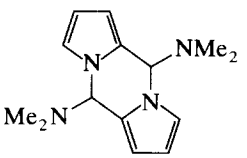
Aldehyde 3 from 1-methyl-2,5-bis(trimethylsilyl)pyrrole (8)

The direct formylation of **8** [6] was carried out as described by Silverstein et al. [22] (solvent CH_2Cl_2; reaction at $-70\,^\circ C$ then at room temperature). The NMR and IR spectra of the main product (isolated in 68% yield by chromatography) were superimposable on those of aldehyde **3** prepared as above.

A solution of **8** (2 g, 8.87 mmol) in 30 mL of THF was cooled in a dry ice–acetone bath and a solution of *N*-bromosuccinimide (1.58 g, 8.87 mmol) in THF (20 mL) was added slowly with stirring. The mixture was stirred at $-25\,^\circ C$ for 3 h and then at $0\,^\circ C$ for 1 h. After hydrolysis, extraction with Et_2O was followed by concentration of the extract and addition of CCl_4. The mixture was filtered and the filtrate evaporated to leave 1.69 g (82%) of 2-bromo-1-methyl-5-trimethylsilylpyrrole (**9**). ^1H NMR ($CDCl_3$): δ 0.32 (s, SiMe), 3.69 (s, NMe), 6.20 (d, $J = 3.6$ Hz, H(3)), 6.37 (d, $J = 3.6$ Hz, H(4)). This crude product was formylated by the standard procedure [13b] involving use of ^{n}BuLi and DMF and aldehyde **3** obtained in 70% yield (based on amount of **8** taken).

Typical procedure for metallation of pyrrole-2-carbaldehyde (2) (Method B)

The C-metallated azafulvene dimers **10–14** were made from the 6-dimethylamino-1-azafulvene dimer (**19**), prepared from **2** and dimethylamine [14].



(19)

In a typical procedure, to a stirred solution of 0.6 g (2.46 mmol) of **19** in 25 mL of anhydrous THF cooled to $-15\,^\circ C$, were added 5.84 mmol of ^{n}BuLi (1.6 *M* in hexane). The mixture was stirred for 15 min at $-15\,^\circ C$ then for 30 min at $0\,^\circ C$ and 1 h at room temperature. The violet solution formed was cooled at $-70\,^\circ C$ and 1.06 g (5.84 mmol) of trimethylchlorosilane were slowly added, and the mixture was stirred for 3 h at room temperature, becoming dark blue then green. Hydrolysis with 0.4 *M* aqueous AcONa was followed by extraction (CH_2Cl_2), drying (Na_2SO_4) and concentration (under reduced pressure) of the residue. Recrystallization from ethyl acetate gave **10** as a brown solid (0.89 g, 93% yield). ^1H NMR ($CDCl_3$): δ 0.25 (s, SiMe), 1.91 and 2.19 (s, 3:1, NMe), 5.83 and 5.86 (d, $J = 0.5$ Hz, 1:3, CHN), 6.11 and 6.18 (dd, $J = 3.5$ and 0.5 Hz, 3:1, H(3)), 6.54 and 6.57 (d, $J = 3.5$ Hz, 3:1, H(4)). The major stereoisomer (75%) has probably the two Me_2N groups in *trans* position. Anal. Found: C, 61.9; H, 9.3. $C_{20}H_{36}N_4Si_2$ calc.: C, 61.79; H, 9.37.

11 (prepared from **19** and Me_3GeCl; 90% yield): brown solid; ^1H NMR ($CDCl_3$): δ 0.38 (s, GeMe), 1.90 and 2.19 (s, 3:1, NMe), 5.82 and 5.84 (d, $J = 0.6$ Hz, 1:3, CHN), 6.12 and 6.20 (dd, $J = 3.5$ and 0.6 Hz, 3:1, H(3)), 6.42 and 6.45 (d, $J = 3.5$ Hz, 3:1, H(4)). Anal. Found: C, 50.2; H, 7.7. $C_{20}H_{36}N_4Ge_2$ calc.: C, 50.28; H, 7.60%.

12 (prepared from **19** and Et_3GeBr; 95% yield): viscous oil; ^1H NMR ($CDCl_3$): δ 1.01 (m, GeEt), 1.84 and 2.13 (s, 5:1, NMe), 5.73 and 5.77 (d, $J = 0.5$ Hz, 1:5, CHN), 6.11 (dd, $J = 3.4$ and 0.5 Hz, H(3)), 6.39 (d, $J = 3.4$ Hz, H(4)). Anal. Found: C, 55.5; H, 8.7. $C_{26}H_{48}N_4Ge_2$ calc.: C, 55.58; H, 8.61%.

13 (prepared from **19** and Me_3SnCl; 88% yield): brown solid; ^1H NMR ($CDCl_3$): δ 0.24 (s, SnMe), 1.96 and 2.26 (s, 9:1, NMe), 5.85 (d, $J = 0.6$ Hz, CHN), 6.19 (dd, $J = 3.4$ and 0.6 Hz, H(3)), 6.46 (d, $J = 3.4$ Hz, H(4)). Anal. Found: C, 42.2; H, 6.4. $C_{20}H_{36}N_4Sn_2$ calc.: C, 42.15; H, 6.37%.

14 (prepared from **19** and n-Bu_3SnCl; 85% yield): viscous oil; ^1H NMR ($CDCl_3$): δ 0.8–1.6 (m, SnBu), 1.91 and 2.18 (s, 6:1, NMe), 5.79 (d, $J = 0.5$ Hz, CHN), 6.16 (dd, $J = 3.4$ and 0.5 Hz, H(3)), 6.42 (d, $J = 3.4$ Hz, H(4)). Anal. Found: C, 55.6; H, 8.8. $C_{38}H_{72}N_4Sn_2$ calc.: C, 55.50; H, 8.83%.

The products **10–14** in THF were hydrolysed as described by Muchowski and Hess [14] with aqueous AcONa under reflux for 15 h for **10**, 35 h for **11** and **12**, and 5 days for **13** and **14**. After extraction with CH_2Cl_2 and evaporation of the extract, the residue was chromatographed with hexane/ethyl acetate/triethylamine (100:15:1) as eluent.

15 (85% yield from **10**): yellow solid, m.p. 64 °C; ^1H NMR ($CDCl_3$): δ 0.30 (s, SiMe), 6.46 (2d, $J = 3.7$ and 2.4 Hz, H(4)), 6.95 (2d, 3.7 and 2.2 Hz, H(3)), 9.52 (s, CHO). ^{13}C NMR ($CDCl_3$): δ −1.3 (SiMe), 119.3 (C(4)), 121.5 (C(3)), 136.2 (C(2)), 141.8 (C(5)), 179.0 (CHO). IR (CCl_4 solution): ν(C=O): 1657; ν(N–H): 3294 and 3450 cm^{-1}. Anal. Found: C, 57.5; H, 7.8. $C_8H_{13}NOSi$ calc.: C, 57.44; H, 7.83%.

16 (76% yield from **11**): yellow solid, m.p. 72 °C; ^1H NMR ($CDCl_3$): δ 0.43 (s, GeMe), 6.40 (2 d, $J = 3.70$ and 2.39 Hz, H(4)), 6.98 (2 d, $J = 3.7$ and 2.2 Hz, H(3)), 9.50 (s, CHO). ^{13}C NMR ($CDCl_3$): δ −1.7 (GeMe), 118.0 (C(4)), 121.6 (C(3)), 135.9 (C(2)), 141.3 (C(5)), 178.6 (CHO). IR (CCl_4 solution): ν(C=O): 1652; ν(N–H): 3286 and 3451 cm^{-1}. Anal. Found: C, 45.3; H, 6.2. $C_8H_{13}NOGe$ calc.: C, 45.37; H, 6.19%.

17 (82% yield from **12**): yellow liquid; ^1H NMR ($CDCl_3$): δ 1.04 (m, GeEt), 6.40 (2 d, $J = 3.7$ and 2.3 Hz, H(4)), 6.99 (2 d, $J = 3.7$ Hz and 2.2 Hz, H(3)), 9.49 (s, CHO). ^{13}C NMR ($CDCl_3$): δ 4.5 ($GeCH_2$), 8.9 (Ge–(C)–Me), 119.1 (C(4)), 121.9 (C(3)), 136.3 (C(2)), 141.6 (C(5)), 178.4 (CHO). IR (CCl_4 solution): ν(C=O): 1652; ν(N–H): 3291 and 3452 cm^{-1}. Anal. Found: C, 52.1; H, 7.6. $C_{11}H_{19}NOGe$ calc.: C, 52.04; H, 7.54%.

18 (50% yield from **14**): yellow liquid; ^1H NMR ($CDCl_3$): δ 0.8–1.6 (m, SnBu), 6.40 (2 d, $J = 3.7$ and 2.3 Hz, H(4)), 7.01 (2 d, 3.7 and 2.2 Hz, H(3)), 9.49 (CHO), 9.8 (NH). ^{13}C NMR ($CDCl_3$): δ 10.1 ($SnCH_2$), 13.7 (Me), 27.3 and 29.0 ((C)–CH_2–(C)), 121.1 (C(4)), 121.8 (C(3)), 136.7 (C(2)), 142.4 (C(5)), 178.1 (CHO). IR (CCl_4 solution): ν(C=O): 1646; ν(N–H): 3282 and 3452 cm^{-1}. Anal. Found: C, 53.2; H, 8.3. $C_{17}H_{31}NOSn$ calc.: C, 53.15; H, 8.14%.

Hydrolysis of stannylated derivative **13** did not take place under the usual conditions, even in the presence of amines (Et_3N, pyridine, TMEDA), or fluoride anion (KF), or upon refluxing with 4N aqueous NaOH.

1-Methyl-2-(trimethylsilyl)pyrrole (20)

The lithium derivative of 1-methylpyrrole was prepared from 10 g (0.123 mol) of 1-methylpyrrole and 77 mL (0.123 mol) of n-butyllithium (1.6 *M* in hexane) in the presence of 14.33 g (0.123 mol) of TMEDA in 80 mL of dry THF [25]. After 30 min stirring, 13.39 g (0.123 mol) of trimethylchlorosilane were added and the mixture was stirred for 12 h at room temperature, hydrolysed, and extracted with Et_2O. The ether was removed and silylpyrrole **20** (13.55 g; 72% yield) isolated by distillation, b.p. 72 °C/16 mmHg (accounting to Ashby [26]: 95–97 °C/40 mmHg).

This method gives better results than those previously described [6,26]. ^{1}H NMR ($CDCl_3$): δ 0.29 (s, SiMe), 3.73 (s, NMe), ethylenic protons: 6.16 (dd, C(4)H), 6.37 (dd, C(3)H), 6.79 (dd, C(5)H), $J_{3,4} = 3.5$ Hz, $J_{4,5} = 2.3$ Hz, $J_{3,5} = 1.6$ Hz. ^{13}C NMR ($CDCl_3$): δ −0.2 (SiMe), 37.0 (NMe), 108.1 (C(4)), 119.3 (C(3)), 127.0 (C(5)), 132.6 (C(2)).

1-Methyl-2-(trimethylgermyl)pyrrole (21)

Prepared by the same procedure from trimethylchlorogermane (70% yield). b.p. 84 °C/15 mmHg. ^{1}H NMR ($CDCl_3$): δ 0.49 (s, $GeMe_3$), 3.76 (s, NMe), ethylenic protons: 6.23 (dd, C(4)H), 6.34 (dd, C(3)H), 6.84 (dd, C(5)H), $J_{3,4} = 3.4$ Hz, $J_{4,5} = 2.4$ Hz, $J_{3,5} = 1.6$ Hz; ^{13}C NMR ($CDCl_3$): δ −0.7 ($GeMe_3$), 36.9 (NMe), 108.1 (C(4)), 116.7 (C(3)), 125.9 (C(5)), 133.5 (C(2)).

1-Methyl-2-(triethylgermyl)pyrrole (22)

Prepared from the same procedure from triethylchlorogermane (75% yield). b.p. 118–120 °C/15 mmHg. ^{1}H NMR ($CDCl_3$): δ 1.07 (m, GeEt), 3.70 (s, NMe), ethylenic protons: 6.21 (dd, C(4)H), 6.29 (dd, C(3)H), 6.81 (dd, C(5)H), $J_{3,4} = 3.4$ Hz, $J_{4,5} = 2.4$ Hz, $J_{3,5} = 1.6$ Hz. ^{13}C NMR ($CDCl_3$): δ 5.2 ($GeCH_2$), 9.2 (Ge–(C)–Me), 37.0 (NMe), 108.1 (C(4)), 118.0 (C(3)), 125.9 (C(5)), 131.0 (C(2)).

1-Methyl-2-(trimethylstannyl)pyrrole (23)

Prepared from the same procedure from trimethyltin chloride (70% yield). b.p. 90 °C/10 mmHg. ^{1}H NMR ($CDCl_3$): δ 0.37 (s, SnMe), 3.74 (s, NMe), ethylenic protons: 6.26 (dd, C(4)H), 6.34 (dd, C(3)H), 6.89 (dd, C(5)H), $J_{3,4} = 3.4$ Hz, $J_{4,5} = 2.2$ Hz, $J_{3,5} = 1.6$ Hz. ^{13}C NMR ($CDCl_3$): δ −8.6 (SnMe), 38.0 (NMe), 108.7 (C(4)), 118.9 (C(3)), 126.0 (C(5)), 132.7 (C(2)).

References

1 (a) K.C. Frisch and R.M. Kary, J. Org. Chem. 21 (1956) 931; (b) idem, US Patent 2,845,435 (1958), Chem. Abstr., 53 (1959) 1380d; (c) Solvay and Cie, Belg. Patent 625,490 (1963), Chem. Abstr., 60 (1964) 12243b; (d) A.G. Rykaert and C. Domen, US Patent 3,397,246 (1968), Chem. Abstr., 69 (1968) 105871n.
2 R. Fessenden and D.F. Crowe, J. Org. Chem., 25 (1960) 598.
3 B.A. Ashby, J. Organomet. Chem., 5 (1966) 405.
4 J.R. Pratt, F.H. Pinkerton and S.F. Thames, J. Organomet. Chem., 38 (1972) 29.
5 J.C. Pommier and D. Lucas, J. Organomet. Chem., 57 (1973) 139.
6 T.J. Barton and G.P. Hussmann, J. Org. Chem., 50 (1985) 5881.
7 U. Frick and G. Simchen, Synthesis, (1984) 929.
8 M.W. Majchrzak and G. Simchen, Tetrahedron, 42 (1986) 1299.
9 D.J. Chadwick and S.T. Hodgson, J. Chem. Soc., Perkin Trans I, (1982) 1833.
10 I. Hasan, E.R. Marinelli, L.C. Chang Lin, F.W. Fowler and A.B. Levy, J. Org. Chem., 46 (1981) 157.
11 R.G. Kostyanovskii and A.K. Prokofev, Dokl. Akad. Nauk SSSR, 164 (1965) 1054.
12 T.R. Bailey, Tetrahedron Lett., 27 (1986) 4407.
13 (a) J. Muchowski and D.R. Solas, Tetrahedron Lett., 24 (1983) 3455; (b) K.P. Stefan, W. Schuhmann, H. Parlar and F. Korte, Chem. Ber., 122 (1989) 169; (c) A.P. Kozikowski and P.W. Shum, Tetrahedron Lett., 31 (1990) 6785; (d) B.L. Bray, P.H. Mathies, R. Naef, D.R. Solas, T.T. Tidwell, D.R. Artis and J.M. Muchowski, J. Org. Chem., 55 (1990) 6317.
14 J.M. Muchowski and P. Hess, Tetrahedron Lett., 29 (1988) 777 and references therein.
15 S.F. Thames and H.C. Odom, Jr., J. Heterocycl. Chem., 3 (1966) 490.
16 S.F. Thames and J.E. McClesky, J. Heterocycl. Chem., 4 (1967) 146.

17 C.L. Loader, G.H. Barnett and H.J. Anderson, Can. J. Chem., 60 (1982) 383.
18 A.J. Carpenter and D.J. Chadwick, Tetrahedron, 41 (1985) 3803.
19 D.L. Comins and J.D. Brown, J. Org. Chem., 49 (1984) 1078; (b) D.L. Comins and M.O. Killpack, ibid., 52 (1987) 104.
20 (a) B.J. Helmer, R. West, R.J.P. Corriu, M. Poirier, G. Royo and A. De Saxe, J. Organomet. Chem., 251 (1983) 295; (b) J. Boyer, C. Brelière, F. Carré, R.J.P. Corriu, A. Kpoton, M. Poirier, G. Royo and J.C. Young, J. Chem. Soc., Dalton Trans., (1989) 43 and references therein.
21 B. Wrackmeyer, Ann. Rep. NMR Spectrosc., 16 (1985) 73 and references therein.
22 R.M. Silverstein, E.E. Ryskiewicz, C. Willard and R.C. Koehler, J. Org. Chem., 20 (1955) 668.
23 C. Jaureguiberry, M.C. Fournié-Zaluski, B. Roques and S. Cambrisson, Org. Magn. Reson., 5 (1973) 165.
24 R.J. Abraham, R.D. Lapper, K.M. Smith and J.F. Unsworth, J. Chem. Soc., Perkin Trans II, (1974) 1004.
25 D.J. Chadwick and I.A. Cliffe, J. Chem. Soc., Perkin I, (1979) 2845.
26 B.A. Ashby, J. Organomet. Chem., 5 (1966) 405.