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Journal of Organometallic Chemistry 556 (1998) 145–149

Journal of Organometallic Chemistry

Synthesis of new elementsubstituted derivatives of 3H-pyrrolizines

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Received 26 September 1997

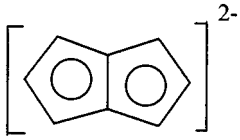
Abstract

The anion of 3H-pyrrolizine was isolated as its lithium **2a** and thallium salts **3** and the anion of 1-methyl-3H-pyrrolizine as its lithium salt **2b**. Reaction of the lithium anions with Group 14 electrophiles led to a number of substituted derivatives of the 3H-pyrrolizine ring system. In the case of **2b** it was shown that the number of isomers obtained was strongly dependent on the reaction solvent.

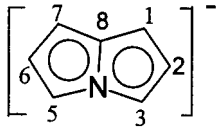
Keywords: 3H-pyrrolizine; Silicon; Tin; Lithium; Thallium

1. Introduction

The simplest heterocycle isoelectronic with 10 π-electron pentalenyl dianion



is the 4-azapentalenyl anion which was first described by Katz et al. [1].



The synthetic utility of pentalenyl diction in the organometallic chemistry group 14 elements has been extensively investigated [2–10]. It has been demonstrated that in forming π-complexes with transition metals that each ring can act as an η^3-fragment and besides that forms 4 electron–4 centers bond between two atoms of transition metal and two bridge carbon atoms [11,12].

However the synthetic utility of the 4-azapentalenyl anion has not been examined. Herein we present new syntheses of 4-azapentalenyl anions and their application to the synthesis of Group 14 derivatives of 3H-pyrrolizine.

2. Results and discussion

The aim of our work was the synthesis of anions of 3H-pyrrolizines as their lithium and thallium salts and subsequent conversion to covalent silicon and tin derivatives. We found that 3H-pyrrolizine **1a** [1] and 1-methyl-3H-pyrrolizine **1b** react rapidly with *n*-butyllithium in hexane at -20°C to give the corresponding lithium salts **2a** and **2b** in nearly quantitative yield. These air and moisture sensitive compounds were isolated as pale yellow crystals insoluble in non-polar organic solvents and characterized by NMR-spectroscopy [1]. The ^{1}H-NMR spectrum of lithium salt of 1-methyl-3H-pyrrolizine **2b** exhibits a singlet due to the methyl group at 1.51 ppm, two multiplets at 5.86 ppm

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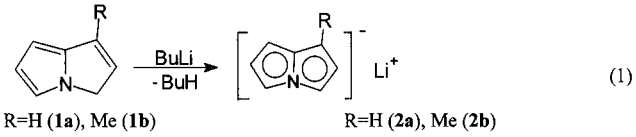
0022-328X/98/$19.00
PII S0022-328X(97)00771-7

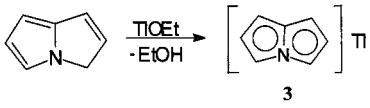
(H2) and 6.12 ppm (H3) corresponding to the substituted ring and three multiplets at 4.85 ppm (H7), 5.36 ppm (H6) and 6.24 ppm (H5) attributable to the protons of non-substituted ring.



(1)

R=H (**1a**), Me (**1b**) R=H (**2a**), Me (**2b**)

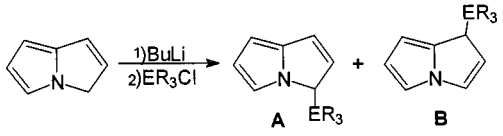
We were also able to isolate the anion of 3H-pyrrolizine as its thallium salt **3** in essentially quantitative yield by reaction of TlOEt with 3H-pyrrolizine in ether at room temperature.



3 (2)

In the solid state compound **3** is quite stable to air and moisture. It is insoluble in hexane, toluene and ether but is soluble in THF. However, the resulting solution is unstable and easily decomposes. The thallium salt was characterized by mass-spectroscopy.

The lithium salts **2a** and **2b** were used in the preparation of silicon and tin substituted 3H-pyrrolizines. Reaction of **2a** with chlorosilanes at -50°C in ether gave a mixture of two possible isomers **A** and **B** (throughout we shall mark the 3-substituted product as **A** and 1-substituted product as **B**):



(3)

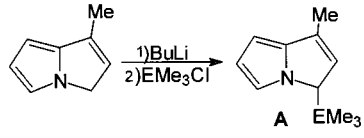
R = Me: E = Si(**4**); **A**:**B** = 4:3; E = Sn(**5**); **A**:**B** = 2:3; R = Ph: E = Si(**6**); **A**:**B** = 4:3.

The trimethylsilyl- and trimethyltin-3H-pyrrolizines were isolated as yellow oils and triphenylsilyl-3H-pyrrolizine as yellow crystals. These compounds are soluble in most of organic solvents and easily oxidize in air.

The ratio of isomers were determined by ^{1}H-NMR spectroscopy. In the case of chlorosilanes the ratio of **A**:**B** was 4:3. The similar reaction of the salt **2a** at -50°C in ether with $SnClMe_3$ also gave the mixture of the two possible isomers, however, in this case the ratio of the isomers **A**:**B** was 2:3. The two reasons are of the great importance in generation of regioselectivity of electrophilic attack. The first reason is the extent of negative charge delocalization in pyrrolizine anion. The unsymmetric delocalization of the charge in the pyrrolizine anion has been convincingly shown by ^{1}H-NMR studies by Katz et al. [1]. The α-carbon atoms of the 3H-pyrrolizines have a higher electron density than the γ-carbon atoms. These synthetic results are in good qualitative agreement with competitive softness and hardness of the used organometallic reagents. Since chlorosilanes are harder electrophiles than $SnClMe_3$, reaction with the lithium salt **2a** occurs preferentially at the α-positions whereas the softer $SnClMe_3$ prefers the γ-carbon atoms.

The second regulation effect arises from Li^+-induced polarization of anion. The precise registration of this effect is rather complicated and requires the series of special experiments. A priori it is clear that the potential energy surface of the pyrrolizine anion is rather flat and therefore the Li^+ can occupy different positions above the aromatic plane without effecting the overall energy of the system. But in any case Li^+-anion interaction will be of unsymmetric nature and such unsymmetrical interactions were found for some lithiated η^3-aza-allyl heterocyclic systems [13,14]. It was shown for instance by X-rays studies for above mentioned aza-allyl lithiated heterocycles that using of the solvents or such reagents as *N*,*N*,*N*′,*N*′-tetramethylethylendiamine which would form helates with Li^+ cation led to increasing of Li–C distances due to more electron density on the metal centre, resulting in weaker metal–nitrogen contact. The difference in Li^+-coordination positions will be apparent, so the easiest way to reveal the results of this coordination on the reaction pathway is to test several solvents with different solvation abilities.

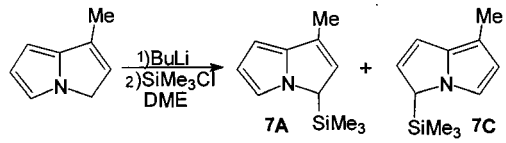
Such effect was found in the case of salt **2b**. When reactions of the lithium salt of the 1-methyl substituted -3H-pyrrolizine **2b** in ether were undertaken with $EClMe_3$ (E = Si, Sn) we found that only one of the four possible isomers was obtained—isomer **A**. (The structure of isomer **7A** was determined by double resonance experiments.)



(4)

E = Si (**7**); E = Sn (**8**)

When we carried out the reaction of $SiClMe_3$ with lithium salt **2b** in DME two isomers **7A** and **7C** were obtained in the ratio 3:1.



(5)

Presumably the steric hindrance of methyl group in **2b** resulted in closer binding of ion Li^+ with α-carbon then in **2a**. Moreover the steric effect of methyl group should prevent the attack of electrophilic species at the positions **1** and **7**.

The structure of compounds **4–8** was confirmed by ^{1}H- and ^{13}C{^{1}H}-NMR spectroscopy. In all cases, the ^{1}H-NMR spectra exhibited singlets due to the EMe_3-groups at -0.07–-0.24 ppm, multiplets of allyl protons cover the range at 2.9–4.9 ppm. Chemical shift of allyl proton in isomer **A** is moved in lower field on ~1 ppm in comparison with the same proton in isomer **B**. Such difference in chemical shifts allows to make the correlation of the signals in both isomers. In compounds **7** and **8** protons of methyl group are located at 1.9–2.5 ppm. Besides that signals of protons of nonsubstituted ring as three multiplets are covered the range at 6.1–7.0 ppm. Signals of vinyl protons of substituted ring are observed at the same field. In all compounds the signals of the protons H5 (or H3 in isomer **7C**) neighboring with nitrogen atom are situated in the lowest field. In isomers **6A** and **6B** it can be noticed that signals of protons neighboring with $SiPh_3$-group are observed in lower field and signals of protons H5 (in **6A**) and H7 (in **6B**) in stronger field due to anisotropy of shielding of phenyl rings. Reference of signals of vinyl protons in Group 14 substituted 3H-pyrrolizine was made on the base of homonuclear decoupling experiments for those compounds and literature data for substituted 3H-pyrrolizines [1,15,16]. In ^{1}H-NMR spectrum of **6** multiplet of phenyl groups at 7.18–7.61 ppm is presents. The magnitude of coupling constants J_{H-H} in pyrrolizine fragment are 1–3 Hz excluding $^3J_{H1-H2}$~6 Hz.

^{13}C{^{1}H}-NMR spectra of compounds **4–8** exhibit signals of EMe_3-groups are observed at -11–-0.1 ppm, and the signals methyl groups in compounds **7** and **8** about 12 ppm. Signals of allyl carbons cover the range at 34–58 ppm and vinyl carbons at 95–141 ppm. Chemical shift of allyl carbon in isomer **A** is moved in lower field on ~20 ppm in comparison with the same carbon in isomer **B**.

In comparison with results found by Ustynyuk et al. [17] when heating the sample of mixture of isomers **5A** and **5B** in DMSO-d_6 at 140°C migration of $SnMe_3$-group did not observed.

3. Experimental

All manipulations were performed under an argon atmosphere. Solvents were freshly distilled from sodium/benzophenone (DME, ether), sodium (hexane). Lithium and thallium salts were prepared using standard Schlenk techniques. $SiClMe_3$ was purified by boiling over aluminum powder. The starting 3H-pyrrolizines were prepared by literature methods [18]. NMR spectra were recorded on VARIAN VXR-400 and JEOL EX-90 spectrometers. All spectra were recorded at room temperature. Elemental analysis were undertaken by the microanalysis group of Moscow State University. Mass-spectra were recorded using an MX-1321 mass-spectrometer by the Zelinsky's Organic Chemistry Institute.

3.1. Synthesis of lithium salts *2a* and *2b*

Butyllithium (4.3 ml of a 2.36 M solution) was added dropwise at -20°C to a vigorously stirred solution of 0.01 mol of starting ligand in 15 ml of hexane. A pale-yellow precipitate immediately formed. The reaction mixture was then warmed to room temperature and stirred for 3 h. The solvent was removed by decantation and the remaining solid washed twice with hexane. The yields of lithium salts **2a** and **2b** were nearly quantitative.

2b ^{1}H-NMR (THF-d_8) δ 6.24 (m, 1H, H5); 6.12 (d, 1H, H3); 5.86 (d, 1H, H6); 5.36 (m, 1H, H6); 4.85 (m, 1H, H7); 1.51 (s, 3H, CH_3)

The ^{1}H-NMR spectrum of lithium salt **2a** is similar to that described by Katz et al. [1].

3.2. Synthesis of thallium salt *3*

To a solution of 0.75 g (7 mmol) of 3H-pyrrolizine in 15 ml of ether 0.5 ml of TlOEt was added at room temperature. A white precipitate immediately formed. The reaction mixture was stirred at room temperature for 4 h and the solvent removed by decantation. The remaining solvent was washed twice with ether affording 2.16 g of the thallium salt **3a** (99.4%); mp = 163°C (with decomposition).

Mass-spectrum (EI, 70 eV) m/z: 309 (23%, M^+ for ^{205}T1); 307 (9.5%, M^+ for ^{203}T1); 205 (100%, $^{205}T1^+$); 203 (43%, $^{203}T1^+$); 104 (76%, $C_7H_6N^+$); 66 (35%, $C_4H_4N^+$); 39 (38%, $C_3H_3^+$).

3.3. Reaction of lithium salts *2* with $SiClMe_3$ and $SnClMe_3$ general procedure

Butyllithium (2.97 ml of a 2.36 M solution) was added dropwise at 0°C to a vigorously stirred solution of 7 mmol of starting ligand in 15 ml of solvent (ether, DME, THF). The solution immediately became dark-red. After stirring at room temperature for 30 min the reaction mixture was cooled to -50°C and a solution of 7 mmol $EClMe_3$ (E = Si, Sn) in 10 ml of solvent was added. The resulting solution was warmed to room temperature and stirred for 20 min. The reaction mixture was filtered and the LiCl precipitate was washed twice with ether. The solvent was removed in vacuo and the residue was distilled under vacuum.

3.3.1. Reactions in ether

4 two isomers: 3-trimethylsilyl-3H-pyrrolizine (**A**) and 1-trimethylsilyl-1H-pyrrolizine (**B**) (**A**:**B** = 4:3), yield 0.72 g (58.5%); bp = 95–108°C/0.1 mmHg

A: ^{1}H-NMR (C_6D_6) δ 6.84 (m, 1H, H5); 6.52 (m, 1H, H6); 6.41 (m, 1H, H1); 6.14 (m, 1H, H7); 5.89 (m, 1H, H2); 3.92 (m, 1H, H3); −0.24 (s, 9H, $SiMe_3$).

B: ^{1}H-NMR (C_6D_6) δ 6.66 (m, 1H, H5); 6.52 (m, 2H, H3, H6); 6.06 (m, 1H, H7); 5.48 (m, 1H, H2); 2.96 (br s, 1H, H1); −0.13 (s, 9H, $SiMe_3$)

A and **B**: ^{13}C{^{1}H}-NMR (C_6D_6) δ 141.93 (C8(**A**)); 138.49 (C8(**B**)); 128.57; 125.94; 120.95; 117.29; 114.97; 112.54; 112.41; 109.62; 98.72; 96.27 (C1, C2, C3, C5, C6, C7 for **A** and **B**); 58.37 (C3(**A**)); 36.42 (C1(**B**)); −3.35 ($SiMe_3$(**B**)); −4.38 ($SiMe_3$(**A**)).

Anal. Found: C, 67.55; H, 8.72; Si, 15.09. $C_{10}H_{15}NSi$ Calc.: C, 67.80; H, 8.47; Si, 15.82%.

5 two isomers: 3-trimethyltin-3H-pyrrolizine (**A**) and 1-trimethyltin-1H-pyrrolizine (**B**) (**A**:**B** = 2:3), yield 0.99 g (52.7%); bp = 114–121°C/0.1 mmHg.

A: ^{1}H-NMR (toluene-d_8) δ 6.77 (m, 1H, H5); 6.47 (m, 1H, H6); 6.34 (m, 1H, H1); 6.07 (m, 1H, H7); 5.99 (m, 1H, H2); 4.34 (m, 1H, $^2J_{Sn-H}$ = 49 Hz, H3); −0.12 (s, 9H, $^2J_{Sn-H}$ = 54.1 Hz, $SnMe_3$).

B: ^{1}H-NMR (toluene-d_8) δ 6.67 (m, 1H, H5); 6.55 (m, 1H, H3); 6.47 (m, 1H, H6); 5.94 (m, 1H, H7); 5.59 (m, 1H, H2); 3.31 (m, 1H, $^2J_{Sn-H}$ = 95 Hz, H1); −0.07 (s, 9H, $^2J_{Sn-H}$ = 53.6 Hz, $SnMe_3$).

A and **B**: ^{13}C{^{1}H}-NMR(toluene-d_8) δ 141.12(C8(**A**)); 140.54 (C8(**B**)); 123.27; 118.26; 118.21; 117.73; 113.52; 112.90; 112.63; 106.60; 95.83; 95.42 (C1, C2, C3, C5, C6, C7 for **A** and **B**); −10.65 ($SnMe_3$(**B**)); −11.08 ($SnMe_3$(**A**)).

^{119}Sn{^{1}H}-NMR δ 115.30 ($SnMe_3$(**A**)); 116.15 ($SnMe_3$(**B**)).

Anal. Found: C, 45.04; H, 5.70; Sn, 44.26. $C_{10}H_{15}NSn$ Calc.: C, 44.78; H, 5.60; Sn, 44.40%.

7 one isomer: 1-methyl-3-trimethylsilyl-3H-pyrrolizine, yield 0.79 g (59.3%); bp = 119°C/0.1 mmHg.

^{1}H-NMR (C_6D_6) δ 6.81 (m, 1H, H5); 6.48 (m, 1H, H6); 6.08 (m, 1H, H7); 5.62 (m, 1H, H2); 3.94 (m, 1H, H3); 1.96 (m, 3H, CH3); −0.20 (s, 9H, $SiMe_3$).

^{13}C{^{1}H}-NMR(C_6D_6) δ 143.87 (C8); 130.60 (C1); 123.50; 115.11; 112.27 (C7); 94.71 (C2, C5, C6); 54.53 (C3); 12.74 (CH_3); −4.26 ($SiMe_3$).

Anal. Found: C, 69.67; H, 8.85; Si, 14.01. $C_{11}H_{17}NSi$ Calc.: C, 69.11; H, 8.90; Si, 14.66%.

8 one isomer: 1-methyl-3-trimethyltin-3H-pyrrolizine, yield 0.92 g (46.5%); bp = 129°C/0.1 mmHg.

^{1}H-NMR (C_6D_6) δ 6.80 (m, 1H, H5); 6.53 (m, 1H, H6); 6.11 (m, 1H, H7); 5.73 (m, 1H, H2); 4.36 (br s, 1H, $^2J_{Sn-H}$ = 42 Hz, H3); 2.01 (d, 3H, CH_3); −0.12 (s, 9H, $^2J_{Sn-H}$ = 54 Hz, $SnMe_3$).

^{13}C{^{1}H}-NMR (C_6D_6) δ 143.61 (C8); 127.52 (C1); 124.95; 113.89; 112.58 (C7); 94.17 (C2, C5, C6); 54.53 (C3); 12.70 (CH_3); −10.91 ($SnMe_3$).

Anal. Found: C, 46.24; H, 5.90; Sn, 43.86. $C_{11}H_{17}NSn$ Calc.: C, 46.81; H, 6.03; Sn, 44.20%.

3.3.2. Reactions in DME

7 two isomers: 1-methyl-3-trimethylsilyl-3H-pyrrolizine (**A**) and 1-methyl-5-trimethylsilyl-3H-pyrrolizine (**C**) (**A**:**C** = 3:1), yield 0.76 g (56.8%); bp = 116–125°C/0.1 mmHg.

C: ^{1}H-NMR (C_6D_6) δ 6.74 (m, 1H, H3); 6.44 (m, 1H, H7); 6.28 (m, 1H, H2); 5.85 (m, 1H, H6); 3.71 (m, 1H, H5); 2.25 (s, 3H, CH3); −0.20 (s, 9H, $SiMe_3$).

^{13}C{^{1}H}-NMR (C_6D_6) δ 139.59 (C8); 130.35 (C1); 126.93; 119.95; 114.57; 113.61 (C2, C3, C6, C7); 58.49 (C5); 11.87 (CH_3); −4.29 ($SiMe_3$).

*3.3.3. Reaction of lithium salt **1** with $SiClPh_3$*

To a vigorously stirred solution of 0.75 g (7 mmol) 3H-pyrrolizine in 15 ml of ether at 0°C was added dropwise 7 mmol of butyllithium. The solution immediately became dark-red. After stirring at room temperature for 30 min, the reaction mixture was cooled to −50°C and a solution of 2.10 g (7 mmol) of $SiClPh_3$ in 10 ml of solvent was added. The resulting solution was warmed to the room temperature and stirred for 30 min. The reaction mixture was filtrated, the precipitate was washed twice with ether and the solvent was removed in vacuo. Recrystallization of the residue from hexane:benzene (5:1) gave a mixture of isomers **6A** and **6B** in the ratio 4:3 respectively. 0.76 g of **5** was obtained (52%).

A: ^{1}H-NMR (C_6D_6) δ 7.10–7.52 (m, 15H, Ph); 6.45 (m, 1H, H5); 6.38 (m, 2H, H1, H6); 6.25 (m, 1H, H2); 6.20 (m, 1H, H7); 4.82 (m, 1H, H3).

B: ^{1}H-NMR (C_6D_6) δ 7.10–7.52 (m, 15H, Ph); 6.66 (m, 1H, H5); 6.38 (m, 2H, H3, H6); 5.80 (m, 1H, H2); 5.73 (m, 1H, H7); 3.95(m, 1H, H1).

A and **B**: ^{13}C{^{1}H}-NMR (C_6D_6) δ 141.22 (C8(**A**)); 140.54 (C8(**B**)); 136.49–97.09 (C1, C2, C5, C6, C7, C8, $SiPh_3$, C2, C3, C5, C6, C7, C8, $SiPh_3$ for **A** and **B**); 56.70 (C3(**A**)); 34.12 (C1 (**B**)).

Anal. Found: C, 79.97; H, 6.61; Si, 7.87. $C_{22}H_{21}NSi$ Calc.: C, 80.73; H, 6.61; Si, 8.50%.

Acknowledgements

Support of this work by Russian Fund for Basic Research (RFBR) is gratefully acknowledged.

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