Synthesis of N,C,C-Trilithio-2,5-diallylpyrrole and its Solvent-Controlled Reactions with Electrophiles

Bernd Wrackmeyer*, Iris Ordung, Bernd Schwarze

Laboratorium für Anorganische Chemie der Universität Bayreuth, Postfach 101251, D-95440 Bayreuth

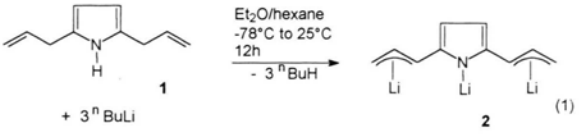
Z. Naturforsch. **52b,** 427–430 (1997); received November 5, 1996

Pyrrole, Solvent Controlled Reactions, NMR Spectra

2,5-Diallylpyrrole **1** reacts with an excess of ^{n}BuLi in hexane/diethylether to give the N,C,C-trilithio reagent **2**. ^{7}Li NMR spectra of **2** in THF/HMPTA at low temperature indicate the presence of an ionic species. Reactions of **2** in THF with electrophiles such as H_2O, D_2O, MeI, Me_3SiCl and Me_3SnCl lead selectively to the *cis*-isomers **3a** – **6a**, whereas the analogous reactions in hexane or diethylether afford mixtures containing both *cis*- and *trans*-isomers (*e.g.* **3b**).

Polymetallated compounds can be regarded as useful starting materials in organic and organometallic synthesis [1,2]. Recently we have reported on the synthesis of N,C-dilithio-2-allylpyrrole, its reactions with electrophiles [3], and on its potential in heterocyclic synthesis [4]. These results prompted us to study the lithiation of 2,5-diallylpyrrole **1**.

Treatment of 2,5-diallylpyrrole **1** in diethylether with an excess of ^{n}BuLi in hexane leads to the N,C,C-trilithio-2,5-diallylpyrrole **2** (eq.(1)) as a bright orange pyrophorous solid, which can be isolated as a dry powder and stored for prolonged time under an inert atmosphere of Ar or N_2. The reaction proceeds stepwise. The lithiation of the first allyl group has no influence on the lithiation of the second one. Therefore, the reaction of **1** with only two equivalents of ^{n}BuLi gives the N-lithiated and the dilithiated products together with **2**. Compound **2** is completely insoluble in diethylether or hydrocarbons but soluble in THF and diluted solutions can be cooled to -80 °C without precipitation.



(1)

Solutions of **2** in THF together with about 10 equivalents of HMPTA were studied by ^{7}Li NMR (see Fig. 1). At low temperature mainly two signals were observed in a 1:2 ratio. The broad signal of lower intensity can be assigned to the N-Li fragment, whereas the sharp ^{7}Li signal shows a splitting into a quintet according to $^2J(^{31}P,^7Li)$ = 7.1 Hz and belongs to the solvated cations $[Li(HMPTA)_4]^+$. The resolved splitting indicates a slow quadrupolar relaxation rate of the ^{7}Li nuclei, which requires an almost perfect tetrahedral environment. Thus, two lithium cations have been removed from **2**, leaving the dianion $\mathbf{2}^{2-}$ for which the structure shown in Fig. 1 can be proposed. This

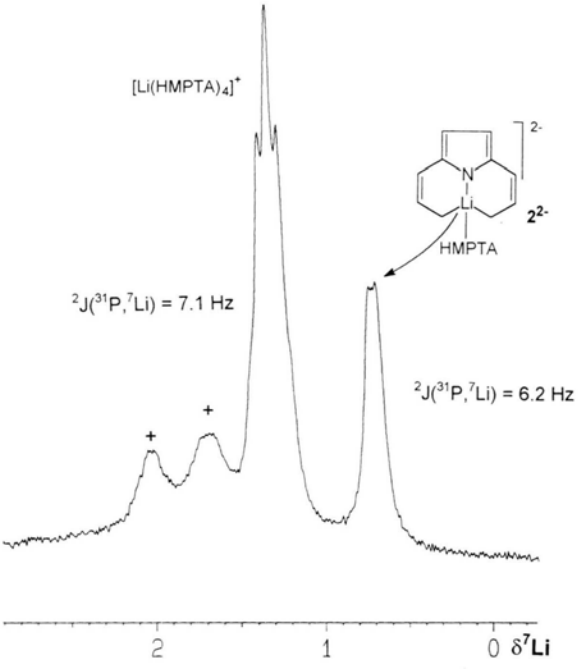


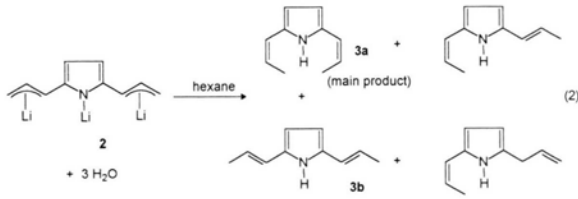
Fig. 1. $^7Li\{^1H\}$ NMR spectrum of **2** in THF with 10 equivalents of HMPTA at -70 °C. The quintet owing to the $^2J(^{31}P\text{-}O\text{-}^7Li)$ coupling is clearly resolved, impurities are marked with +. The splitting of the resonance assigned to $\mathbf{2}^{2-}$ indicates that a further HMPTA molecule coordinates to the lithium atom of the dianion.

* Reprint requests to Prof. Dr. B. Wrackmeyer.

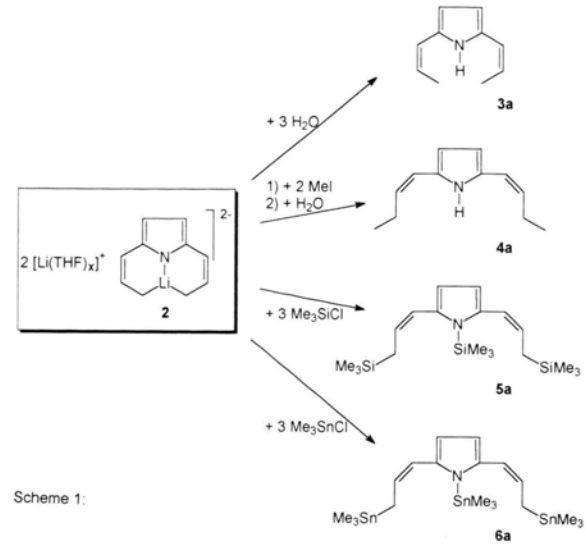
0932–0776/97/0300–0427 $06.00 D

result is comparable to the result of the ^{7}Li NMR study of N,C-dilithio-2-allylpyrrole [1].

If the preferred structure of **2** in donor solvents corresponds to that shown in Fig. 1, it is likely that the reaction of **2** with electrophiles proceeds in a stereospecific way, leading selectively to products **3a** – **6a** with *cis*-configuration as shown in Scheme 1. If the reactions, *e.g.* the hydrolysis, are carried out in hexane or in diethylether complex mixtures of isomers are obtained (eq. (2)), but the *cis*-product **3a** is still the main product. This indicates that

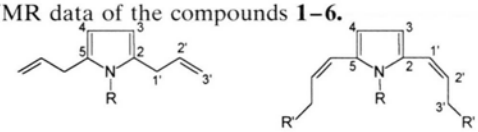


a tricyclic form of **2** (similar to $\mathbf{2}^{2-}$) is also present to some extent in non donor solvents, in contrast to the situation found for N,C-dilithio-2-allylpyrrole [3] where the selective formation of the *trans*-products in non donor solvents indicates a non-cyclic constitution. The assignment of *cis*- or *trans*-configuration follows conclusively from the ^{1}H and ^{13}C NMR spectra [6] (Table I) (for NMR data of side chains with *trans*-configuration see [3,4]).



Scheme 1:

Table I. ^{13}C, ^{14}N, ^{29}Si and ^{119}Sn NMR data of the compounds **1**–**6**.



1 **2 - 6**

No		**1** [a]	**2** [b]	**3a** [a]	**4a** [a]	**5a** [a]	**6a** [c]
N–R			Li	H	H	$SiMe_3$	$SnMe_3$
3′–R′			Li	H	CH_3	$SiMe_3$	$SnMe_3$
δ^{14}N		–229.5	n.o.	n.m.	–237.0	–227.2	n.o.
δ^{29}Si/δ^{119}Sn	N–R	–	–	–	–	10.8	57.7
	3′–R′	–	–	–	–	1.7	4.9
δ^{13}C	C-2/5	129.4	131.7	129.9	129.7	133.2	136.7 [18.8]
(J(^{29}Si^{13}C))	C-3/4	106.5	97.4	110.4	110.2	111.7	112.1 [21.0]
[J(^{119}Sn^{13}C)]	C-1′	33.1	73.9	120.2	118.5	120.3	118.5 [50.2]
	C-2′	136.7	142.2	122.0	130.0	125.8	126.3 [55.4]
	C-3′	116.5	47.1	14.9	22.5	19.6 (45.2)	15.8 [293.7]
	N–R	–	–	–	–	2.9 (57.8)	–1.9 [396.0]
	3′-R′	–	–	–	14.0	–1.8 (52.0)	–9.0 [316.0]

[a] $CDCl_3$, 25 °C; [b] THF, 25 °C; [c] C_6D_6, 25 °C.

Experimental

All preparative work and handling of samples was carried out in an N_2 atmosphere, using dry glassware and dry solvents. 2,5-Diallylpyrrole **1** [7] was prepared by a modified literature procedure [8]. ^{n}BuLi in hexane (1.6 M), pyrrole, MeI, Me_3SiCl and Me_3SnCl were commercial products and used without further purification. EI-MS spectra (70 eV): VARIAN-MAT CH 7 with direct inlet. NMR spectra: Jeol EX270 (^{1}H, ^{13}C) and Bruker ARX 250 (^{1}H, ^{13}C, ^{14}N, ^{29}Si, ^{119}Sn); chemical shifts are given with respect to Me_4Si [δ^1H($CHCl_3$/$CDCl_3$) = 7.24, (C_6D_5H) = 7.15; δ^{13}C($CDCl_3$) = 77.0, (C_6D_6) = 128.0; δ^{29}Si: Ξ(^{29}Si) = 19.867184 MHz], neat $MeNO_2$ [δ^{14}N: Ξ(^{14}N) = 7.223656 MHz] and Me_4Sn [δ^{119}Sn: Ξ(^{119}Sn) = 37.290665 MHz].

2,5-Diallylpyrrole **1**

A mixture of 280 g (2 mol) of K_2CO_3 in 70 ml of H_2O, 700 ml of toluene and 140 ml (2 mol) of pyrrole was heated to 80 °C. While stirring was continued 350 ml (4 mol) of allylbromide was added dropwise. Then the mixture was stirred at 80 °C for 15 h; the organic phase was separated and the water phase was extracted twice with ether. The combined organic phases were dried with Na_2SO_4 and the solvent was removed in vacuo. Fractional distillation gave 105 g (49%) of 2-allylpyrrole (b.p.: 50 °C/0.1 Torr, NMR data see [3]) and 93 g (41%) of **1** as colourless liquids (b.p.: 62 °C/0.1 Torr). **1**: ^{1}H NMR ($CDCl_3$, 25 °C): δ^1H [^nJ(^{1}H,^{1}H)]= 6.16 (s) (H-3/4); 3.53 (d) [6.6 Hz] (H-1'); 6.19 (m) (H-2'); 5.42 (m) (H-3'); 7.91 [br] (NH). EI-MS: m/z(%) = 147 (100) [M$^+$]; 120 (77) [M$^+$- $CHCH_2$]; 106 (80) [M$^+$- allyl]; 65 (10) [M$^+$- 2 allyl].

N,C,C-Trilithio-2,5-diallylpyrrole **2**

A solution of ^{n}BuLi (480 mmol) in 300 ml of hexane and 100 ml of diethylether was added dropwise to a stirred solution of 20 g (136 mmol) of 2,5-diallylpyrrole in 400 ml of diethylether at -78 °C. The mixture was stirred for 12 h and warmed up to room temperature. Then the bright orange reaction mixture was filtered, the precipitate was washed with pentane and dried in a vacuum; 18 g (80%) yield of **2**, were obtained as an extremely air-sensitive orange powder. ^{1}H NMR (THF, 25 °C): δ^1H = 6.13 (H-2'); 5.51 (H-3/4); 5.00 (H-1'); 2.25 (H-3').

Adduct of **2** *with HMPTA*

3.1 g HMPTA (17 mmol) was added to a solution of 0.28 g (1.7 mmol) **1** in 5 ml of THF at -78 °C. The colour changed from dark orange to dark red. The solutions of the adduct are stable at r.t. for several hours.

Reactions of **2** *with electrophiles in THF*

10.5 mmol of H_2O, Me_3SiCl, or Me_3SnCl, respectively, or 7.0 mmol of MeI followed by 7.0 mmol of H_2O was added in one portion to a stirred solution of 0.5 g (3.5 mmol) of **2** in 50 ml of THF at -78 °C. The colour of the dark red solution became lighter. After warming up to r.t. the solvent was removed, the residue was extracted with hexane, and the products remained after filtration and removing of the hexane in a vacuum.

3a: 0.4 g (80%) yield, yellow solid. ^{1}H NMR ($CDCl_3$, 25 °C): δ^1H [^nJ(^{1}H,^{1}H)]= 6.31 (s) (H-3/4); 6.24 (d) [11.3 Hz] (H-1'); 5.60 (m), (H-2'); 1.98 (dd) [7.3 Hz][1.4 Hz], (H-3').

With D_2O: ^{13}C NMR ($CDCl_3$, 25 °C): δ^{13}H [^nJ(^{13}C,^{2}D)]= 15.1 (t) [38.4 Hz] (C-3'). ^{1}H NMR ($CDCl_3$, 25 °C): δ^1H = 5.60 (m) (H-2'); 1.99 (m) (H-3').

4a: 0.49 g (80%) yield, yellow powder. ^{1}H NMR ($CDCl_3$, 25 °C): δ^1H [^nJ(^{1}H,^{1}H)]= 8.04 s (br), (N-H); 6.34 (s), (H-3/4); 6.19 (dt) [11.5][1.9] (H-1'); 5.50 (dt) (H-2'); 2.50 (m) (H-3'): 1.24 (t) (CH_3). EI-MS: m/z(%) = 175 (55) [M$^+$]; 160 (100) [M$^+$ – Me]; 144 (10) [M$^+$ – 2Me – H].

5a: 0.76 g (60%) yield, brown liquid. ^{1}H NMR ($CDCl_3$, 25 °C): δ^1H [^nJ(^{1}H,^{1}H)]= 6.26 (m) (H-3/4); 6.21 (m) [11.2 Hz] (H-1'); 5.53 (m) (H-2'); 1.88 (m), (H-3').

6a: 1.3 g (60%) yield, brown liquid. ^{1}H NMR (C_6D_6, 25 °C): δ^1H [^nJ(^{1}H,^{1}H)]= 6.33 (t) [3.78 Hz], (H-3/4); 5.96 (d) [11.6 Hz] (H-1'); 5.57 (m) (H-2'); 2.13 (d) [9.7 Hz] (H-3'); 0.27 (s), (N-Sn(CH_3)$_3$); 0.09 (m) ($C^{3'}$-Sn(CH_3)$_3$). EI-MS: m/z(%) = 635 (5) [M$^+$]; 472 (12) [M$^+$ – $SnMe_3$]; 310 (65) [M$^+$ – 2 $SnMe_3$]; 165 (100) [$SnMe_3^+$]; 144 (75) [M$^+$ – 3 $SnMe_3$].

Reaction of **2** *in hexane with water*

10.5 mmol of H_2O was added in one portion to a stirred suspension of 0.5 g (3.5 mmol) of **2** in hexane at 0 °C. After one minute the colour of the suspension became lighter and finally yellow; then the suspension was filtered. Removing of the solvent from the filtrate gave a mixture of **3a** as the main product, **3b** and further isomers.

Acknowledgements

Support of this work by the Fonds der Chemischen Industrie and Volkswagen-Stiftung is gratefully acknowledged.

[1] a) S. A. Burns, R. J. P. Corriu, V. Huynh, J. J. E. Moreau, J. Organomet. Chem. **333**, 281 (1987);
b) B. Wrackmeyer, H. Zhou, J. Organomet. Chem. **375**, 1 (1989);
c) G. W. H. Cheeseman, S. G. Greenberg, J. Organomet. Chem. **166**, 139 (1979);
d) A. G. Mal'kina, R. den Besten, A. C. H. T. M. van der Kerk, L. Brandsma, B. A. Trofimov, J. Organomet. Chem. **493**, 271 (1995).

[2] a) A. Bretschneider-Hurley, C. H. Winter, J. Am. Chem. Soc. **116**, 6468 (1994);
b) K. N. Seneviratne, A. Bretschneider-Hurley, C. H. Winter, J. Am. Chem. Soc. **118**, 5506 (1996).

[3] B. Wrackmeyer, I. Ordung, B. Schwarze, J. Organomet. Chem. (1996) in press.

[4] B. Wrackmeyer, I. Ordung, B. Schwarze, J. Organomet. Chem. (1997) in press.

[5] B. Wrackmeyer, B. Schwarze, J. Organomet. Chem., submitted.

[6] H. Günther, NMR-Spektroskopie, pp. 105–112, G. Thieme Verlag, Stuttgart (1983).

[7] K. Heß; Ber. Dtsch. Chem. Ges. **46**, 3125 (1913).

[8] E. P. Papadopoulos, C. A. Van der Werf; Heterocycles **19**, 343 (1982).