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SYNTHESIS OF 5-AMINO-2-CYANO-4-SILYLPYRROLES FROM SILYLACETYLENES AND TRIMETHYLSILYL CYANIDE

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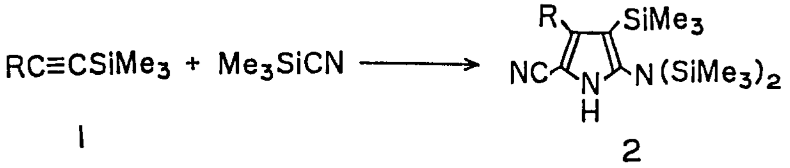
Summary: The reaction of silylacetylenes with trimethylsilyl cyanide in the presence of palladium catalysts gives 3-substituted 5-[N,N-bis(trimethylsilyl)amino]-2-cyano-4-silylpyrroles with high regioselectivity.

Introduction of silicon as well as carbon functional groups into silylacetylenes is expected to provide new silylated material which might be useful for organic synthesis and polymer science. Along this line, hydrosilylation1) and carbometallation2) of 1,4-bis(trimethylsilyl)butadiyne (**1a**) have been studied. Herein reported is silylcyanation3) of silylacetylenes in which unexpectedly 3-substituted 5-[N,N-bis(trimethylsilyl)amino]-2-cyano-4-silylpyrroles (**2**) are produced with the aid of palladium catalysts.



a: R = $Me_3SiC{\equiv}C$– b: R = Ph–
c: R = $CH_3(CH_2)_5$– d: R = Me_3Si–

In a typical procedure, a mixture of 0.4 mmol of **1a**, 1.5 mmol (0.2 ml) of trimethylsilyl cyanide and 0.01 mmol of palladium chloride was heated at 120 °C for 9 h under an argon atmosphere in a sealed vial. The reaction mixture was diluted with ether (10 ml) and the precipitated material was filtered off. Concentration of the filtrate followed by preparative TLC on silica gel gave 5-[N,N-bis(trimethylsilyl)amino]-2-cyano-4-trimethylsilyl-3-(trimethylsilylethynyl)pyrrole (**2a**) in 84% yield, mp 223-4 °C (hexane); i.r. (KBr) 3320 (NH), 2220 (CN), 2126 (C≡C) cm^{-1}; ^{1}H n.m.r. (CDCl$_3$) δ 0.1 (s, 18H),

Table 1 Synthesis of pyrroles from silylacetylenes.

Entry	Silylacetylene **1**	Catalyst$^{b)}$	Conditions	% Yield$^{a)}$ of **2**
1	**1a**	$PdCl_2$	120 °C, 9 h	**2a** 84
2	**1a**	$Pd(OAc)_2$	120 °C, 4 h	**2a** 76
3	**1a**	$Pd(CN)_2$	120 °C, 9 h	**2a** 72
4	**1a**	$PdCl_2(PhCN)_2$	120 °C, 9 h	**2a** 77
5	**1a**	$PdCl_2(PPh_3)_2$	140 °C, 12 h$^{c)}$	**2a** 84
6	**1a**	Pd black	120 °C, 8 h	**2a** 75
7	**1a**	10% Pd-C	160 °C, 4.5 h	**2a** 55
8	**1b**	$PdCl_2$	140 °C, 3 h	**2b** 76$^{d)}$
9	**1c**	$PdCl_2$	160 °C, 8 h	**2c** 49$^{e)}$
10	**1d**	$PdCl_2$	140 °C, 24 h	**2d** 0$^{f,g)}$

a) Isolated yield after purification by preparative TLC. The structure was determined by i.r., ^{1}H and ^{13}C n.m.r., and mass spectrometries as well as elementary analysis.

b) The amount of the catalyst was 3 to 10 mol%.

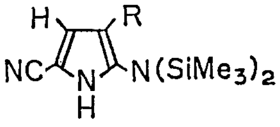
c) This reaction did not occur at 120 °C.

d) Only a trace amount of **3b** and **4b** is formed.

e) By-products are **3c** (9%) and **4c** (7%).

f) Two products having molecular formula of $C_{29}H_{64}N_6Si_7$ and $C_{23}H_{48}N_6Si_5$ were mainly obtained, but the structure of these was not determined.

g) Desilylated pyrroles **3d** (7%) and **4d** (3%) were isolated.



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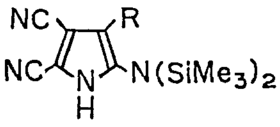

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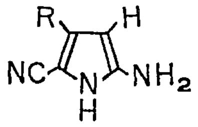

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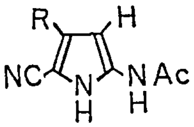

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0.23 (s, 9H), 0.32 (s, 9H), 8.3-8.6 (br, 1H); ^{13}C n.m.r. (CDCl$_3$) δ -0.26, 0.04, 1.69, 98.53, 100.52, 100.97, 113.70, 116.16, 122.02, 144.73; m/z 419 (M$^+$). The structure was unambiguously determined by single crystal X-ray analysis (Figure 1).

The pyrrole formation is achieved by means of various palladium catalysts at the reaction temperature of 120 °C (Table 1). Phosphine ligand tends to inhibit the reaction (entry 5 vs entry 1). Other silylacetylenes **1b** and **1c** gave pyrroles **2b** and **2c** as the main products. When dimethylphenyl(phenylethynyl)silane was allowed to react with trimethylsilyl cyanide (PdCl$_2$ catalyst, 160 °C, 3 h), again **2b** was obtained in 76 % yield along with **4b.** Thus, silyl exchange reaction is found to be remarkable. The formation of by-products **3** or **4** observed in these cases may be ascribed to palladium catalyzed desilylation followed by protonation[4] or cyanation respectively. The structure of these products was determined by transformation to **5** and/or **6** through proto-desilylation with KF in methanol and/or proto-desilylative N-acetylation with acetyl chloride respectively, and by observation of ^{1}H n.m.r. absorptions at 5-6 ppm (H at C-4) for **5** and **6** and those at 6.5-7.0 ppm (H at C-3) for **3**.

Now that the structure of pyrroles **2** and **3** is established, particular attention should be paid to the regiochemistry of the pyrrole formation. The less bulky groups (R vs Me$_3$Si, H vs R) always reside at C-4. The high selectivity contrasts the Ni-catalyzed pyrrole formation from acetylenes and t-BuNC.[5]

The mechanism of the palladium catalyzed pyrrole formation may be explained in terms of palladium isonitrile or cyanide complex which takes a reaction pathway like carbene-metal complex. Actually, when palladium chloride and trimethylsilyl cyanide was heated at 120 °C, colorless solid (i.r. 2220 cm^{-1}) is obtained which is insoluble in common organic solvents and clearly different from commercially available palladium cyanide with respect

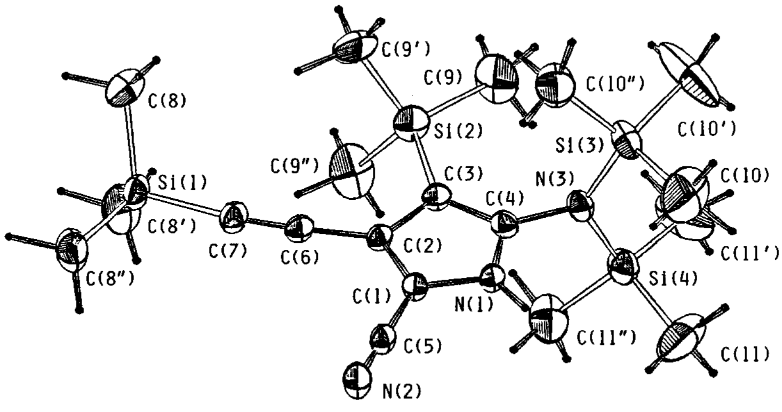

Figure 1. ORTEP drawing of the molecule **2a.**[6]

to elemental analysis. Though further characterization of the complex is unsuccessful at moment, it actually catalyzed the pyrrole formation: **2a** (78%) from **1a** (120 °C, 2 h). At any event, the reaction reported here provides us with a new and regioselective method for pyrrole synthesis.[7,8]

We are indebted to Professor M. Yokoyama (Chiba University) for helpful discussions and kind assistance.

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1) T. Kusumoto and T. Hiyama, Chem. Lett., **1985**, 1405.
2) T. Kusumoto, K. Nishide, and T. Hiyama, Chem. Lett., **1985**, 1409.
3) N. Chatani and T. Hanafusa, J. Chem. Soc., Chem. Commun., **1985**, 838. N. Chatani, T. Kakeyasu, and T. Hanafusa, Tetrahedron Lett., **27**, 1841 (1985).
4) When a terminal acetylene was heated with trimethylsilyl cyanide and $PdCl_2$ catalyst at 120 °C, a fair amount of pyrrole **3** is formed. For example, phenylacetylene gave **3b** (14%) as well as (Z)-3-(trimethylsilyl)-2-phenylpropenenitrile (32%); 1-octyne gave **3c** (7%) and (Z)-(trimethylsilylmethylidene)octanenitrile (53%); trimethylsilylacetylene (140 °C, 9 h) gave **3d** (9%) only.
5) J. Jautelat and K. Ley, Synthesis, **1970**, 539.
6) Crystal data for **2a**: Large triclinic crystals were obtained by slow evaporation of a methanol solution; $C_{19}H_{37}N_3Si_4$: space group P1; a=18.170(4), b=8.900(5), c=8.902(4) Å, β=99.40, 100.65, 79.83°, v=1377.8 $Å^3$, d(calcd.)=1.01 gcm^{-3}, Z=2. Lattice constants and intensity data were measured using graphite monochromated Cu-Kα radiation on a Rigaku AFC-5 diffractometer. A total of 4675 unique reflections with $I > \sigma(I)$ were obtained using the $w < 30° < w-2\theta$ scanning method with a 2θ scan speed of 4° min^{-1} to 2θ=155°, R=0.061. The structure was solved by the UNICS-III system (Library of Computer of Tokyo University) based on the direct method. Selected bond lengths (Å) are: N(1)-C(1) 1.383(5), C(1)-C(2) 1.386(5), C(2)-C(3) 1.430(6), C(3)-C(4) 1.382(5), C(4)-N(1) 1.369(5), C(1)-C(5) 1.416(6), C(5)-N(2) 1.138(6), C(2)-C(6) 1.435(5), C(6)-C(7) 1.186(5), C(7)-Si(1) 1.834(4), C(3)-Si(2) 1.856(4), C(4)-N(3) 1.415(5), N(3)-Si(3) 1.759(3).
7) For recent methods for the preparation of 5-amino-2-cyano(or carboxy)-pyrroles, see; K. W. Law, T. -F. Lai, M. P. Sammes, A. R. Katritzky, and T. C. W. Mak, J. Chem. Soc., Perkin Trans I, **1984**, 111. K. Gewald and U. Hain, Synthesis, **1984**, 62. R. Verhe, N. D. Kimpe, L. D. Buyck, M. Tilley, and N. Schamp, Tetrahedron, **36**, 131 (1980).
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