Tetrahedron Letters,Vol.27,No.28,pp 3261-3262,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

A NOVEL DIMERIZATION OF ISONITRILE BY ORGANOSILYLLITHIUM

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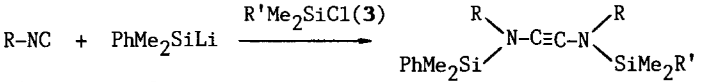
Summary: Reactions of alkyl isocyanides with phenyldimethylsilyllithium followed by treatment with trialkylchlorosilane afforded 1-[*N*-(phenyldimethylsilyl)-*N*-alkylamino]-2-[*N*-(trialkylsilyl)-*N*-alkylamino]acetylenes in moderate yields.

Synthetically useful methods have been developed on the basis of the selective lithiation of isonitriles.1) Primary- and secondary-alkyl isocyanides are selectively lithiated at the α carbon atom to the isocyano group to generate α-lithioalkyl isocyanides.1) On the other hand, tert-alkyl isocyanides having no α-hydrogen are susceptible to α,α-addition with alkyllithium to give lithium aldoimine intermediates.2)

Herein, we wish to describe that alkyl isocyanides (**1**) are readily dimerized by organosilyllithium (**2**) to produce di-[*N*-(organosilyl)-*N*-alkylamino]acetylenes (**4**) in moderate yields, after quenching with trialkylchlorosilanes (**3**). The diaminoacetylene structure of **4** was unambiguously supported by Raman spectral band at $\nu_{C\equiv C}$ 2210 cm^{-1}.



1 **2** **4**

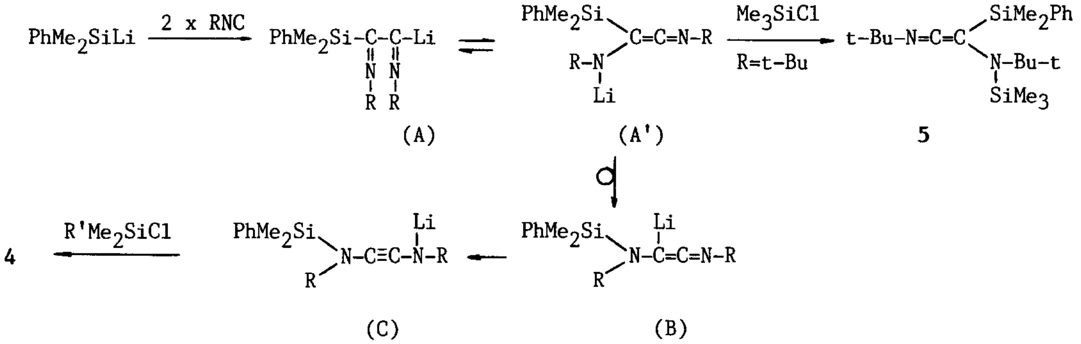
a:	R=c-C_6H_{11},	R'=Me	79%
b:	R=sec-C_4H_9,	R'=Me	67%
c:	R=sec-C_4H_9,	R'=Ph	70%
d:	R=iso-C_3H_7,	R'=Me	56%
e:	R=iso-C_3H_7,	R'=Ph	53%

A general procedure for the dimerization of isonitrile is as follows. To a stirred solution of phenyldimethylsilyllithium (3 mmol) in tetrahydrofuran (3 ml) at -20°C under nitrogen atmosphere, sec-butyl isocyanide (3 mmol) was dropwise added and stirred for 4 hrs. The reaction mixture was treated with phenyldimethylchlorosilane (4.5 mmol) and stirred for 2 hrs at room temperature, and then distilled in vacuo to afford 1,2-bis[*N*-(phenyldimethylsilyl)-*N*-sec-butylamino]acetylene (**4c**): ^1H NMR (CCl_4 with c-C_6H_{12} internal reference) δ 0.37 (s, 12H), 0.76 (t, 6H), 0.98 (d, 6H), 1.13-1.75 (m, 4H), 2.40-2.82 (m, 2H), 7.14-7.32 (broad m, 6H), 7.38-7.62 (broad m, 4H); ^{13}C NMR (C_6D_6) δ -1.86 and -1.80, 11.70 and 11.72, 20.93 and 20.95, 28.53 and 28.57, 54.25 and 54.26, 66.42, 129.57, 134.28, 138.57; Exact Mass (m/e) Calcd for $C_{26}H_{40}N_2Si_2$ 436.2728. Found 436.2722.

A similar treatment of *tert*-butyl isocyanide with phenyldimethylsilyllithium followed by quenching with trimethylchlorosilane afforded a desired diaminoacetylene (**4f**)3) only in 11% yield together with a keteneimine derivative (5)(7%), which was tentatively assigned on the basis of IR and ^{13}CNMR.4)

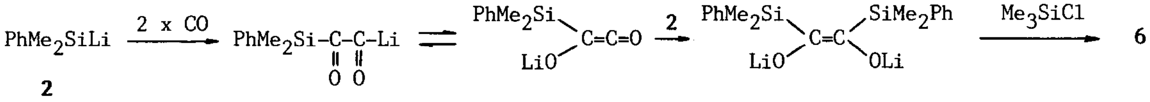
The present dimerization may be explained by a reaction scheme involving a successive insertion of two isonitriles into the lithium-silicon bond of organosilyllithium, and an anionic 1,2-migration of silyl group in the resulting intermediate (A').

Scheme 1.



Carbon monoxide, which is isoelectronic to isonitrile, also reacts with phenyldimethylsilyllithium followed by treatment with trimethylchlorosilane to afford a dimeric 1,2-bis-(phenyldimethylsilyl)-1,2-bis(trimethylsilyloxy)ethylene **(6)** in moderate yield.[5] Based upon the findings of the isonitrile dimerization mentioned above, the formation of **6** may be rationalized by Scheme 2.

Scheme 2.



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(3) 4f: ^{1}H NMR (CCl_4 with $c\text{-}C_6H_{12}$ internal reference) δ 0.18 (s, 9H), 0.44 (s, 6H), 1.13 (s, 9H), 1.22 (s, 9H), 7.23-7.38 (broad m, 3H), 7.52-7.66 (broad m, 2H); ^{13}C NMR (C_6D_6) δ 1.9, 3.1, 30.1, 30.3, 56.3, 56.7, 70.1, 70.2, 129.4, 133.8, 141.2; Exact Mass (m/e) Calcd for $C_{21}H_{38}N_2Si_2$ 374.2571. Found 374.2565.

(4) 5: IR (neat) 1965 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.12 (s, 9H), 0.36 and 0.42 (2s, 6H), 1.08 (s, 9H), 1.31 (s, 9H), 7.29-7.34 (broad m, 3H), 7.43-7.72 (broad m, 2H); ^{13}C NMR (C_6D_6) δ -0.27, 3.07 and 3.24 and 3.25, 30.58 and 31.72, 55.76 and 57.78, 70.04, 127.85, 128.81, 134.19, 143.53, 183.93; Exact Mass (m/e) Calcd for $C_{21}H_{38}N_2Si_2$ 374.2571, Found 374.2571. The spectral data do not exclude another possible struture; $t\text{-}C_4H_9\text{-}N\text{=}C\text{=}C[N(t\text{-}C_4H_9)(SiMe_2Ph)](SiMe_3)$.

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(Received in Japan 1 May 1986)