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# SYNTHESIS AND THERMAL REARRANGEMENTS OF (TRIMETHYLSILYL)METHYL ISOCYANIDES*

ROBERT WEST AND GERALD A. GORNOWICZ
*Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706 (U.S.A.)*

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## SUMMARY

Mono- (I), bis- (II), and tris(trimethylsilyl)methyl isocyanide (III) have been prepared and characterized. All three rearrange upon heating to 150°. (I) gives (trimethylsilyl)acetonitrile; II yields bis(trimethylsilyl)acetonitrile, which undergoes further thermal disproportionation; and III is transformed into tris(trimethylsilyl)keteneimine.

During attempts to prepare a linear, triatomic trianion[1] by treating methyl isocyanide with excess n- or tert-butyllithium, we obtained, after quenching the reaction with trimethylchlorosilane, tris(trimethylsilyl)methyl isocyanide (III), the first example of a new class of organosilicon compounds. This paper describes the synthesis and thermal reactions of three members of this new type of compound.

Subsequent to our initial work, Schöllkopf and Gerhart[2] published the synthesis of lithiomethyl isocyanide. This organolithium reagent reacts readily with trimethylchlorosilane to form (trimethylsilyl)methyl isocyanide (I):

$$CH_3NC + n\text{-}BuLi \xrightarrow[-78^\circ]{\text{THF/hexane}} LiCH_2NC \xrightarrow{Me_3SiCl} \underset{\text{(I), 80\%}}{Me_3SiCH_2NC}$$

(I) is a stable, clear, offensive smelling liquid. It shows a strong isocyanide stretching absorption at 2140 $cm^{-1}$ in the infrared. Its NMR spectrum shows two singlets at $\tau$ 7.25 ($CH_2$) and $\tau$ 9.83 ($Me_3Si$) in the ratio 2/9.

Bis(trimethylsilyl)methyl isocyanide (II) was prepared by a stepwise process of metalation followed by derivatization:

$$CH_3NC + n\text{-}BuLi \rightarrow LiCH_2NC \xrightarrow{Me_3SiCl} Me_3SiCH_2NC \xrightarrow{n\text{-}BuLi}$$

$$Li(Me_3Si)CHNC \xrightarrow{Me_3SiCl} \underset{\text{(II), 40\%}}{(Me_3Si)_2CHNC}$$

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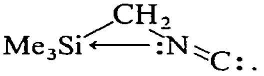
(II) is a yellow, evil smelling oil. It exhibits a strong isocyanide absorption at 2110 $cm^{-1}$ in the IR and two singlets at $\tau$ 7.51 and $\tau$ 9.83, ratio being 1/18, in the NMR spectrum.

The $\alpha$-protons of compounds (I) and (II) do not exhibit long range spin–spin coupling to $^{14}N$ as many simple alkyl isocyanides do. This $^{1}H$–$^{14}N$ coupling is observed in alkyl isocyanides because the high electronic symmetry about nitrogen reduces the quadrupolar relaxation effect of $^{14}N$[3]. The broadness ($\sim$5 Hz at half-height) of the $CH_2$ and CH resonances of (I) and (II) indicates that the $^{14}N$ quadrupolar relaxation effect prevents $^{1}H$–$^{14}N$ coupling in these compounds. Possibly there is some interaction between silicon and nitrogen that destroys the electronic symmetry about nitrogen:



Tris(trimethylsilyl)methyl isocyanide (III) has been prepared by three different procedures. Addition of methyl isocyanide to 3 or more equivalents of n- or tert-butyllithium in alkane or alkane/ether solvents at −78° followed by quenching with trimethylchlorosilane gives (III) in 10–20% yields*. A large amount of black tar is also formed which makes isolation of pure (III) very difficult. (III) is also formed in low yield when methyl isocyanide is metalated and then derivatized with trimethylchlorosilane in a stepwise fashion similar to that used to prepare (II). A large amount of black tar is formed also. However (III) is formed in good yield by metalation of pure (II) with n-butyllithium followed by quenching with trimethylchlorosilane:

$$\underset{(II)}{(Me_3Si)_2CHNC} + n\text{-}BuLi \xrightarrow[-78^\circ]{\text{THF/hexane}} Li(Me_3Si)_2CNC \xrightarrow{Me_3SiCl} \underset{(III),\ 40\%}{(Me_3Si)_3CNC}$$

No difficulty is encountered in isolating pure (III) from the crude yellow product obtained in this manner. (III) is a white, crystalline, offensive smelling solid, m.p. 133–136° with dec. It shows a strong isocyanide band at 2090 $cm^{-1}$ in the IR and a sharp singlet at $\tau$ 9.77 in the NMR. This singlet remains sharp even upon cooling to −50°.

(I) upon heating at 150° in a sealed tube rearranges slowly and cleanly to (trimethylsilyl)acetonitrile[1-3,6]:

$$\underset{(I)}{Me_3SiCH_2NC} \xrightarrow[150^\circ]{} Me_3SiCH_2CN$$

(II) at 150° rearranges to the expected bis(trimethylsilyl)acetonitrile, but the latter undergoes a thermal redistribution reaction to form (trimethylsilyl)acetonitrile and tris(trimethylsilyl)ketenimine:

$$\underset{(II)}{(Me_3Si)_2CHNC} \xrightarrow[150^\circ]{} (Me_3Si)_2CHCN \xrightarrow[150^\circ]{}$$

$$Me_3SiCH_2CN + (Me_3Si)_2C{=}C{=}NSiMe_3$$

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* Trilithiomethyl isocyanide most likely is *not* a precursor to (III). (III) is probably formed by a process of metalation during derivatization, see ref. 1.

These two reactions have similar rates because both unchanged (II) and bis(trimethylsilyl)acetonitrile were still present after 24 h. When bis(trimethylsilyl)acetonitrile is heated at 150°, (trimethylsilyl)acetonitrile and tris(trimethylsilyl)ketenimine are formed.

(III) rearranges quantitatively to tris(trimethylsilyl)ketenimine in 24 h at 150°. Presumably tris(trimethylsilyl)acetonitrile is an unstable intermediate:

$$\underset{\text{(III)}}{(Me_3Si)_3CNC} \xrightarrow[150^\circ]{} [(Me_3Si)_3CCN] \xrightarrow[150^\circ]{} (Me_3Si)_2C{=}C{=}NSiMe_3$$

Increasing the number of trimethylsilyl groups in silylmethyl isocyanides increases the rate of thermal rearrangements. After 24 h at 150° about 50% of (I) and 15% of (II) remained unchanged but (III) had reacted completely. Probably the large bulk of the trimethylsilyl group decreases the stability of the isocyanide.

With the recent resurging interest in isocyanide chemistry[4] silylalkyl(aryl) isocyanides should prove to be valuable intermediates for the synthesis of new organosilicon compounds and complexes.

## EXPERIMENTAL SECTION

n-Butyllithium was obtained from Foote Mineral Co. Methyl isocyanide was prepared by the method of Casanova, Schuster and Werner[5]. Trimethylchlorosilane was purchased from Dow Corning Corp. NMR spectra were run on a Varian A60 spectrometer. Infrared spectra were obtained on a Perkin–Elmer Model 457 spectrometer. Boiling points and melting points are uncorrected. Gas chromatography (GLC) separations were made on a Varian Aerograph Model 700 chromatograph using a column packed with General Electric Co SE-30 or QF-1 silicone on chromosorb W. Analyses were obtained from Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.

### *(Trimethylsilyl)methyl isocyanide (I)*

Lithiomethyl isocyanide was prepared by the procedure of Schollkopf and Gerhart[2]. A solution of 3.3 ml (0.06 mole) of methyl isocyanide in 50 ml of THF was added slowly to a solution of 45 ml of 1.6 *M* n-butyllithium (0.07 mole) in hexane and 50 ml of THF at −78°. After 30 min the mixture was added, via a 100 ml syringe, to a solution of 13 ml (0.1 mole) of trimethylchlorosilane in 50 ml of THF at −78°. Reaction was stirred 2 h (negative Gilman Test) then warmed to room temperature. THF was removed by distillation and replaced with 50 ml of hexane. Lithium chloride was removed by filtration. Distillation of the filtrate on a 6-inch Vigreux column gave 5.4 g of liquid, b.p. 65–100°/80 mm. NMR showed this liquid to be 85% (I) and 15% n-butyltrimethylsilane. (I) could not be purified by preparative GLC because it rearranged to (trimethylsilyl)acetonitrile. Therefore the sample was redistilled to give 2.5 g of (I), b.p. 80–90°/80 mm, $n_D^{22}$ 1.4160. Yield of (I) was about 80% and of (II) about 5%. (I) was characterized as follows: IR (neat), $\nu$ (cm$^{-1}$) 2140 (−NC), 1255 ($Me_3Si$); NMR ($CCl_4$, TMS) $\tau$ 7.25 (s, 2, $CH_2$) and $\tau$ 9.83 (s, 9, $Me_3Si$). (Found: C, 53.6; H, 10.1; N, 11.0. $C_5H_{11}NSi$ calcd.: C, 53.0; H, 9.8 N, 12.4%.)

### *Bis(trimethylsilyl)methyl isocyanide (II)*

Lithiomethyl isocyanide was prepared from 2.2 ml (0.04 mole) of methyl isocyanide and 25 ml of 1.6 *M* n-buthyllithium (0.04 mole) in hexane as described above. After 30 min, 5.0 ml (0.04 mole) of trimethylchlorosilane was added rapidly. After a negative Gilman Test was obtained ($\frac{1}{2}$ h) and additional 25 ml of 1.6 *M* n-butyllithium solution was added slowly. After 30 min, another 5.0 ml (0.04 mole) of trimethylchlorosilane was added. Mixture was worked-up in the manner described above to give 3 g (40%) of (II), b.p. 70–75°/1 mm; $n_D^{22}$ 1.4469, IR (neat); $\nu$ (cm$^{-1}$) 2110 (–NC) and 1250 ($Me_3Si$). NMR ($CCl_4$, TMS): $\tau$ 7.51 (s, 1, CH) and $\tau$ 9.83 (s, 18, $Me_3Si$). (Found: C, 52.0; H, 10.6; N, 7.6. $C_8H_{19}NSi_2$ calcd.: C, 51.8; H, 10.3; N, 7.6%.)

*Tris(trimethylsilyl)methyl isocyanide (III)*

A solution of 1.8 g (0.01 mole) of bis(trimethylsilyl)methyl isocyanide (II) in 10 ml of THF was added slowly to 6 ml of 1.6 *M* n-butyllithium (0.01 mole) in hexane and 10 ml of THF at −78°. After 20 min 1.6 ml (0.015 mole) of trimethylchlorosilane was added. Reaction was stirred for 6 h at −78° (negative Gilman Test) and warmed to room temperature. Solvent was removed with a rotary evaporator to give a yellowish white solid. Product was slurried with 25 ml of ether and filtered. Evaporation of ether gave 2 g of oily, yellow solid, which was recrystallized twice from hexane (2 ml) giving 1 g (40%) of (III)· m.p. 133–136° with dec. (III) was characterized in the following manner: IR (KBr pellet); $\nu$ (cm$^{-1}$) 2090 (–NC) and 1250 ($Me_3Si$); NMR ($CCl_4$, TMS): $\tau$ 9.77 (s, $Me_3Si$). (Found: C, 51.3; H, 10.8; N, 5.4; Si, 32.7. $C_{11}H_{27}NSi_3$ calcd.: C, 51.4; H, 10.6; N, 5.4; Si, 32.4%.)

*Decomposition of silylmethyl isocyanides*

(I) (0.1 ml) was sealed in a glass tube and heated in an oven at 150°. Periodically the tube was opened and the contents analyzed by IR and GLC. Even though the liquid turned black only one product, (trimethylsilyl)acetonitrile, could be found: time (ratio of isocyanide to nitrile): 24 h (1/1); 48 h (1/2); 72 h (1/4).

In a similar manner (II) was heated at 150° for 24 h. IR and GLC analysis showed unreacted (II) and three products (GLC area %): (trimethylsilyl)acetonitrile (30), bis(trimethylsilyl)actonitrile (15), (II) (15), and tris(trimethylsilyl)ketenimine (40). Under identical conditions bis(trimethylsilyl)acetonitrile undergoes a thermal redistribution reaction to give (trimethylsilyl)acetonitrile and tris(trimethylsilyl)-ketenimine.

(III) rearranges quantitatively to tris(trimethylsilyl)ketenimine at 150° in 24 h.

(Trimethylsilyl)acetonitrile (2230 cm$^{-1}$), bis(trimethylsilyl)acetonitrile (2180 cm$^{-1}$), and tris (trimethylsilyl)ketenimine (2020 cm$^{-1}$) were identified by their nitrile and ketenimine stretching bands in the infrared spectra and by comparison of their GLC retention times with those of authentic samples.

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