We are left with the overall conclusion that Mu and H, despite having binding energies and polarizabilities within 0.5% of each other, respond in opposite senses toward the uneven electron distributions of N-heterocyclic aromatic rings. This results in different reaction mechanisms predominating and therefore different reaction products being formed.

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Registry No. H, 12385-13-6; muonium, 12587-65-4; benzene, 71-43-2; pyridine, 110-86-1; pyridazine, 289-80-5; pyrimidine, 289-95-2; pyridine conjugate acid, 16969-45-2; pyridazine conjugate acid, 17009-97-1; pyrimidine conjugate acid, 17009-95-9; pyrazine conjugate acid, 17009-93-7; pyrazine, 290-37-9.

The First Stable Functional Silyl Anions: (Aminosilyl)lithiums

Kohei Tamao,* Atsushi Kawachi, and Yoshihiko Ito*

Department of Synthetic Chemistry
Faculty of Engineering
Kyoto University, Kyoto 606, Japan
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Carbanion chemistry plays a central role in the whole field of organic chemistry:[1] many of a large number of carbanions are functional carbanions stabilized by heteroatoms,[2] including α-heteroatom-substituted carbanions (A). Reported herein are our initial results on the analogous species in silicon chemistry (B).

(A) (B)

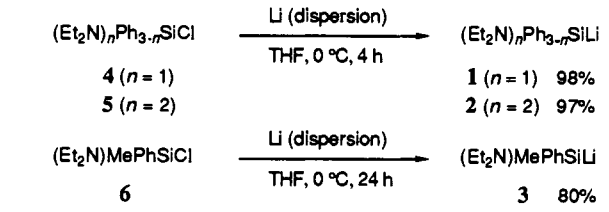
$(Et_2N)Ph_2SiLi$ $(Et_2N)_2PhSiLi$ $(Et_2N)MePhSiLi$

1 2 3

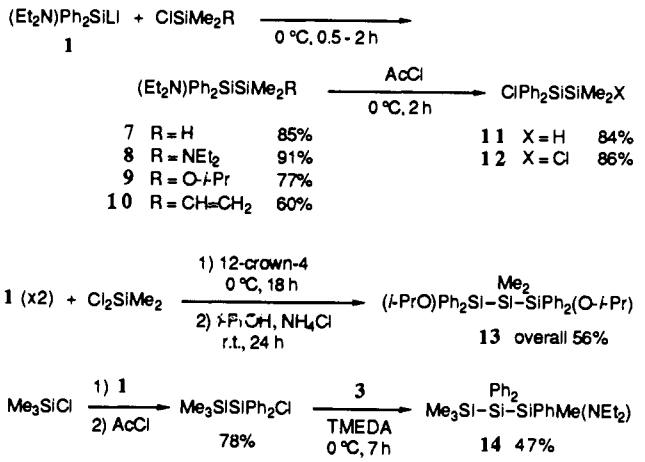
Silyl anions have been studied much less extensively than carbanions.[3,4] Synthetically useful silyl anions have long been limited to only several simple triorganosilyl anions such as Ph_3Si^-,[5,6] Ph_2MeSi^-,[6] $PhMe_2Si^-$,[6] Me_3Si^-,[7] and $(Me_3Si)_3Si^-$.[8] Although three functional silyl anions, Cl_3Si^-,[9] $(RO)_nMe_{3-n}Si^-$,[10] and HPh_2Si^-,[11] have been reported, the first two are postulated active species generated in situ in the presence of quenching agents, and the last is obtained in about 10% yields and tends to polymerize readily. Thus, stable functional silyl anions have never been prepared.

Amino groups (X = NR_2) were chosen as functional groups on silicon because of their high stability toward organometallic reagents;[12] it was thus anticipated that aminosilyl anions must be stable with respect to both intermolecular substitution and intramolecular α-elimination to silylene species. It is noted here

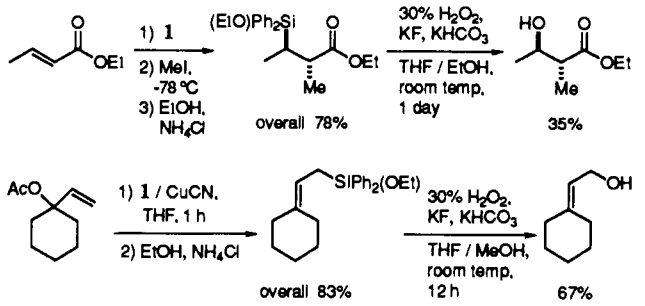
Scheme I



Scheme II



Scheme III



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that recent theoretical studies[4b,c] have predicted the comparable stability of two model systems MeH_2Si^- and $(H_2N)H_2Si^-$, as well as their much higher stability than the corresponding carbanions.

We have now succeeded in the preparation of three stable (amino)(phenyl)silyl anions **1-3** by the standard direct reaction of aminochlorosilanes[13] **4-6** with lithium metal (Scheme I).[14] Thus, the reactions of **4** and **5** with lithium dispersion in THF set in at 0 °C to give immediately deep blue-green solutions; after 4 h, (aminosilyl)lithium **1** and (diaminosilyl)lithium **2** were formed in quantitative yields.[15] The reaction of **6** proceeded slowly to give **3** in 80% yield in 1 day at 0 °C. Significantly, the (aminosilyl)lithium **1** is stable at 0 °C for 6 days, and **2** and **3** are stable for 3 days without a drop in activity.

Functional silyl anions in solution are observable by ^{13}C and ^{29}Si NMR spectroscopy. Thus, aromatic carbons in $(Et_2N)Ph_2SiLi$ (**1**) in THF appear at 158.5 (ipso), 135.6 (ortho), 126.6 (meta), and 123.9 (para) ppm (cyclohexane δ 27.7 ppm as internal standard),[16] and chemical shift changes from the corresponding chlorosilane precursors $\Delta\delta$(SiLi - SiCl)[4j] are +24.3 (ipso), 0 (ortho), -21 (meta), and -7.3 (para) ppm (positive signs denote downfield shifts). The data are quite similar to those for $MePh_2SiLi$[4j] and imply that the Et_2N group exhibits essentially the same effect as the Me group on the charge distribution in the anions. The ^{29}Si resonance of **1** appears at -24.7 ppm in THF (TMS as external reference).

The versatility of the (aminosilyl)lithiums in organosilicon chemistry is apparent from some representative transformations shown in Scheme II.[17] All of the (aminosilyl)lithiums **1-3** undergo coupling with a variety of chlorosilanes to form the corresponding disilanes **7-12**: the Si-N bonds in the primary products can be converted into the Si-Cl bonds by mixture with an acyl chloride such as acetyl chloride, as exemplified by the transformations from **7** and **8** to **11** and **12**, respectively. A one-step introduction of two functional silyl groups into a dichlorosilane and a stepwise Si-Si bond elongation by sequential treatment of a chlorosilane with (aminosilyl)lithiums are exemplified by the formation of trisilanes **13** and **14**, respectively. It is noted that all of the functional disilanes and trisilanes prepared herein are structurally rather simple, but are new compounds barely accessible by conventional methods.

(Aminosilyl)lithiums are also useful reagents for organic synthesis. Thus, **1** or the corresponding copper reagent serves as the hydroxy anion equivalent through the conjugate addition to α,β-unsaturated esters or the allylic substitution followed by oxidative cleavage of the silicon-carbon bonds,[18] as shown in Scheme III.[17] The present procedure is complementary to the known $PhMe_2Si^-$ chemistry,[19] which requires an acid treatment prior to the oxidation. In particular, the latter method cannot be applied to allylic silane systems, because the acid treatment must cleave the particular allyl-silicon bond much faster than the phenyl-silicon bond.[20] The present aminosilyl anion chemistry has afforded a solution to this problem.

The present development, 40 years after the first practical synthesis of silyl anions,[5] has opened up the possibility of preparing a large variety of functional organosilicon compounds, including tailor-made polyfunctional disilanes, oligosilanes, and eventually polysilanes of current interest,[21] as well as new synthetic reagents for organic synthesis.

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Registry No. 1, 140438-35-3; **2**, 140438-36-4; **3**, 140438-37-5; **4**, 33935-31-8; **5**, 87651-58-9; **6**, 140438-38-6; **7**, 140438-39-7; **8**, 140438-40-0; **9**, 140438-41-1; **10**, 140438-42-2; **11**, 140438-43-3; **12**, 140438-44-4; **13**, 140438-45-5; **14**, 140438-46-6; $ClSiMe_2H$, 1066-35-9; $ClSiMe_2(NEt_2)$, 6026-02-4; $ClSiMe_2(O\text{-}i\text{-}Pr)$, 1825-71-4; $ClSiMe_2CH{=}CH_2$, 1719-58-0; Cl_2SiMe_2, 75-78-5; (*E*)-$CH_3CH{=}CHCO_2Et$, 623-70-1; (R*,S*)-$CH_3CH(SiPh_2(OEt))CH(CH_3)CO_2Et$, 140438-47-7; (R*,R*)-$CH_3CH(OH)CH(CH_3)CO_2Et$, 51898-36-3; $\overline{CH_2(CH_2)_4C}{=}CHCH_2SiPh_2(OEt)$, 140438-48-8; $\overline{CH_2(CH_2)_4C}{=}CHCH_2OH$, 932-89-8; 1-acetoxy-1-ethenylcyclohexane, 6318-49-6.

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(15) Typically, under a nitrogen atmosphere, to a suspension of lithium dispersion (16 mg-atom; commercial 25 wt % in mineral oil was washed with dry hexane three times) in dry THF (8 mL) was added dropwise aminochlorosilane **4** (4 mmol) at room temperature. After a few minutes of stirring, the resulting greenish mixture was stirred at 0 °C for 4 h to give a solution of **1**. Lithium wire (fresh cuts) can also be used. Yields of the silyl anions were estimated by GLC analysis of the corresponding disilanes obtained by quenching with Me_3SiCl.

(16) Diaminosilyl anion **2** showed similar chemical shifts: 160.0 (ipso), 134.9 (ortho), 126.6 (meta), and 123.2 (para) ppm.

(17) Isolated yields are shown. All new compounds show satisfactory spectral and analytical data.

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Stereospecific Recognition of Tryptophan Agarose by in Vitro Selected RNA

Michael Famulok† and Jack W. Szostak*

Department of Molecular Biology, Massachusetts General Hospital, Boston, Massachusetts 02114

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RNA molecules can recognize substrates by forming binding pockets and clefts similar to those found in proteins.[1] A better understanding of RNA-substrate recognition would facilitate the development of new ribozymes and receptor molecules based on RNA. Most protein enzymes bind substrates with enormous specificity, and in many cases the recognition is highly stereoselective. Here we show that this high degree of specificity can also be achieved by RNA.

The only well-characterized example of small-molecule recognition by a macromolecular RNA is the binding of guanosine (and its analogues, including arginine) by the self-splicing group I intron from *Tetrahymena*.[2] L-Arginine inhibits GTP binding and subsequent splicing of group I introns from several organisms with a 2-fold higher K_i than the D enantiomer,[3] corresponding to a $\Delta\Delta G$ of 0.4 kcal mol^{-1}. We have addressed the question of stereospecific substrate recognition by RNA by using in vitro selection[4] to isolate RNA molecules that are able to discriminate between D- and L-tryptophan coupled to an agarose matrix (D-tryptophan agarose, D-**Trp-A**). We have previously used in vitro selection to isolate RNAs and DNAs that specifically bind to small organic dye molecules from a large pool of random sequence RNA

† Present address: Institut fur Biochemie der Ludwig-Maximilians-Universität München, c/o Max Planck Institut fur Biochemie, Am Klopferspitz 18a, W-8033 Martinsried, FRG.

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