appropriate geometry to form an intramolecular hydrogen bond, there is insufficient data on the gas-phase basicities of guanidine compounds to determine whether cyclization occurs for this amino acid on the basis of the measurements reported here.

Table II compares prior measurements of the proton affinities of six amino acids with the measurements reported here. To facilitate the comparison, the proton affinity values in the table are referenced to the proton affinity ladder used in the earliest study.[2] We find excellent agreement with Meot-Ner's measurements of the proton affinities of alanine, valine, leucine, and proline and close agreement for glycine and phenylalanine.[2] Likewise, we find excellent agreement with the proton affinity value of alanine reported by Locke and McIver.[3] Our value for the proton affinity of glycine is lower than, but similar to, that measured by Locke and McIver. The comparisons show no systematic differences between ours and prior measurements. Our relative ordering of the proton affinities of the amino acids agrees with that proposed by Bojensen with a few notable exceptions.[13] Bojensen places histidine as the second most basic amino acid, while we find it sixth on our list. In Bojensen's study, glutamine is more basic than glutamic acid, opposite to our finding. We find alanine, methionine, and threonine to be more basic than does Bojensen. While the exact reason for the differences between the two measurements is not known, it should be emphasized that the measurements reported here are based on well-established ion–molecule techniques and theory. Bojensen relates ion abundances in a metastable ion mass spectrum to thermodynamic properties of the product ions, a technique proposed by Cooks and co-workers for measuring relative proton affinities of closely related, monofunctional compounds.[14] The discrepancies between our measurements and those of Bojensen may be a limitation of Cook's method, which has never been tested with structurally diverse, polyfunctional molecules such as the amino acids.

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Different Reaction Paths Taken by Hydrogen Isotopes

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Kinetic isotope effects usually reveal differences in *degree* but not in *kind*. However, in studying the chemistry of muonium (hydrogen's light isotope with a positive muon as nucleus) we find it to behave as a nucleophile in its reactions with aromatic N-heterocyclic solutes in water. This contrasts with the electrophilic character of ^{1}H.[1,2] Muonium (Mu) has one-ninth the atomic mass of ^{1}H but virtually the same reduced mass, ionization energy, size, etc. as all hydrogen isotopes. Hitherto Mu has shown kinetic and spectroscopic isotopic effects which are understandable in terms of its different atomic mass from that of ^{1}H;[3] but in the present study it shows a different *type* of reaction.

Table I. Rate Constants[a] for the Reaction of Muonium Atoms with Aromatic N-Heterocyclic Solutes in Water at ~295 K. Comparison with Published Data on ^{1}H[b]

solute	k_M	k_M/C	k_H	k_H/N	k_M/k_H
benzene	33 ± 3	5.5	9	(1.5)[c]	3.7
pyridine	58 ± 4	12	7.8[d]	7.8	7.4
pyridazine	50 ± 3	12.5	2.7[e]	1.4	18.5
pyrimidine	37 ± 2	9	0.92[f]	0.46	40.2
pyrazine	77 ± 5	19	3.0[g]	1.5	25.7

[a] All k values are in units of 10^8 dm^3 mol^{-1} s^{-1}; k_M/C and k_H/N are described in the text. See footnotes *c* to *g* for pH dependence. [b] Reference 8. [c] Calculated as k_H per C atom. [d] The 7.8 refers to natural pH. At pH ~1, however, $k_H = 1.7 \times 10^8$ M^{-1} s^{-1} for pyridine where >99% of the solutes were protonated; so protonation decreases k_H by ~4.5-fold. This contrasts with Mu, where k_M increased from 58 to 74 ($\times 10^8$) on changing from pH ~7 to pH 1.2, for pyridine. Thus k_M/k_H increases from 7.4 at pH ~7 to 44 at pH ~1. [e] k_H measured at pH ~1, where ~99% of the solutes have one of their N atoms protonated; so the number of unprotonated N atoms is half that relevant to the k_M data. [f] k_H measured at pH ~1, where ~65% of the solutes have one of their N atoms protonated. [g] k_H measured at pH ~1, where ~30% of the solutes have one of their N atoms protonated.

Recently we found that Mu produces the free radical which arises from addition into the aromatic ring of pyrazine at its C atoms.[4] Now we report the rate constants measured for that reaction and Mu's reaction with other N-heterocyclic compounds. Table I gives our observed rate constants (k_M) for reaction of Mu with benzene, pyridine, and the 1,2-, 1,3-, and 1,4-diazines. These data were obtained by measuring the chemical decay rate of muonium using the muon-spin-rotation technique[5] on millimolar aqueous solutions of these compounds at natural pH. They are compared in Table I with the published data for reaction of ^{1}H atoms with the same solutes under similar conditions. Since Mu adds to a ring C,[4] whereas ^{1}H attaches at the more electronegative N atoms,[6] these data have been normalized in columns 3 and 5 of Table I by dividing k_M by the number of C sites on the solutes and k_H by the number of N sites.

Mu is seen to react 3.7 times faster than ^{1}H with benzene. This is not inconsistent with Mu's 3-fold-higher mean thermal velocity stemming from its one-ninth atomic mass: a kinetic isotope effect expected for diffusion-limited reactions.[3] The overall rate constants ratio, k_M/k_H, then increases to 7.4 due to the presence of one ring N, and up to 40 with two N atoms. This ratio rises partly by k_M increasing and partly by k_H decreasing.

The enhancement of k_M by ring nitrogens implies that Mu is "nucleophilic", because N draws electron density from the C atoms where Mu reacts. Preliminary results even suggest that there is a direct proportionality between $-\log(k_M)$ and the Hückel molecular orbital localization energy on each C.[7] By contrast, the presence of the ring N of pyridine seems to switch H's reaction site from C to N (as seen through ESR data[6]). This results in a minor overall decrease in k_H (but an increase per atom where reaction takes place). The presence of a second N atom then reduces the rate further. Also, ^{1}H has already been shown to display a negative Hammett ρ parameter,[1,2] and the differences between the diazines have been interpreted as consistent with this electrophilic character.[1]

There is additional information to be gleaned from the pH dependence of these rate constants arising from protonation of the solute. For pyridine, which is the only N-heterocycle for which data are available, k_M/k_H jumps from 7.4 at pH ~7 to 44 at pH ~1. Almost all of this jump (see footnotes to Table I) emerges from a decrease in k_H. This consequently corroborates the view that reaction of H, but not Mu, occurs on the N atom.

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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

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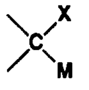
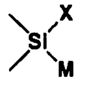
Carbanion chemistry plays a central role in the whole field of organic chemistry:[1] many of a large number of carbanions are functional carbanions stabilized by heteroatoms,[2] including α-heteroatom-substituted carbanions (A). Reported herein are our initial results on the analogous species in silicon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



(A)



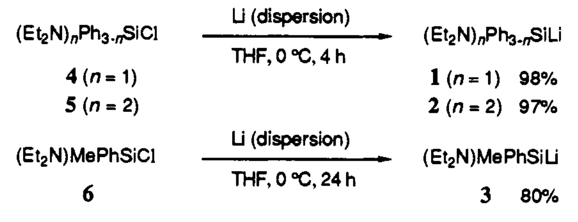
(B)

$(Et_2N)Ph_2SiLi$ **1** $(Et_2N)_2PhSiLi$ **2** $(Et_2N)MePhSiLi$ **3**

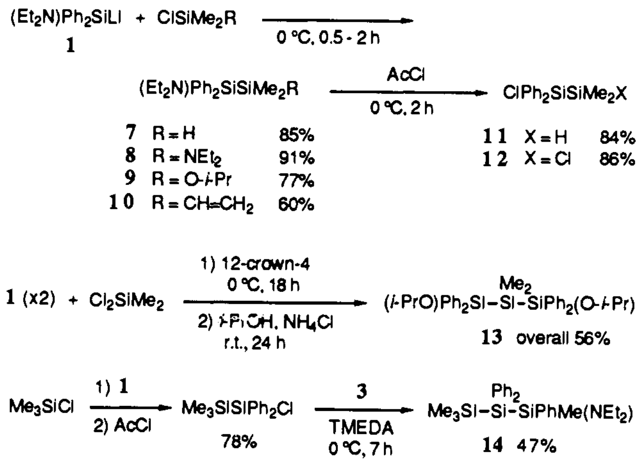
Silyl anions have been studied much less extensively than carbanions.[3,4] Synthetically useful silyl anions have long been limited to only several simple triorganosilyl anions such as Ph_3Si^-,[5,6] Ph_2MeSi^-,[6] $PhMe_2Si^-$,[6] Me_3Si^-,[7] and $(Me_3Si)_3Si^-$.[8] Although three functional silyl 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

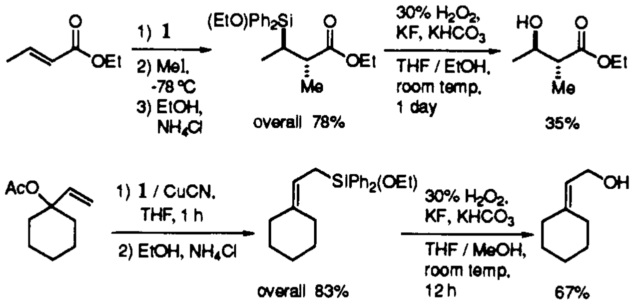
Scheme I



Scheme II



Scheme III



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