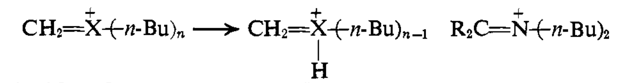
Site-Specific Hydrogen Transfer in Even-Electron Ions

Sir:

The McLafferty rearrangement of a γ-hydrogen to an unsaturated center accompanied by the expulsion of an olefinic fragment is a much studied example of a hydrogen transfer reaction which can be extremely site specific.[1,2] Several authors have documented the importance of localized *radical* character at the receptor site in the odd-electron species as a necessary requirement for a reasonable rate for this reaction[3] as well as for the observed site specificity.[4]

Not all odd-electron ions, however, show this site specificity in the elimination of neutral molecules. While the loss of water from acyclic alcohols is highly site specific,[5] the loss of water from cyclic alcohols[6] and the loss of HX from acyclic halogen compounds is less than site specific.[6b]

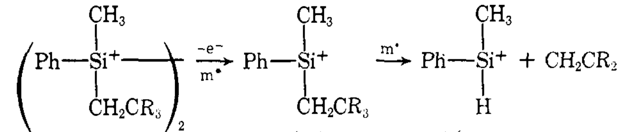
There are also many examples of olefin eliminations accompanied by hydrogen rearrangement from even electron ions, such as **1a–c**. These reactions of **1a–c** → **2a–c** were originally formulated as site specific but more recently have been shown to be extremely *non*-site specific.[7] Recent work suggests that the lack of site specificity in **1a** may be due to scrambling of hydrogen and deuterium atoms in the alkyl chain prior to olefin elimination.[8] Loss of water from even electron ions is also a nonspecific hydrogen abstraction reaction.[6a] To our knowledge the only report of a site-specific hydrogen transfer in an even-electron ion is a somewhat dubious one involving an extremely weak ion derived from **3**.[3]



$$\mathrm{CH_2{=}\overset{+}{X}{-}(\textit{n}\text{-}Bu)_{\textit{n}}} \longrightarrow \mathrm{CH_2{=}\overset{+}{X}(H){-}(\textit{n}\text{-}Bu)_{\textit{n}-1}} \qquad \mathrm{R_2C{=}\overset{+}{N}{-}(\textit{n}\text{-}Bu)_2}$$

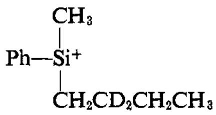
1a, X = O; *n* = 1 **2a**, X = O; *n* = 0 **3**
b, X = S; *n* = 1 **b**, X = S; *n* = 0
c, X = N; *n* = 2 **c**, X = N; *n* = 1

We have discovered several such processes in the course of our investigations of organosilane fragmentation mechanisms.[9] Olefin elimination accompanied by hydrogen rearrangement from R_3Si^+ cations is a well known process,[10] and in fact it has been postulated without evidence that the hydrogen involved was one of the β-hydrogens. We have generated cation **4** (R = H) by electron impact on the appropriate disilane and observed a loss of ethylene to produce the *m/e* 121 ion **5** (R = H). Use of the specifically deuterium-labeled disilane produces **4** (R = D) and subsequent loss of ethylene results in a clean shift of ion **5** to *m/e* 122, indicative of >98% specificity.[12] In order to eliminate any question of the importance of chain length in this process, ion **6**, *m/e* 177 (68), was generated in a similar manner, and the loss of butene was accompanied by >95% site-specific transfer of deuterium to give ion **5** (R = D),[12] again the base peak in the spectrum.



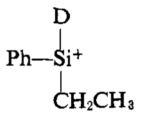
$$\left(\mathrm{Ph{-}\overset{CH_3}{\underset{CH_2CR_3}{Si^+}}{-}}\right)_2 \xrightarrow[m^*]{-e^-} \mathrm{Ph{-}\overset{CH_3}{\underset{CH_2CR_3}{Si^+}}} \xrightarrow{m^*} \mathrm{Ph{-}\overset{CH_3}{\underset{H}{Si^+}}} + \mathrm{CH_2CR_2}$$

(**9**)[11] **4** (51) **5** (100)



$$\mathrm{Ph{-}\overset{CH_3}{\underset{CH_2CD_2CH_2CH_3}{Si^+}}}$$

6



$$\mathrm{Ph{-}\overset{D}{\underset{CH_2CH_3}{Si^+}}}$$

7

Several silicon hydrides were investigated in initial efforts to delineate the scope of this specificity. In spite of the quite different stability and chemistry of these substances, site specificity is maintained in olefin elimination from **7** and related ions.

Although a six-membered ring intermediate has been postulated to account for other rearrangements in even-electron silicon ions[13] and such an intermediate could be envisioned here with transfer of the hydrogen atom to the *ortho* position of the aromatic ring, we believe that this rearrangement represents the first documented case of a site-specific 1,2 elimination of a neutral molecule from an even-electron ion for two reasons. The known difficulty of generating pentacoordinate or double bonded silicon species, both in solution and in other mass spectral studies,[9] suggests great instability for **8**, the expected product ion of hydrogen transfer to an *ortho* position. Secondly, the phenyl ring is not a prerequisite for this rearrangement, and successive olefin eliminations are well documented for trialkylsiliconium ions,[14] as well as for phenyldi-*n*-butylsiliconium ion[15] in which successive hydrogen transfer to the *ortho* position is extremely unlikely.

A possible explanation for the high specificity in this 1,2-elimination reaction could be in the relative size of the silicon atom. Other workers have proposed that as the size of the abstracting atom increases, hydrogen atoms nearer the abstracting atom are more readily transferred.[16] Experiments are under way in our laboratory to study the effects of other metal(loid) atoms and other structural changes on this elimination.

In a parallel study, we have noted a loss of ethylene accompanied by phenyl migration in ions such as **9** and **10**. This rearrangement of an organosilyl cation is much more complex since **9** loses CH_2CD_2 cleanly,

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(10) D. B. Chambers, F. Glockling, and J. R. C. Light, *Quart. Rev.* (London), **22**, 317 (1968).

(11) Relative intensities at 70 eV are shown in parentheses.

(12) Determined from the nominal 20-eV spectrum. The calculation of label retention at 70 eV was complicated by the loss of H(D) from the *m/e* 122 ion, but the specificity was still >90%.

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(15) Unpublished spectrum from this laboratory.

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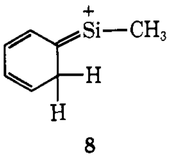

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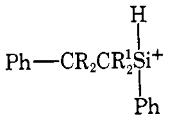

$$\mathrm{Ph{-}CR_2CR'_2\overset{H}{\underset{Ph}{Si^+}}}$$

9, R = H; R′ = D

10, R = D; R′ = H

yet deuterium atoms are scrambled prior to the loss of ethylene from **10**. Our work on this rearrangement and other interesting electron-impact-induced rearrangements of organosilanes is continuing.

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[17] NDEA Fellow, 1967–1968.

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Crystal and Molecular Structure of Narcissidine[1]

Sir:

Despite extensive studies, the chemistry of the Amaryllidaceae alkaloid narcissidine has remained anomalous. The initial formulation, **1a**, which resulted from degradation studies,[2] was revised to **1b** after mass spectral studies on other members of this class of alkaloids showed a fragmentation pattern for C_1–C_2 inconsistent with **1a**.[3] No definitive reaction sequence or spectroscopic study was able to elucidate the configuration of the hydroxyl at C_4. Although most alkaloids containing this ring system but lacking the C_4 substituent have been shown to undergo relatively simple degradations, comparable degradations of narcissidine have failed. Two additional alkaloids, parkacine[4] (**1c**) and ungiminorine[5] (**1d**), have been reported to possess structures related to that of narcissidine. To determine the structure unambiguously, we carried out a single-crystal X-ray structure determination of narcissidine hydrobromide and found the structure to be significantly different from either **1a** or **1b**.

Narcissidine hydrobromide crystallizes in the orthorhombic system with $a = 16.10 \pm 0.01$ Å, $b = 15.53 \pm 0.01$ Å, and $c = 7.34 \pm 0.01$ Å. Density measurements indicate four molecules per unit cell and the systematic extinctions $h00$ ($h = 2n + 1$), $0k0$ ($k = 2n + 1$), and $00L$ ($L = 2n + 1$) uniquely determine the space group $P2_12_12_1$ (D_2^4). The unique reflections ($2\theta \leq 110°$) were collected on an automated Hilger–Watts four-circle diffractometer using filtered Cu (1.5418 Å) radiation. Of the 1376 reflections measured, 1259 were judged observed after background and LP corrections.

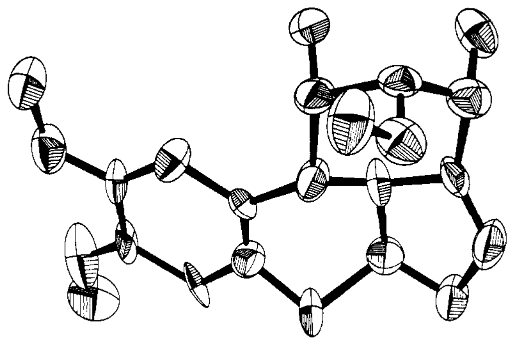
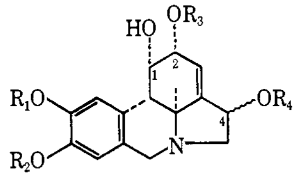
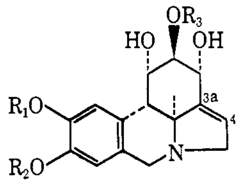


Figure 1.



1a, $R_1 = R_2 = R_4 = CH_3$; $R_3 = H$
1b, $R_1 = R_2 = R_3 = CH_3$; $R_4 = H$
1c, $R_1 = R_2 = CH_3$; $R_3 = R_4 = H$
1d, $R_1{-}R_2 = CH_2$; $R_3 = CH_3$; $R_4 = H$

The initial position of the bromine atom was determined from the three-dimensional Patterson synthesis, and the 24 nonhydrogen atoms were located in subsequent electron density syntheses. Full matrix least-squares refinements in which all atomic positions and anisotropic temperature factors were varied and the atomic scattering factor of bromine was corrected for anomalous dispersion gave a final unweighted R of 0.124 for the 1259 observed reflections. A final difference map showed no peaks larger than 0.4 e/Å^3. The estimated standard deviations are ±0.02 Å for bond lengths and ±1.0° for bond angles. All distances and angles compare well with generally accepted values.[6] Figure 1 is a drawing of the final X-ray model, less the Br. The absolute configuration shown for narcissidine is that found for dihydrolycorine.[7] No abnormally short intermolecular contacts were found.



2a, $R_1 = R_2 = R_3 = CH_3$
2b, $R_1 = R_2 = CH_3$; $R_3 = H$
2c, $R_1{-}R_2 = -CH_2-$; $R_3 = H$

Ironically, this structure (**2a**) was once considered for narcissidine, but discarded because a satisfactory vicinal

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(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Additional support was derived from a grant from the National Institutes of Health (HE-07503).

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