

Journal of Organometallic Chemistry, 217 (1981) 151–156
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

VINYLMETALLOIDS

IV *. INTRAMOLECULAR BOND-FORMING REACTIONS OF VINYLSILANES UPON ELECTRON IMPACT

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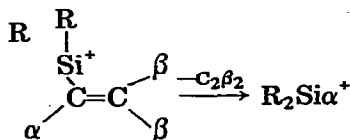
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(Received March 2nd, 1981)

Summary

The behavior of a number of alpha-substituted vinylsilanes upon electron impact in the mass spectrometer is reported. All such compounds exhibit fragment ions which can be understood by a process involving prior loss of a radical fragment from the molecular ion followed by bond formation between the alpha-substituent and the silicon center with loss of the remaining portion of the vinyl moiety. Using the alpha-deuterated vinyltrimethylsilane, this process was shown to be an important one which had not been previously considered for such systems. MIKE ** data were also obtained on alpha bromovinyltrimethylsilane to add support for such a process.

We wish to report an important fragmentation process which occurs for ions derived from vinylsilanes in the mass spectrometer. This process occurs when vinyl-substituted trivalent silicon cations undergo bond formation with groups alpha to the silicon center with loss of the vinylidene portion of the vinyl moiety.



Our studies [1] on vinyl derivatives of silicon, germanium and tin required the preparation and characterization of a wide variety of new compounds. Their behavior upon electron-impact proved to be diagnostically useful. The

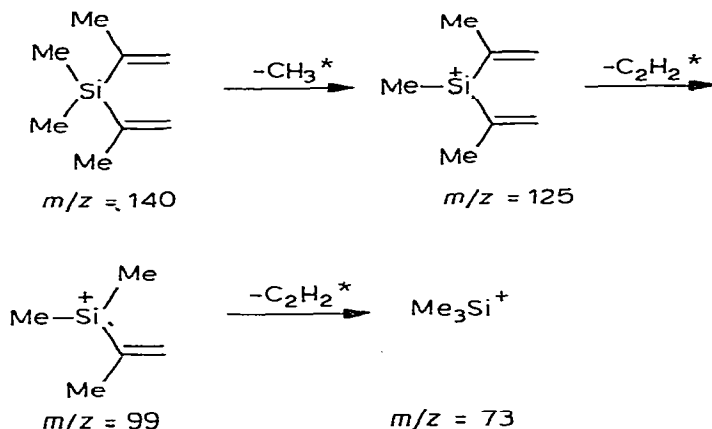
* For part III see ref. 1b.

** MIKE = mass-analyzed kinetic energy.

detailed study of Smolinsky and Vasile [2] on the mass spectral behavior of vinyltrimethylsilane proved to be helpful as a model for our systems. However, in our alpha-substituted vinylsilanes it was evident that another decomposition pathway, which had not been previously considered, must be occurring.

For example, in dimethyl(diisopropenyl)silane, a major fragment at $m/z = 73$ evidently arose from the formation of a trimethylsilyl cation by a complex pathway. Metastable ions at $m/z = 111.6$, 78.5 and 53.8 supported the following unimolecular decomposition sequence to this ion at an operating pressure of 10^{-7} Torr.

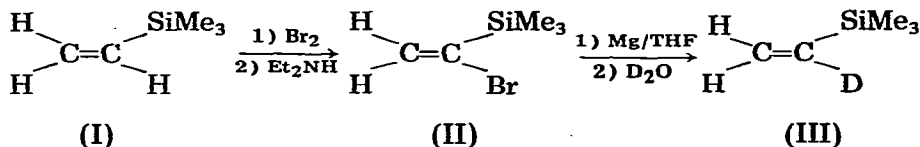
SCHEME 1



While other pathways to the $m/z = 73$ fragment could also be occurring, we were unable to find metastable peaks supporting these other possible pathways (e.g. $140 \rightarrow 99$).

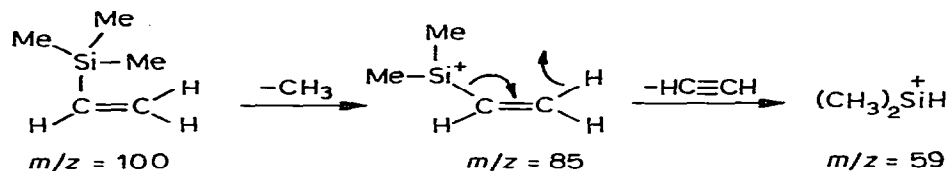
Using a number of different mass spectrometers including a Dupont 21-491B, Varian Mat CH5, CEC-110B or Finnigan 4000 instrument, good qualitative reproducibility of the ion fragment intensities were observed. As a representative case, the CEC-110B instrument was operated using a 7.5 kV accelerating voltage, an electron ionizing energy of 70 eV and a source temperature of 150°C . Samples were introduced using a heated all-glass inlet system.

Wishing to examine the generality of this process, we prepared alpha-bromo-vinyltrimethylsilane (II) using the method of Ottolenghi and coworkers [3] which we converted to alpha-deuteriovinyltrimethylsilane (III) using a Grignard method.

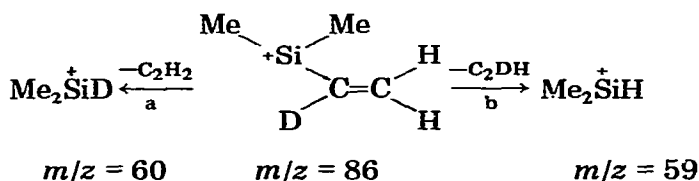


Like Smolinsky and Vasile, we also found that I decomposes in the mass spectrometer to give major ion fragments at $m/z = 85$ and 59 . From their studies and with the results obtained from the corresponding deuterated methyl compound, $(\text{CD}_3)_3\text{SiCH}=\text{CH}_2$, the authors proposed that the major pathway

to the $m/z = 59$ fragment occurred through successive loss of methyl radicals and acetylene.



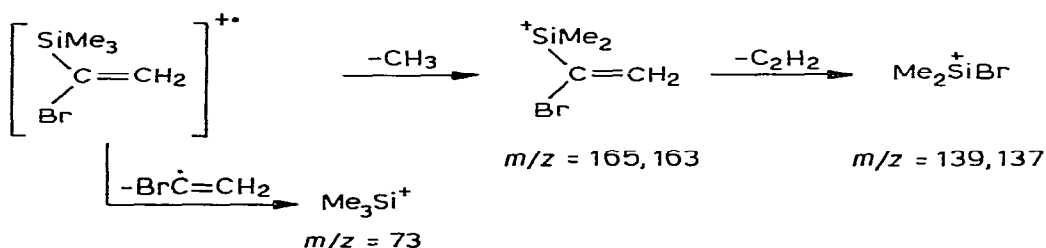
The $85 \rightarrow 59$ transition shown considered only bond formation between the beta hydrogens and the silicon center. This pathway has evidently been accepted by others in related systems [4]. We felt that examination of the behavior of III in the mass spectrometer would be useful in determining whether or not the alpha hydrogen could be involved in this process.



Indeed, operating at 70 eV, we found that both ions were formed in a near statistical ratio of ca. 1 : 1.8 for the 60 and 59 peaks using either the Dupont or CEC instruments. Diminution of the ionization voltage to 13 eV lowered this ratio to ca. 1 : 1.5 using the former instrument, but had little effect on this ratio using the latter instrument. Scrambling processes have been found to increase at lower ionizing voltages [5], suggesting that this mechanism is not wholly responsible for the formation of the $m/z = 59$ and 60 ions. Additionally, decomposition of the trimethylsilyl cation to give the $m/z = 59$ fragment was shown to become more significant at low ionizing voltages [2]. Thus, the modest increase in the $m/z = 60$ fragment at 13 eV relative to the $m/z = 59$ fragment over the values observed at 70 eV adds support to our view that two major pathways are responsible for the formation of the $m/z = 59$ fragment derived from vinyltrimethylsilane.

The behavior of II upon electron impact was also examined. The major fragments can be explained using the following scheme.

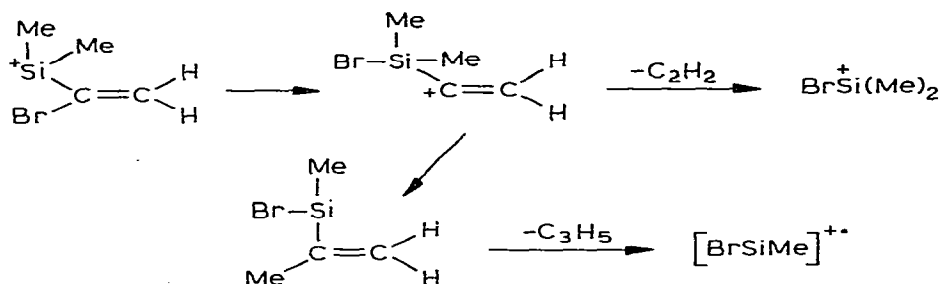
SCHEME 2



Using a mass-analyzed ion kinetic energy spectrometer [6], we examined the decomposition of the $m/z = 163$ ion and found it to give the $m/z = 137$ ion as well as several minor (ca. 13% of the 137 peak) ion fragments. It is impor-

tant to point out that none of these minor pathways included loss of a $\text{BrC}\equiv\text{CH}$ moiety, which may have been expected from the previous studies on I and related compounds [2,4]. However, one of the minor processes occurring for the $m/z = 163$ ion corresponded to loss of C_3H_5 fragment. This suggested that this ion may well be undergoing a non-synchronous bromine-silicon bond formation with loss of the C_2H_2 moiety (Scheme 3).

SCHEME 3



Three-center bond-forming reactions are quite rare in the mass spectrometer [7]. While we cannot be certain of the exact nature of the process, it is clear that bond formation occurs between the alpha substituent and the silicon moiety in a wide variety of vinylsilanes (see Table 1). It is important

TABLE 1

REPRESENTATIVE VINYLILANES WHICH FORM FRAGMENTS BY MIGRATION OF THE alpha-SUBSTITUENT^a

Entry	Compound	Base ion (m/z)	Fragment (% base)
1.	$\text{Me}_3\text{SiCD}=\text{CH}_2$	$\text{Me}_2^+\text{SiCD}=\text{CH}_2$ (86)	Me_2^+SiD (28)
2.	$\text{Me}_3\text{SiCBr}=\text{CH}_2$	Me_2^+SiBr (137, 139)	Me_2^+SiBr (100)
3.	$\text{Me}_3\text{SiC(OMe)}=\text{CH}_2$	Me_3Si^+ (73)	$\text{Me}_2^+\text{SiOMe}$ (47)
4.	$\text{Me}_2(\text{Ph})\text{SiC(OMe)}=\text{CH}_2$	$\text{Me}_2(\text{Ph})\text{Si}^+$ (135)	MePhSiOMe (21) $\text{Me}_2\text{Si}^+\text{OMe}$ (19) $\text{Me}_2\text{Si}^+\text{OMe}$ (100)
5.	$Z\text{-Me}_3\text{SiC(OMe)}=\underset{\text{CH}=\text{CH}_2}{\text{CH}}$	Me_3Si^+ (73), $\text{Me}_2^+\text{SiOMe}$ (89)	$\text{Me}_2\text{Si}^+(\text{CH}_2\text{CH}=\text{CH}_2)$ (46)
6.	$Z\text{-Me}_3\text{SiC}=\underset{\text{CH}_2\text{CH}=\text{CH}_2}{\text{CH}}(\text{n-C}_7\text{H}_{15})$	Me_3Si^+ (73)	$\text{Me}_2^+\text{SiOSiMe}_3$ (85)
7.	$\text{Me}_3\text{SiC(OSiMe}_3)=\text{CH}_2$	Me_3Si^+ (73)	$\text{Me}_2^+\text{SiOMe}$ (86)
8.	$E\text{-Me}_3\text{SiC(OMe)}=\text{CHPh}$	M^+ (206)	$\text{Me}_2^+\text{SiOMe}$ (100)
9.	$\text{Me}_2\text{Si}(\text{CPh}=\text{CH}_2)\text{C(OMe)}=\text{CH}_2$	Me_2SiOMe (89)	$\text{Me}_2^+\text{SiOMe}$ (100)
10.	$\text{Me}_2\text{Si}(\text{C(Me)}=\text{CH}_2)_2$	$\text{MeSi}(\text{C(Me)}=\text{CH}_2)_2$ (125)	Me_3Si^+ (100)
11.	$\text{Me}_2\text{Si}(\text{CPh}=\text{CH}_2)_2$	$\text{Me}_2\text{Si}^+\text{Ph}$ (135)	Me_2^+SiPh (100)
12.	$\text{Ph}_2\text{Si}(\text{C(OMe)}=\text{CH}_2)_2$	Ph_2SiOMe (213)	Ph_2SiOMe (100)
13.	$\text{MeSi}(\text{C(OMe)}=\text{CH}_2)_3$	MeSi(OMe)_2 (105)	$^+\text{Si(OMe)}_3$ (58)
14.	$\text{Si}(\text{C(OMe)}=\text{CH}_2)_4$	M^+ (256)	$^+\text{Si(OMe)}_3$ (58)

^a For entries 1, 5, 7, 8, 13, and 14, a Dupont 21-491B instrument was used to obtain the tabulated data. Except for 6 (CEC) and 12 (Finnigan), the remaining compounds were analyzed on a Varian MAT CH5 or CH7 mass spectrometer. However, compounds 1 and 3 were also analyzed on the CEC instrument which gave similar fragment ion intensities.

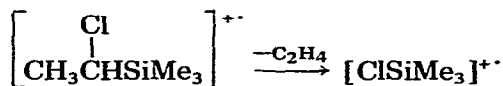
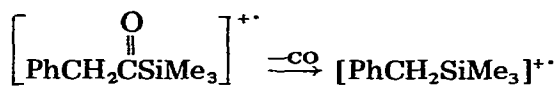
to point out that we have not observed fragments corresponding to bond formation from the molecular ion of vinylsilanes. This process evidently occurs only after the initial loss of a radical fragment.

We have also examined a variety of vinyl derivatives of germanium and tin. Bond formation of the type described for the silicon compounds probably occurs for these compounds as well.

For example, as was found for α -methoxyvinyl(trimethyl)silane (cf. entry 3, Table 1), the corresponding germanium and tin derivatives gave fragment ions corresponding to a Me_2MOMe^+ formulation with an intensity of ca. 50% of the base ion fragment (Me_3M^+). Owing to the complex isotopic distribution observed for these metalloids, we were unable to obtain conclusive metastable ion data to support a similar fragmentation pathway to these ions as was found for the silicon compounds.

In addition to the migrating groups mentioned above, we have found that methoxy, allyl, phenyl, and trimethylsiloxy groups also undergo this process (see Table 1). We have even observed up to three migrations in the methoxy case to give formulation of the type $\text{Si}(\text{OMe})_3^+$ (i.e. see entries 13 and 14, Table 1).

In order to determine whether or not such bond-forming reactions were important for other types of functionalized organosilanes, the behavior of benzoyltrimethylsilane and alpha-chloroethylsilane in the mass spectrometer were examined. However, both compounds gave ions which corresponded to bond formation from the molecular ion*.



While we were able to attribute peaks to loss of a methyl radical from the molecular ion, we were unable to find support for the alpha-substituent to silicon bond formation from these fragments.

Thus, it would appear that vinylsilanes exhibit a special behavior in that prior loss of a radical fragment is necessary in order to initiate bond formation with an alpha substituent, with loss of the remaining portion of the vinyl moiety.

Acknowledgement

We thank Professors R.H. Shapiro and R.G. Cooks for helpful discussions regarding this work. In addition, we would like to express our thanks to Ms. Marylou Sigsby for carrying out the MIKE experiment and to Dr. James Campbell for providing us with the spectrum of *Z*-4-trimethylsilyldodeca-1,4-diene.

* For other examples of systems showing related behavior see ref. 8.

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