

Rearrangement of TMS of halogenated saturated aliphatic alcohols in EI mass spectra

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Introduction

Analysis of electron ionization mass spectra of trimethylsilyl (TMS) of halogenated saturated aliphatic alcohols reveal characteristic ions $^+\text{CH}_2\text{-O-Si(CH}_3)_2\text{X}$ and $^+\text{Si(CH}_2)_n\text{X}$ ($\text{X}=\text{Cl, Br or I}$) from rearrangement and halogen migration. This fragmentation pathway does not appear to have been previously reported. It enables the enhancement of spectrum prediction by the NIST MS interpreter software tool.

Materials and Methods

Six compounds were purchased from Sigma and dissolved in acetonitrile at concentrations of 1mg/ml, and spectra were acquired at 70eV on a triple quadrupole GC/MS instrument equipped with a 15m x 0.25mm x 0.25um non-polar column with a helium flow rate of 1ml/min. The collision gas of GC/MS/MS was using N_2 and the collision energy was 5V, 10V, 20V, and 40V. Other spectra of compounds in the below table were from the NIST mass spectra library.

$\text{X-(CH}_2)_n\text{-CH}_2\text{-O-Si(CH}_3)_3$

No	X	n	M, m/z	b, m/z(%)	c, m/z(%)	No	X	n	M, m/z	b, m/z(%)	c, m/z(%)	No	X	n	M, m/z	b, m/z(%)	c, m/z(%)
1	Cl	3	180	123 (100)	93 (58)	7	Br	1	210	No	137 (100)	12	I	5	300	215 (18)	185 (21)
2	Cl	4	194	123 (40)	93(33)	8	Br	2	210	167 (60)	137 (87)	13	I	9	356	215 (10)	185 (8)
3	Cl	5	208	123 (33)	93 (22)	9	Br	5	252	167 (22)	137 (11)	14	I	10	370	215 (7)	185 (8)
4	Cl	7	236	123 (21)	93(12)	10	Br	6	266	167 (17)	137(11)						
5	Cl	9	264	123 (19)	93 (10)	11	Br	7	280	167 (13)	137 (6)						
6	Cl	10	278	123 (18)	93 (9)												

Table 1. Studied compounds and their characteristic ions b and c

Results

1. Mass spectrum of 4-chlorobutan-1-ol, TMS has characteristic ion b (m/z 123) and ion c (m/z 93).

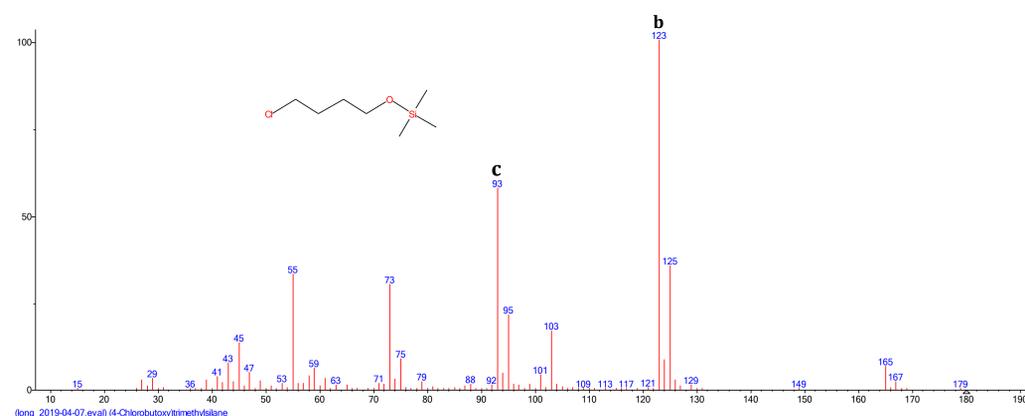


Figure 1. EI Mass spectrum of 4-chlorobutan-1-ol, TMS [compound 1]

2. GC/MS/MS Product ion scan of the ion a (M-CH_3) $^+$ (m/z 165) by collision energy of 5V. The ion b (m/z 123) and ion c (m/z 93) are daughter ions of the ion a (M-CH_3 , m/z 165).



Figure 2. MS/MS Product ion scan of 4-chlorobutan-1-ol, TMS with the ion a (M-CH_3) $^+$, (m/z165).

3. GC/MS/MS Product ion scan of the ion (m/z 123) by collision energy of 5V. The ion c (m/z 93) is a daughter ion of the ion b (m/z 123).

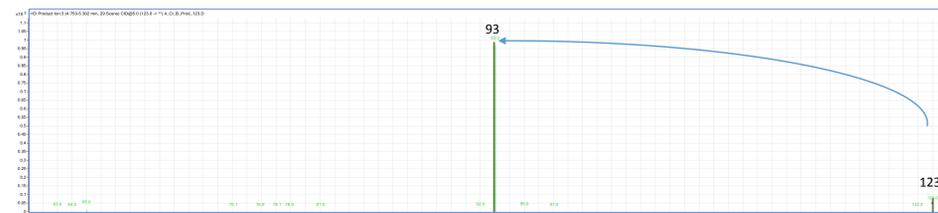
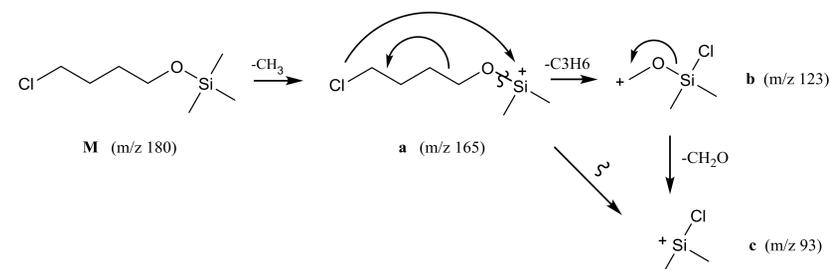


Figure 3. MS/MS Product ion scan of 4-chlorobutan-1-ol, TMS with the ion (b) (m/z 123).

The mass spectrum of 4-chlorobutan-1-ol, TMS (Figure 1) shows a base peak at m/z 123 (ion b) and a second most intense peak at m/z 93 (ion c). They can't be recognized by the MS interpreter software tool. It cannot be explained by a simple reaction. Based on above GC/MS/MS results, the formation of the ion b begins with CH_3 cleavage (ion a) and migration of the chlorine from the carbon to the siliconium center with simultaneous loss of cyclopropane. The ion c results from the ion b by losing CH_2O or direct from the ion a by migration of chlorine and inductive cleavage of O-Si bond.



Spectra of compounds (1-14) generated similar fragment ions b ion c in EI mass spectrometer (Table 1). The ion b and ion c are characteristic ions $^+\text{CH}_2\text{-O-Si(CH}_3)_2\text{X}$ and $^+\text{Si(CH}_2)_n\text{X}$ ($\text{X}=\text{Cl, Br or I}$) for the trimethylsilyl (TMS) derivatives of halogenated saturated aliphatic alcohols. In this case m/z 123, 93 are for $\text{X}=\text{Cl}$; m/z 167, 137 are for $\text{X}=\text{Br}$; m/z 215, 185 are for $\text{X}=\text{I}$. The fragmentation pathway is illustrated on the next panel:

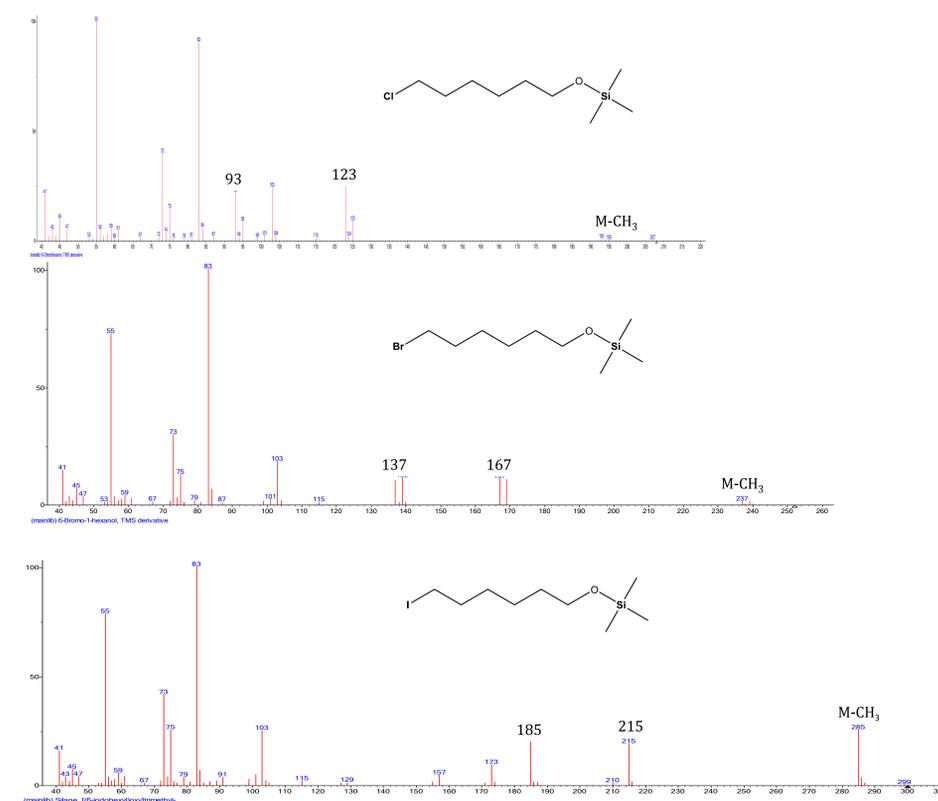
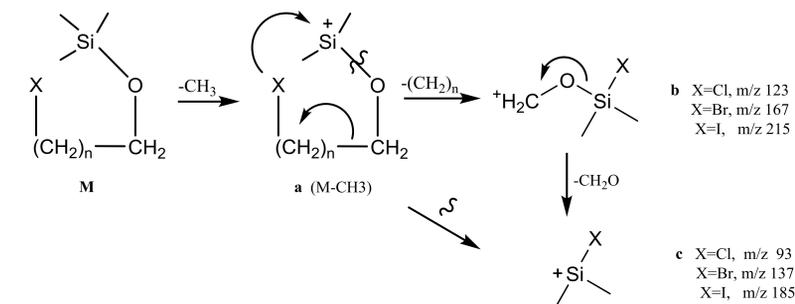


Figure 4. Mass spectrum of 6-halogenhexan-1-ol, TMS [compound 3, 9 and 12]

Conclusions

The ion b $^+\text{CH}_2\text{-O-Si(CH}_3)_2\text{X}$ and ion c $^+\text{Si(CH}_2)_n\text{X}$ ($\text{X}=\text{Cl, Br or I}$) are characteristic ions of the trimethylsilyl (TMS) derivatives of halogenated saturated aliphatic alcohols. Both ions result from migration of a halogen atom from the carbon to the siliconium ion center with simultaneous loss of $(\text{CH}_2)_n$ or $[(\text{CH}_2)_n+\text{CH}_2\text{O}]$ from $(\text{M-CH}_3)^+$. The ion c is derived by loss of CH_2O from ion b.

The driving force for this facile rearrangement of electronegative groups such as halogen is the considerably greater strengths of silicon-halogen bonds compared to corresponding carbon-halogen bonds. A Si-Cl bond is 91 kcal/mol compared to a C-Cl bond is 81 kcal/mol. (C. Eaborn, "Organosilicon Compounds", Butterworths, London, 1960, p 90)