Silicon-Directed Carbon-Carbon Bond Cleavage in the Removal of Angular Substituents on Octalins

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The silicon directing effect on the cleavage of C–C bonds in radical cations was investigated. Electron impact induced fragmentation was performed in the gas phase on six pairs of cis and trans isomers of 5-(trimethylsilyl)bicyclo[4.4.0]dec-1-enes with an angular CHO, COOEt, or CH_2OH group at the C-6 position. For aldehydes including *trans*-6-formyl-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-en-3-one (**2**), *trans*-6-formyl-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-ene (**4**), *trans*-6-formyl-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-en-3-one 3-(ethylene thioacetal) (**6**), and 1-butyl *r*-3-[*c*-6-formyl-*t*-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-enyl] sulfide (**8**), their parent radical cations underwent fragmentation to give $(M^{\bullet+} - {}^{\bullet}CHO)$ as the main species. By the same fashion, the radical cation of the ester ethyl *trans*-3-oxo-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-ene-6-carboxylate 3-(ethylene thioacetal) (**10**) gave $(M^{\bullet+} - {}^{\bullet}COOEt)$; the radical cation of the alcohol *trans*-6-(hydroxymethyl)-5-(trimethylsilyl)bicyclo-[4.4.0]dec-1-ene (**12**) gave $(M^{\bullet+} - {}^{\bullet}CH_2OH)$. In contrast, the corresponding cis radical cations, resulting from *cis*-6-formyl-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-en-3-one (**1**), *cis*-6-formyl-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-ene (**3**), *cis*-6-formyl-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-en-3-one 3-(ethylene thioacetal) (**5**), and 1-butyl *r*-3-[*c*-6-formyl-*c*-5-(trimethylsilyl)bicyclo[4.4.0]dec-1-enyl] sulfide (**7**) produced $(M^{\bullet+} - {}^{\bullet}CH_3)$ as the main species. These results from mass spectrometry indicated that the trimethylsilyl group at the β-position directed the angular C–C bond cleavage in octalin radical cations. The trimethylsilyl group, being trans to the angular substituent, provided greater driving force than the trimethylsilyl group being cis in the cleavage of the C–C bond. The fragmentation pattern was independent of the functionalities on the octalin framework and the oxidation state of the angular oxygenated methyl substituent.

Introduction

Trialkylsilyl groups can stabilize carbocations,[1-3] carbanions,[4,5] and carbon radicals.[6-11] The stabilizing ability of silyl groups has been utilized to direct the carbon–carbon bond cleavage.[12] Generally these reactions are performed in solution. The directing effect is thus likely influenced by counterions and solvents. We intended to investigate the "net" effect of the trimethylsilyl group on carbon–carbon bond cleavages.

Information from mass spectrometry can reveal the influence of a functional group on unimolecular fragmentations. The counterion and solvent effects do not exist during molecular ion fragmentations induced by electron impact in the gas phase. The fragmentation patterns in mass spectrometry could also reveal clues for the understanding of photochemical reactivity of related organic species.[13] In addition, establishment of new fragmentation patterns may be useful in the identification of the stereoconfiguration of isomers.[14-19]

Regarding the fragmentation pattern of molecular radical cations, little information is available on the anchimeric effect resulting from organosilyl groups. We found that the trimethylsilyl group can direct the C_β–C_γ bond cleavage in radical cations; the C_β–C_γ bond connected an angular oxygenated methyl substituent to an octalin framework.

Results

Octalins possess a rigid skeleton and thus provide us an ideal geometry to study the Me_3Si-directed C–C bond cleavage. The alignment of the Me_3Si–C bond and the C_β–C_γ bond to be broken may significantly influence the efficiency of the bond cleavage. The trimethylsilyl group in trans isomers (e.g., **2**, **4**, **6**, **8**, **10**, and **12**) could be axial. Axial substituents in cyclohexanes generally cause an upfield shift of the carbons at the α-position in ^{13}C NMR spectroscopy.[20] Comparing ^{13}C NMR spectra of **1** and **2** in $CDCl_3$, we found that the carbon attached to the trimethylsilyl group in **2** (δ 27.07 ppm) was 6.27 ppm more upfield than that in **1** (δ 33.34 ppm). Therefore, the Me_3Si–C bond should be near trans coplanar to the C–C

Scheme I

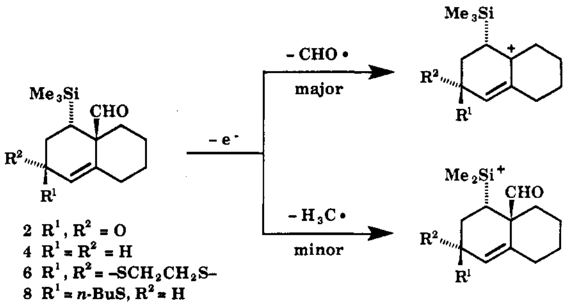

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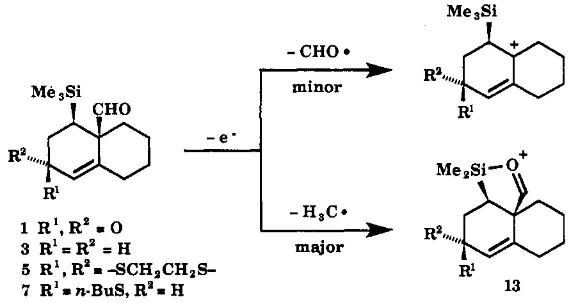
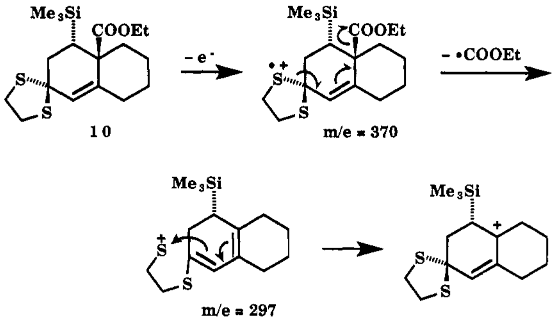
Table I. Relative Abundances (% Base) of ($M^{\bullet +}$ - $^{\bullet}CH_3$) and ($M^{\bullet +}$ - $^{\bullet}CHO$) in Mass Spectra of Compounds 1-8

ion	1		2	3		4	5		6	7		8
($M^{\bullet +}$)	0		0	9.1		0.7	2.8		3.0	4.5		0
($M^{\bullet +}$ - $^{\bullet}CH_3$)	8.6	>	3.9	11.0	>	5.6	18.4	>	0.6	0.2	>	0
($M^{\bullet +}$ - $^{\bullet}CHO$)	4.8	<	65.3	7.2	<	36.1	5.6	<	39.7	0	<	1.0

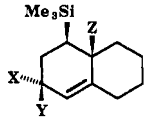
Scheme II



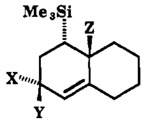
Scheme III



bond that connected the oxygenated methyl substituent (i.e., CHO) to the octalin framework. The trimethylsilyl group in cis isomers (e.g., 1, 3, 5, 7, 9, and 11) should be equatorial; thus the Me_3Si–C bonds were skewed to the C–C bonds.



1 X,Y = O; Z = CHO
3 X = Y = H; Z = CHO
5 X,Y = -SCH2CH2S-; Z = CHO
7 X = H; Y = n-BuS; Z = CHO
9 X,Y = -SCH2CH2S-; Z = COOEt
11 X = Y = H; Z = CH2OH



2 X,Y = O; Z = CHO
4 X = Y = H; Z = CHO
6 X,Y = -SCH2CH2S-; Z = CHO
8 X = H; Y = n-BuS; Z = CHO
10 X,Y = -SCH2CH2S-; Z = COOEt
12 X = Y = H; Z = CH2OH

We studied the fragmentation pattern on molecular radical cations of six pairs of cis and trans trimethylsilyl octalins (1–12). These isomers had different functionalities on the octalin framework and on the angular substituent.

We observed two main fragmentation pathways in the mass spectra of the molecular radical cations resulting from 1–12 (Schemes I–IV): expulsion of the angular substituent (i.e., $M^{\bullet +}$ - $^{\bullet}CHO$, $M^{\bullet +}$ - $^{\bullet}COOEt$, or $M^{\bullet +}$ - $^{\bullet}CH_2OH$) and removal of a methyl radical ($M^{\bullet +}$ - $^{\bullet}CH_3$). All of the trans isomers (i.e., 2, 4, 6, 8, 10, and 12) preferred to expel the angular substituent; most of the cis isomers (1, 3, 5, 7, and 9) mainly lost a methyl radical. The relative intensities are listed in Tables I and II. These fragmentation patterns of cis and trans isomers were independent of the functionalities present on the octalin framework.

Scheme IV

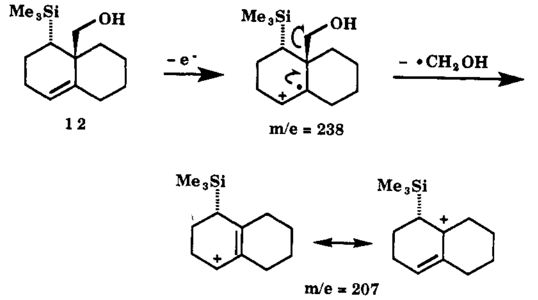


Table II. Relative Abundances (% Base) of ($M^{\bullet +}$ - $^{\bullet}CH_3$), ($M^{\bullet +}$ - $^{\bullet}CH_2OH$), and ($M^{\bullet +}$ - $^{\bullet}COOEt$) in Mass Spectra of Compounds 9-12

ion	9		10	11		12
($M^{\bullet +}$)	4.0		3.6	0		0.4
($M^{\bullet +}$ - $^{\bullet}CH_3$)	8.3	>	3.6	4.1	>	0
($M^{\bullet +}$ - $^{\bullet}CH_2OH$)	–		–	11.1	<	37.2
($M^{\bullet +}$ - $^{\bullet}COOEt$)	5.2	<	20.9	–		–

In all spectra of silyl octalins 1–12, we observed strong peaks resulting from Me_3Si^+ and its fragments. A series of silyl cations was assigned as follows:[21-23] $CH_3Si^+ = 43$, $(CH_3)H_2Si^+ = 45$, $(CH_3)_2HSi^+ = 59$, and $Me_3Si^+ = 73$. Two peaks were related to oxygenated silyl cationic species:[24,25] $CH_3Si^+OH = 45$ and $(CH_3)_2Si^+OH = 75$.

Discussion

Trans trimethylsilyl aldehydes gave a large ratio for ($M^{\bullet +}$ - $^{\bullet}CHO$):($M^{\bullet +}$ - $^{\bullet}CH_3$); it was 17:1 for 2, 6.4:1 for 4, 66:1 for 6, and 1.0:0 for 8 (Scheme I and Table I). Conversely, cis trimethylsilyl aldehydes gave a small ratio for ($M^{\bullet +}$ - $^{\bullet}CHO$):($M^{\bullet +}$ - $^{\bullet}CH_3$); it was 1:1.8 for 1, 1:1.5 for 3, 1:3.3 for 5, and 0:0.2 for 7 (Scheme II and Table I). Trimethylsilyl octalins 9 and 10 had an angular ester group. Similarly to aldehydes 2, 4, 6, and 8, the radical cation of trans ester 10 had a great tendency to expel $^{\bullet}COOEt$ (Scheme III).[26] The ratio for ($M^{\bullet +}$ - $^{\bullet}COOEt$):($M^{\bullet +}$ - $^{\bullet}CH_3$) was 5.8:1 (Table II). The radical cation of the corresponding cis isomer (9), however, favored the loss of a methyl radical; the ratio for ($M^{\bullet +}$ - $^{\bullet}COOEt$):($M^{\bullet +}$ - $^{\bullet}CH_3$) was 1:1.6. Furthermore, the ratio for ($M^{\bullet +}$ - $^{\bullet}CH_2OH$):($M^{\bullet +}$ - $^{\bullet}CH_3$) of trans trimethylsilyl alcohol 12 was much larger than that of the corresponding cis isomer 11: 37:0 for 12 and 2.7:1 for 11.

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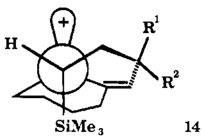
Kirkien-Konasiewicz et al.[27] found that the radical cations of cholesterol derivatives lost the 10β-hydroxymethyl group mainly in the form of $CH_2{=}O$. They suggested that H$^\bullet$ transfer occurred between the OH group and the C=C bond. Shoppee et al.[28] found that radical cations of cholestanol derivatives underwent fragmentation to expel the angular group in the form of $^\bullet CH_2OH$. These cholestanol derivatives do not possess C=C bonds; thus H$^\bullet$ transfer cannot occur. Trimethylsilyl octalinol **12** had a C=C double bond; however we found that the angular group in the radical cation of **12** was expelled in the form of $^\bullet CH_2OH$. The discrepancy could come from the stabilizing ability of the trimethylsilyl group: the species ($M^{\bullet+} - {}^\bullet CH_2OH$) from **12** had a trimethylsilyl group which resided at the β-position to the carbocationic center.

The antiplanarity of the Me_3Si–C and the C–CX (X = (=O)H, (=O)OEt, or H_2OH) bonds in trans isomers **2**, **4**, **6**, **8**, **10**, and **12** may be responsible for the expulsion of the angular oxygenated substituents from the parent radical cations. Because the steric congestion did not exist between the trimethylsilyl group and the angular substituents in trans isomers, the electronic factor must govern the cleavage of the C–CX bond.

The hyperconjugation resulting from silicon at the β-position can stabilize carbocations.[29-31] Wierschke et al.[32,33] calculated the acceleration factor contributed by the hyperconjugation of the trimethylsilyl group in the solvolysis of 2-(trimethylsilyl)cyclohexyl trifluoroacetate. The acceleration from the species in which the Me_3Si–C and the C–O bonds are antiplanar is 10^8 times larger than that from the species in which the Me_3Si–C and the C–O bonds are skewed. Our results showed that trans isomers preferred to lose the angular oxygenated methyl substituent. This phenomenon could also be explained by the hyperconjugation. Stabilization from the hyperconjugation of the Me_3Si–C bond to the carbocationic center in **14** could provide driving force for the silicon-directed carbon–carbon bond cleavage of radical cations.

Minimal hyperconjugation effect existed in cis isomers **1**, **3**, **5**, **7**, **9**, and **11**. Also, the oxygen atom in the angular substituent could interact with the silicon atom nearby. The cis radical cations thus preferred to lose a methyl radical to give, possibly, a five-membered oxonium intermediate (e.g., **13**).



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Conclusion

Radical cations of octalins **2**, **4**, **6**, **8**, **10**, and **12** in the gas phase underwent fragmentation to give ($M^{\bullet+} - {}^\bullet CHO$), ($M^{\bullet+} - {}^\bullet COOEt$), or ($M^{\bullet+} - {}^\bullet CH_2OH$) as the main species. All of these octalins possessed a trimethylsilyl group, which was adjacent and trans to the angular oxygenated methyl substituent. In contrast, the corresponding cis radical cations, resulting from **1**, **3**, **5**, **7**, and **9**, mainly produced the ($M^{\bullet+} - {}^\bullet CH_3$) species.

These experimental results indicated that the trimethylsilyl group influenced the C_β–C_γ bond cleavage. The main fragmentation pathways depended upon the orientation of Me_3Si–C and C_β–C_γ bonds. Octalins with different functionalities on the framework or with different oxidation states on the angular methyl substituent gave the same fragmentation pattern. These findings provide further information on the directing effect exerted by silicon and will be useful for the identification of the stereoconfiguration of trimethylsilylated compounds by mass spectrometry.

Experimental Section

Electron impact induced fragmentations were recorded at 70-eV electron energy with a VG Analytical 70-S mass spectrometer. The accelerating potential was set at 8 keV, and the source temperature was 180 °C. The mass spectral data and the preparation of compounds **1**–**12** are presented in the supplementary material.

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Supplementary Material Available: Mass spectroscopic and other spectral data for compounds 1–12 (28 pages). Ordering information is given on any current masthead page.

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