

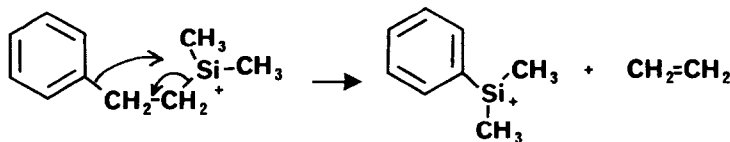
MASS SPECTRAL REARRANGEMENTS OF SILICONIUM IONS-PHENYL
MIGRATION FROM CARBON TO SILICON

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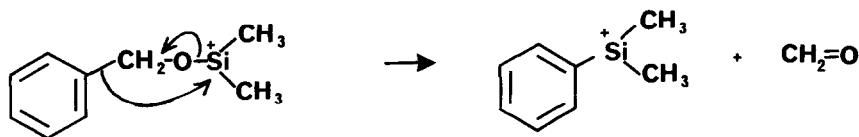
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We have observed in the mass spectrum of 1-phenyl-2-trimethylsilylethane¹ a novel intramolecular rearrangement of the phenyl group from carbon to a positively charged silicon center.

The base peak at $m/e = 73$ is due to the trimethylsilylionium ion, while the peak at $m/e = 163$ results from loss of a methyl group from the parent ion. Fragmentation at such a highly branched silicon center producing these two ions is a highly favored process^{2,3}. The third most intense peak at $m/e = 135$ is due to the dimethylphenylsilylionium ion. This ion results from migration of the electron rich phenyl group from carbon to the siliconium ion center with simultaneous loss of ethylene. The composition of these ions was proved by examination of the mass spectrum of 1-phenyl-1,1-dideuterio-2-trimethylsilylethane. While both the parent and the parent-15 ions showed the expected shifts to higher mass due to the two deuterium atoms, the peak due to the dimethylphenylsilylionium ion was still at $m/e = 135$.

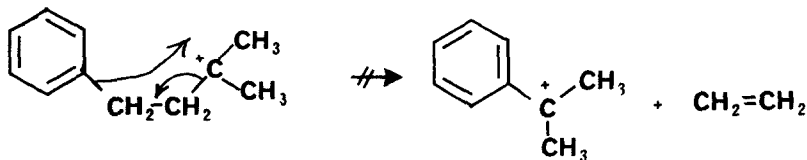


A similar rearrangement of trimethylsilylbenzyl ethers has been reported by Diekman⁴ in which the dimethylphenylsilylionium ion is produced by rearrangement of the parent-15 ion with simultaneous loss of formaldehyde.

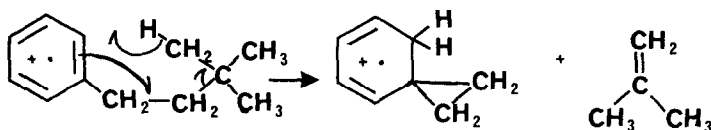


Quick examination of the mass spectrum of 1-phenyl-2-trimethylsilylethane reveals that the most notable feature of the spectrum is its extreme simplicity. (Essentially four ions dominate the entire spectrum.) The reason for this may be the great stability of these silylionium ions which permits little secondary fragmentation. In support of this idea is our finding that in the mass spectrum of trimethylsilylbenzene the dimethylphenylsilylionium ion carries almost 50% of the total ion current. Additional evidence comes from the observation that while in the mass spectra of alkyl benzenes the tropylium ion $m/e = 91$ is usually very important, in the mass spectrum of 1-phenyl-2-trimethylsilylethane it is not. Possibly the lower electronegativity of silicon compared to carbon permits charge localization on silicon more easily than on carbon-stabilizing the siliconium ions.

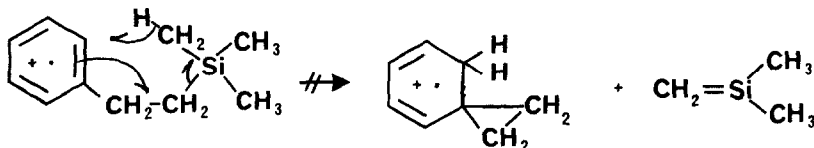
Examination of the mass spectrum of 1-phenyl-2-t-butylethane, the carbon analog of our silyl compound reveals certain distinct differences⁵. Cleavage at the quaternary carbon center is important in the mass spectrum of 1-phenyl-2-t-butylethane⁵. This fragmentation yields peaks at $m/e = 57$ due to the t-butyl cation and at $m/e = 147$ due to loss of a methyl group from the parent ion. No peak, however, occurs at $m/e = 119$ due to the dimethylphenylcarbonium ion.



The tropylium ion, $m/e = 91$ is important, as is the peak at $m/e = 106$. This ion is the product of a hydrogen migration from a methyl group to the positively charged phenyl ring with simultaneous loss of isobutylene.

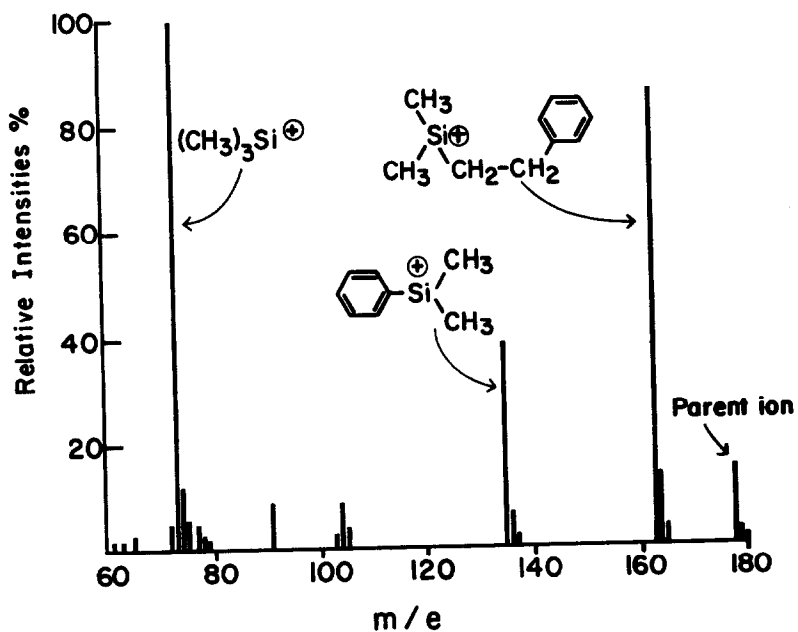


No such peak appears in the spectrum of the analogous silicon compound. This is reasonable in the light of silicon's well known tendency not to form compounds containing carbon-silicon double bonds^{5,6,7}.



Possibly the significant differences in the mass spectra of these two compounds are caused by three factors. First, the greater stability of siliconium ions which minimizes secondary fragmentation. Second, the greater charge localization on silicon which facilitates phenyl migration, leading to formation of the dimethylphenylsilanium ion. Third, silicon's inability to form multiple bonds prevents a rearrangement which is facile in the case of 1-phenyl-2-t-butylethane.

Clearly this tendency for charge localization to occur on silicon even in the presence of a phenyl ring, makes mass spectroscopy a most valuable tool for the investigation of the properties of siliconium ions. This is of great interest because siliconium ions are species which are produced in solution only with great difficulty^{8,9,10,11}.



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13. All mass spectra were run on a Varian M-66 and a Perkin-Elmer Hitachi RMU-6E mass spectrometers at an ionizing voltage of 70 ev.