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Preliminary Communication

Analogies between photolysis and mass spectrometry of organocyclopolysilanes

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SUMMARY

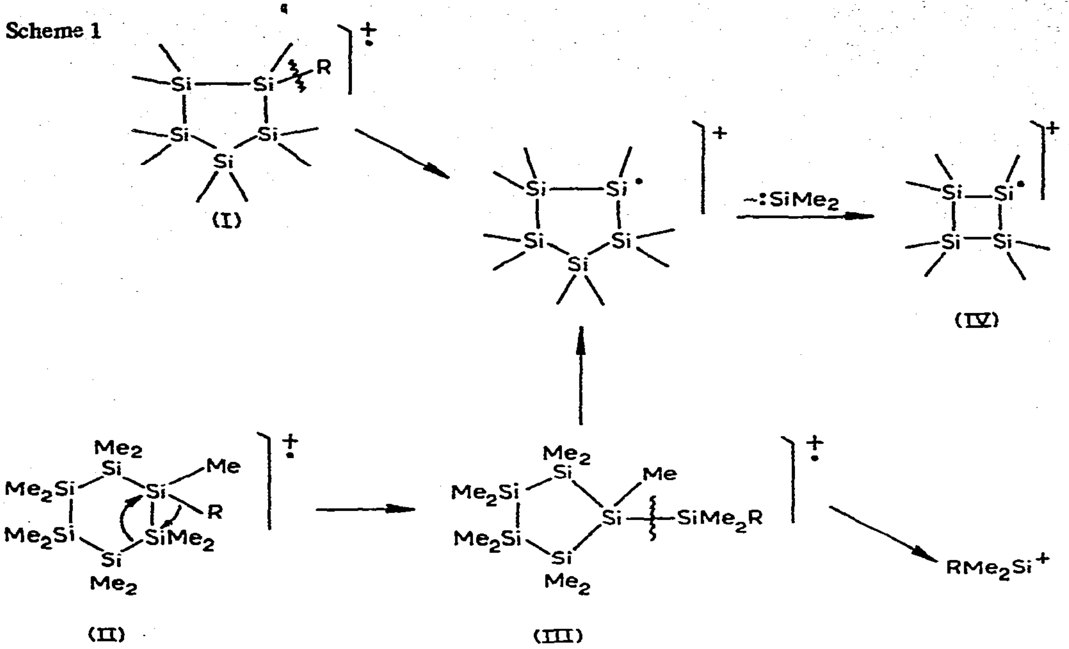
Analogies between photolysis and mass spectrometry of organocyclopentasilane and organocyclohexasilane derivatives are shown and the importance of phenyl substituent is noted in the formation of ions by electron bombardment. The stability of these may be explained by $p_\pi-d_\pi$ interaction or by ring extension.

The importance of phenyl substituent has been reported in the formation of diphenylsilylene ion by mass spectrometry of perphenylcyclopolysilanes[1] and 1,1-diphenyl 1-silacyclopentanols[2]. These silylenes are commonly observed by photolysis[3–7].

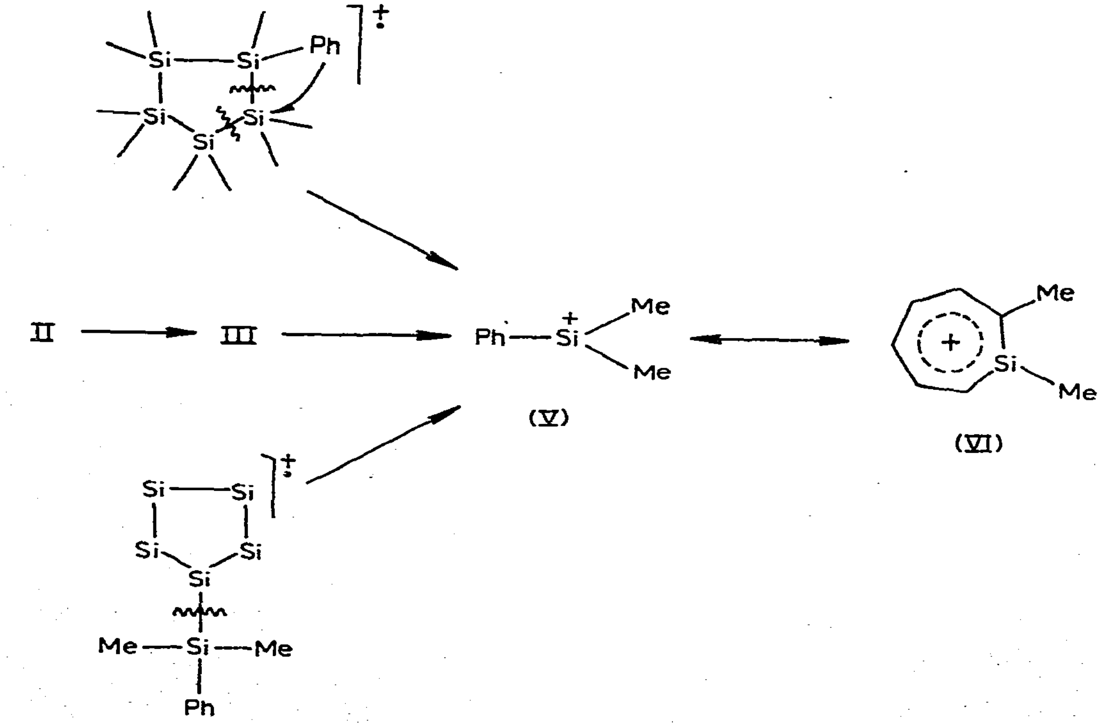
The role of the R substituent in compounds of the type $Si_n(CH_3)_{2n-1}R$ is shown in Scheme 1. For $n = 5$, R = H, F, Cl or C_6H_5; for $n = 6$, R = Cl, C_6H_5, OC_2H_5, $Si(CH_3)_2Cl$ or $Si(C_6H_5)_2Cl$.

For a five-membered silicon ring of type I the expulsion of the R radical is a very common mechanism; this expulsion is followed by the elimination of dimethylsilylene to give ions of type IV. For a six-membered ring of type II a ring contraction takes place in the first step and then the exocyclic silicon–silicon bond in the resulting ion is cleaved. This mechanism is based on the fact that Me_3Si^+ is an important fragment from the compounds of $Si_n(CH_3)_{2n-1}R$ type; the mass spectra of phenylundecamethylcyclohexasilane and phenylnonamethylcyclopentasilane indicate that Me_3Si^+ is as important a species as $PhMe_2Si^+$. So in this case this ring contraction is similar to the results obtained by photolysis[6] or catalysis[7]. In the same way analogies between photolysis[8,9], thermolysis[10] and mass spectrometry of other cyclic silicon compounds have been shown.

Scheme 1



Scheme 2



If the expulsion of R or $Si(CH_3)_2R$ radicals is one of the most important mechanisms, on the other hand when $R = C_6H_5$ the formation of ions $m/e = 135$ also occurs as shown in Scheme 2. When $R = Si(CH_3)_2C_6H_5$ ions of $m/e = 135$ are produced by simple breaking of Si–Si exocyclic bonds, whereas these ions in the upper case are pentacyclic compounds formed by double breaking of Si–Si endocyclic bonds followed by phenyl migration.

The stability of these ions may have two origins: a $p_\pi{-}d_\pi$ interaction[2] between the aromatic ring and the siliconium ion (structure V) or a ring extension of this ion V to give a "silatropylium" ion derivative (structure VI); these tropylium ions are very common in mass spectrometry[11].

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