Unexpectedly Low Reactivity for Spirosilanes: 4-Sila-spiro[3,3]heptane

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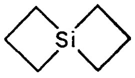
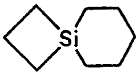
Summary Competitive cleavages of 4-silaspiro[3,3]heptane (I), 4-silaspiro[3,5]nonane (III), and 1,1-dimethylsilacyclobutane (III) by hydrogen chloride in diethyl ether have been carried out; the unexpectedly low reactivity of (I) is discussed in terms of a model controlled by steric considerations.

Cleavages of carbon–silicon bonds by electrophilic reagents have been investigated in many systems[1] although little mechanistic information is available for simple alkyl–silicon bond cleavages[1,2] As observed in carbon chemistry, the introduction of angular strain into organosilicon compounds increases reactivity toward electrophilic reagents[1,3] In particular, silacyclobutanes can be readily cleaved by hydrogen chloride, sulphuric acid, bromine, and ethanolic silver nitrate.[3]

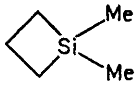
We have examined the relative reactivities of compounds (I)—(III), all of which are readily cleaved by hydrogen chloride in yields greater than 85%. Compounds (I)—(III), treated in pairs with a deficiency of hydrogen chloride in diethyl ether by the standard competition method,[4] gave the following relative rates: (I), 1·0; (II), 2·6; (III), 9·3. These may be compared with results obtained by Nametkin and his co-workers[5] for $\overline{CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}Si}(Me)R$: R = Me, 1·0; Bu, 0·8; $OSiMe_3$, 0·5; Cl, quite unreactive. Their results indicate that the effects of alkyl substituents are small (steric and inductive) while compounds with substituents bearing lone-pair electrons are more dramatically affected. Our results are important in two respects: (i) the range of relative reactivities is quite large when compared with Nametkin's[1,5] alkyl substituted compounds, and (ii) the order of reactivity is not what might have been predicted on the basis of ground-state strain considerations.



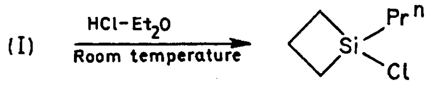
(I)



(II)



(III)



We tentatively suggest that the low reactivity of (I) and (II) is caused by steric hindrance to attack by hydrogen chloride. The current opinion[5] that the reaction proceeds with the electrophilic portion of the hydrogen chloride reagent attacking at the α endocyclic carbon atom of the silacyclobutane ring seems to be somewhat oversimplified. The attacking reagent is probably a $HCl–Et_2O$ complex[6] (1 : 1 hydrogen bonded ?), indicating a larger attacking species than simple hydrogen chloride. Further, the actual position and dynamics of attack of such a reagent seems open to question until more detailed studies are undertaken. Models of (I)—(III) indicates that attack of an electrophilic reagent along a lateral pathway with respect to the silicon–carbon bond (*i.e.* parallel to the ring being attacked and roughly perpendicular to the other ring) appears favoured over a face-on attack. In addition, such an approach is less hindered for (II) than (I) while both of these offer more resistance to approach than (III) does. The Ingold-Thorpe *gem*-dimethyl effect[7] also may play an important role in allowing more ready attack of an electrophilic reagent on (III).

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