

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

By R. DAMRAUER,* R. A. KARN, and M. T. BURKE

(Chemistry Department, University of Colorado, Denver Centre, Denver, Colorado 80202)

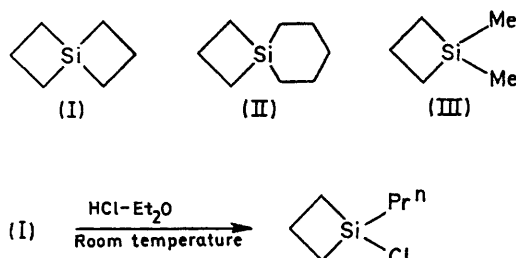
Summary Competitive cleavages of 4-silaspiro[3,3]heptane (I), 4-silaspiro[3,5]nonane (III), and 1,1-dimethylsilacyclobutane (III) by hydrogen chloride in diethyl ether have been carried out; the unexpectedly low reactivity of (I) is discussed in terms of a model controlled by steric considerations.

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

CLEAVAGES of carbon-silicon bonds by electrophilic reagents have been investigated in many systems¹ although

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-workers⁵ for $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{Me})\text{R}$: R = Me, 1.0; Bu, 0.8; OSiMe₃, 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.

We tentatively suggest that the low reactivity of (I) and (II) is caused by steric hindrance to attack by hydrogen chloride. The current opinion⁵ 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-Et₂O complex⁶ (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 effect⁷ also may play an important role in allowing more ready attack of an electrophilic reagent on (III).

We thank the National Science Foundation for support.

(Received, 18th July 1972; Com. 1241.)

¹ C. Eaborn and R. W. Bott in 'Organometallic Compounds of the Group IV Elements,' vol. 1, part I, The Bond to Carbon, ed. by A. G. MacDiarmid, Marcel Dekker, New York, 1968.

² D. H. O'Brien and T. J. Hairston, *Organometallic Chem. Rev. (A)*, 1971, **7**, 95.

³ R. Damrauer, *Organometallic Chem. Rev. (A)*, 1972, **8**, 67.

⁴ W. von E. Doering and W. A. Henderson, jun., *J. Amer. Chem. Soc.*, 1958, **80**, 5274.

⁵ N. S. Nametkin, E. D. Babich, V. N. Karel'sky, and V. M. Vdovin, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1971, 748.

⁶ S. Searles, jun., and M. Tamres in 'The Chemistry of the Ether Linkage,' ed. S. Patai, Interscience, London, 1967.

⁷ E. Eliel, 'Stereochemistry of Carbon Compounds,' McGraw-Hill, New York, 1962, pp. 197.