viously thought to be formed. Complete details of the synthesis, and the crystallographic measurements, will be reported later.

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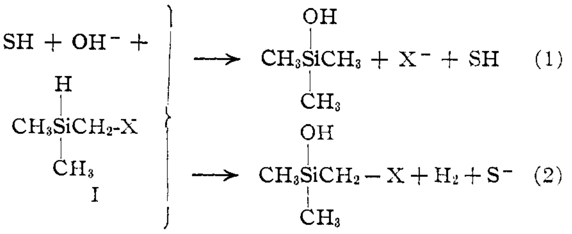
BASE-CATALYZED REARRANGEMENT OF HYDRIDE ION FROM SILICON TO CARBON WITH DISPLACEMENT OF HALIDE ION AT THE MIGRATION TERMINUS

Sir:

The concept of a pentacovalent silicon intermediate, Si(5), in the base-catalyzed solvolyses of triorganosilanes,[1] whose geometry approximates a trigonal bipyramid in which the entering group (hydroxide) and the group ultimately displaced (hydrogen) may form an angle near 90° with the central silicon,[2] leads to the view that the original four bonds to silicon must undergo considerable excitation and loosening in the conversion of Si(4) to Si(5) since this change would also involve the conversions: Si(4), sp^3 bonding, neutral $\rightarrow$ Si(5), sp^3d bonding, unit formal negative charge.[3] On the basis of these considerations it was of considerable interest to determine whether the hydrogen functions in chloromethyldimethylsilane (I, X = Cl) and in iodomethyldimethylsilane (I, X = I) become sufficiently activated in the Si(5) complex formed with hydroxide ion to act as intramolecular reducing groups for the carbon-halogen bonds, which must, themselves, undergo considerable activation in the change from Si(4) to Si(5)

We wish to report the synthesis of these silanes, their novel and rapid rearrangement upon treatment with KOH in 95% ethanol, and the proof that these rearrangements are intramolecular



$$\left.\begin{array}{c} SH + OH^- + \\ \overset{H}{\underset{CH_3}{CH_3SiCH_2\text{-}X}} \\ I \end{array}\right\} \begin{array}{ll} \longrightarrow \overset{OH}{\underset{CH_3}{CH_3SiCH_3}} + X^- + SH & (1) \\ \longrightarrow \overset{OH}{\underset{CH_3}{CH_3SiCH_2}} - X + H_2 + S^- & (2) \end{array}$$

Reduction of chloromethyldimethylchlorosilane with lithium aluminum hydride in ether solution gave chloromethyldimethylsilane (I, X = Cl) in 59% yield having b.p. 81.5° (732 mm.). Found: Si, 25.6; Cl, 32.14. Treatment of I with sodium iodide in dry acetone gave iodomethyldimethylsilane (I, X = I) in 35% yield having b.p. 128° (731 mm.), $n^{20}D$ 1.5043, and d^{20} 1.542. Found: Si, 14.1; *MR*D, 38.5.

Treatment of chloromethyldimethylsilane (I, X = Cl) with 0.0539 *M* KOH in 95% ethanol gave an extremely rapid evolution of hydrogen (reaction was complete in less than 15 seconds) which corresponded to 31% of the theoretical (31% solvolysis, reaction 2) and a precipitate of KCl, 67% yield (in good accord with the expected 69% rearrangement, reaction 1). The expected disiloxanes, condensation products of the silanols from (1) and (2), also were obtained in good yields. A similar experiment with iodomethyldimethylsilane (I, X = I) gave 11% solvolysis (2) and 89% rearrangement (1).

Base-catalyzed solvolysis of phenyldimethylsilane in the presence of bis-(chloromethyl)-tetramethyldisiloxane gave 100% hydrogen and no reduction of the C–Cl bonds in the latter. Furthermore, treatment of I (X = Cl) with 0.04 *M* KOH in 70% dioxane–30% D_2O gave 77% rearrangement product which contained no C–D bonds as shown by an infrared spectrum.

The relatively small change in the ratio (1)/(2) with change from $-CH_2Cl$ to $-CH_2I$, compared to the large change in solvolysis rates with change from RCl to RI (iodides are generally more reactive by a factor of $\sim 10^2$),[4] suggests a common Si(5) intermediate for (1) and (2) in which the $-CH_2X$ group and the hydrogen function form an angle near 90° with the silicon atom (a geometry exceedingly favorable for back attack by the activated hydrogen function on the $-CH_2X$ group). These interesting rearrangements are receiving further study.

[1] $R_3SiH + OH^- + SH \rightarrow R_3SiOH + H_2 + S^-$, where SH represents solvent (95% ethanol) and $-d[\text{silane}]/dt = k_2[\text{silane}][OH^-]$.

[2] L. H. Sommer and O. F. Bennett, THIS JOURNAL, **79**, 1008 (1957); L. H. Sommer, O. F. Bennett, P. G. Campbell and D. R. Weyenberg, *ibid.*, **79**, 3295 (1957).

[3] The sp^3d hybrid orbital, although present in PF_5 and PCl_5 in the vapor state, is uncommon and certainly of much higher energy than sp^3. Formation of an Si(6) intermediate containing two hydroxide groups is untenable on kinetic grounds, and such an intermediate containing one hydroxide and one solvent molecule is unlikely on steric grounds and contrary to other evidence which cannot be detailed here.

[4] A. Streitwieser, Jr., *Chem. Revs.*, **56**, 602 (1956).

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REACTIVITY AT BRIDGEHEAD SILICON. II. 1-SILABICYCLO[2.2.2]OCTANE

Sir:

The special geometry associated with bridgehead atoms in medium-sized bicyclic systems has led to an important use of these compounds in the determination of the stereochemical requirements of S_N1 and S_N2 displacements on carbon.[1,2]

In previous work,[3] reactivity at the bridgehead silicon atom of 1-silabicyclo[2.2.1]heptane (I) was found to be greatly enhanced relative to $(C_2H_5)_3$-SiH. The objective of synthesizing a bridgehead silicon compound that would be almost free of strain (in order to obviate unusual reactivity at

[1] Bridgehead chlorides containing the bicyclo[2.2.1]heptane system are inert toward nucleophilic reagents (back attack is not possible) and have greatly reduced reactivity toward halophilic reagents: P. D. Bartlett and L. H. Knox, THIS JOURNAL, **61**, 3184 (1939); P. D. Bartlett and E. S. Lewis, *ibid.*, **72**, 1005 (1950); W. von E. Doering and E. F. Schoenewalt, *ibid.*, **73**, 2333 (1951).

[2] The bridgehead bromide, 1-bromobicyclo[2.2.2]octane shows greatly *enhanced reactivity* compared to the more strained 1-bromobicyclo[2.2.1]heptane in solvolysis reactions with or without added Ag^+ as a catalyst. However, even the former is less reactive than *t*-butyl bromide by a factor of five powers of ten. W. von E. Doering, M. Levitz, A. Sayigh, M. Sprecher and W. P. Whelan, Jr., THIS JOURNAL, **75**, 1008 (1953).

[3] L. H. Sommer and O. F. Bennett, *Ibid.*, **79**, 1008 (1957); L. H. Sommer, O. F. Bennett, P. G. Campbell and D. R. Weyenberg, *ibid.*, **79**, 3295 (1957).