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

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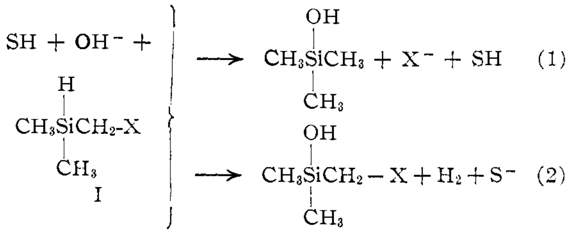
BASE-CATALYZED REARRANGEMENT OF HYDRIDE ION FROM SILICON TO CARBON WITH DISPLACEMENT OF HALIDE ION AT THE MIGRATION TERMINUS

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 → 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



$$\left.\begin{array}{c} SH + OH^- + \\ \overset{\displaystyle H}{\underset{\displaystyle CH_3}{CH_3SiCH_2\text{-}X}} \\ \text{I} \end{array}\right\} \begin{array}{l} \longrightarrow CH_3\overset{OH}{\underset{CH_3}{Si}}CH_3 + X^- + SH \quad (1) \\ \longrightarrow CH_3\overset{OH}{\underset{CH_3}{Si}}CH_2-X + H_2 + S^- \quad (2) \end{array}$$

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 ~ 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.

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(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

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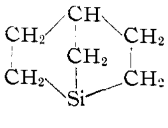
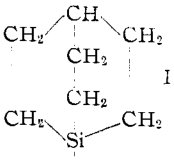
(1) Bridgehead chlorides containing the bicyclo[2.2.1]heptane system are inert toward nucleophilic reagents (back attack is not possible) and have greatly reduced reactivity toward halophilic reagents: P. D. Bartlett and L. H. Knox, THIS JOURNAL, **61**, 3184 (1939); P. D. Bartlett and E. S. Lewis, *ibid.*,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

bridgehead silicon due to possible changes in bond hybridization which might invalidate general conclusions) has led to the synthesis of 1-silabicyclo-[2.2.2]octane (II) for comparison of reactivity with I.[4]


I


II

Treatment of 4-(2-hydroxyethyl)-tetrahydropyran[5] with equimolar amounts of thionyl chloride and pyridine gave 4-(2-chloroethyl)-tetrahydropyran, b.p. 71° (6 mm.); *Anal.* Calcd. for $C_7H_{13}OCl$: Cl, 23.9. Found: Cl, 23.5. The Grignard reagent prepared from 4-(2-chloroethyl)-tetrahydropyran in tetrahydrofuran was added to excess silicon tetrachloride and gave 4-(2-trichlorosilylethyl)-tetrahydropyran (III) in 63% yield, b.p. 97° (3 mm.); *Anal.* Calcd. for $C_7H_{13}SiOCl_3$: Si, 11.3; Cl, 43.1. Found: Si, 11.1; Cl, 43.1. Treatment of III with boron trichloride and then thionyl chloride gave 1,5-dichloro-3-(2-trichlorosilylethyl)-pentane (IV) in 70% yield, b.p. 130° (2.5 mm.). *Anal.* Calcd. for $C_7H_{13}SiCl_5$: Si, 9.3; Cl (attached to Si), 35.2. Found· Si, 9.2; Cl (attached to Si), 35.3. Ring-closure of IV with excess magnesium in ether gave a 30% yield of the bridgehead chloride, 1-chloro-1-silabicyclo[2.2.2]-octane (V), b.p. 59° (8 mm.). *Anal.* Calcd. for $C_7H_{13}SiCl$: Si, 17.4; Cl, 22.1. Found: Si, 17.2; Cl, 22.5. The infrared spectrum of V showed the absence of Si-H, C=C and $Si-CH_3$. Compound V is readily hydrolyzable and gives rapid quantitative reaction of the silicon–chlorine bond with 0.1 *N* alkali. Treatment of V with lithium aluminum hydride in ether at 0° gave 1-silabicyclo[2.2.2]-octane (II), b.p. 158° (733 mm.), m.p. 133° (sealed capillary), with an infrared spectrum showing the strong Si–H band at 4.7 μ and lacking maxima for C=C, $Si-CH_3$ and Si-O-Si. *Anal.* Calcd. for $C_7H_{13}SiH$: Si, 22.2; H (attached to Si), 0.80; mol. wt. (cryoscopically in benzene), 126. Found: Si, 21.9; H (attached to Si), 0.80; mol. wt. (cryoscopically in benzene), 128.

The kinetics and rate constant for II in the base-catalyzed solvolysis with hydroxide ion in 95% ethanol, $R_3SiH + OH^- + SH \rightarrow R_3SiOH + H_2 + S^-$, where SH represents solvent, have been determined. For reactions of R_3SiH with OH^- in 95% ethanol at 35° relative rates (k_2) are, for $(C_2H_5)_3SiH = 1$; II, 10; I, 10^3; $(CH_2)_4Si(CH_3)H$, 10; $(CH_2)_5Si(CH_3)H$, 10^{-1}.

The new reactivity data offer additional support for our earlier, preliminary hypothesis.[3]

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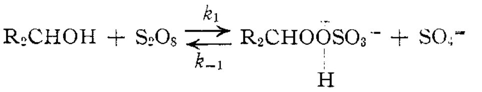
(4) A molecular model of II using accurately scaled Stuart–Briegleb atom models is easily constructed and shows only small strain at Si and complete shielding of that atom to back attack. A corresponding model of I cannot be made.

(5) D. Kohlback, E. Cekovnikov, A. Rezek and M. Piantanida, *Ann.*, **532**, 69 (1937).

PERSULFATE OXIDATION OF ISOPROPYL ALCOHOL

Sir:

In a recent paper[1] Malinowski and Levitt have proposed a mechanism for the persulfate oxidation of isopropyl alcohol which involves in the first step a reaction between isopropyl alcohol and the persulfate ion



$$R_2CHOH + S_2O_8 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_2CH\underset{\displaystyle H}{\underset{|}{\overset{-}{O}}}OSO_3^- + SO_4^=$$

The intermediate is then assumed to decompose to the ketone and bisulfate ion.

This may be shown to be incorrect by our observation that induced exchange of radioactive sulfate with persulfate ion in the presence of isopropyl alcohol does not occur, whereas it is required by the above mechanism. When the reaction was carried to 25% completion in the presence of S-35 labeled sulfate, the recovered persulfate had only 10^{-4} of the activity calculated for complete exchange.

We also have observed that the addition of allyl acetate decreased the rate of disappearance of persulfate from 2.30×10^{-4} sec.$^{-1}$ (0.02 *M* isopropyl alcohol, 0.02 *M* persulfate, 0.02 *M* sulfate, *p*H 5, 60°) to the value observed in the absence of isopropyl alcohol (4×10^{-6} sec.$^{-1}$).[2] The inhibition of the oxidation of isopropyl alcohol by allyl acetate indicates that the reaction must be a chain process, that the initiation step is the first order decomposition of persulfate ion (probably to the sulfate ion-radical) and does not involve isopropyl alcohol, and that the propagation steps involve the induced decomposition of persulfate ion. The species formed in the decomposition of the persulfate ion is, in the presence of allyl acetate, consumed in initiating the polymerization of the latter. In the absence of allyl acetate, it affects the oxidation of isopropyl alcohol.

The species which initiates the oxidation of the alcohol may be either the sulfate ion-radical or the hydroxyl radical. The latter species has been shown to be involved in the decomposition of persulfate ion in water[3] and may reasonably be expected to be involved in this case also. It appears that only a reaction utilizing the hydroxyl radical can accommodate the kinetics of the reaction (first order in persulfate and independent of the alcohol concentration). Evidence for the participation of this species may be obtained from the observation that whereas the rate constant is independent of the hydroxyl ion concentration between *p*H 5–8, in more basic solution it decreases and levels off at $k = 0.2 \times 10^{-4}$ sec.$^{-1}$ between *p*H 9.5–10.5. The simplest interpretation is that the hydroxyl radical is converted to the less reactive oxygen ion-radical in the more basic solution.[4]

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(1) E. R. Malinowski and L. S. Levitt, THIS JOURNAL, **80**, 5334 (1958).

(2) This technique was first used by I. M. Kolthoff, E. J. Meehan and E. M. Carr, *ibid.*, **75**, 1439 (1953), in studying the persulfate oxidation of methanol.

(3) I. M. Kolthoff and I. K. Miller, *ibid.*, **73**, 3055 (1951).

(4) E. J. Hart, S. Gordon and D. A. Hutchison, *ibid.*, **75**, 6165 (1953), have presented evidence for the hydroxyl radical having a *pk* of about 9.