FRAGMENTATION OF THE SILACYCLOHEXANE RING

II*. REACTION OF TRITYL FLUOROBORATE WITH 1,1-DIMETHYL-SILACYCLOHEXANE

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Summary

The title reaction proceeds in dichloromethane with a pseudo-first-order rate constant of $1.19 \times 10^{-3} \text{ sec}^{-1}$, 5000 times faster than the reaction of trityl fluoroborate with tetraethylsilane, yielding as products 4-pentenyldimethylfluoro silane, triphenylmethane, and boron trifluoride The enhanced reactivity of the title silane is attributable to $\sigma \rightarrow \pi$ conjugation

The phenomenon of reactivity at a σ bond β to a silicon atom i e. the Y—Z bond in Si—X—Y—Z, has been of continuing interest Whether manifested in the greater rate of solvolysis of β-haloalkylsilanes[1], or in their β elimination [2,3], or in the specific insertion of carbenoid reagents into carbon—hydrogen bonds β to silicon, or in the hydridic character of these C—H bonds [4,5], and whether explained by "limiting siliconium ions" [6], carbon—metal hyperconjugation [7], or by vertical stabilization [8,9], this phenomenon is clearly real

We report here on the reaction of a carbonium ion with 1,1 dimethyl-1-silacyclohexane (DMSCH), a system known to be particularly reactive toward dichlorocarbene [4], in fact the most reactive of all compounds with CH_2 β to silicon That the stereochemistry and geometry of the reactant is the determining factor in reaction β to silicon is shown by the lessened reactivity of dimethylsila-cyclopentane toward dichlorocarbene [4] and the observation that insertion of the latter reagent into sec-butyltrimethylsilane is directed into that β-hydrogen which is *trans* to silicon in the predominant conformation of the substrate [10]
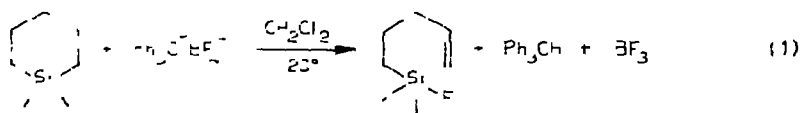
The report by Jerkunica and Traylor [5] that the reaction of tetraethylsilane with trityl cation in acetonitrile at 29.8° produced ethylene with a rate con-

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stant of 6.8 X 10^{-7} mol^{-1} sec^{-1} prompted a detailed study of the reaction of a presumedly more reactive silane, DMSCH, with trityl ion.

Results

DMSCH reacts with trityl fluoroborate (TF) in dichloromethane. GLPC anal ysis shows that the reaction is more than 90% complete after 90 min at 23°, when the initial concentration of the reactants is ca. 0.4 M. Three products were isolated and characterized: fluorodimethyl-4-pentenylsilane (FDPS), triphenylmethane, and boron trifluoride (eqn. 1). The GLPC curve showed no other volatile products in greater than 0.2% yield. A control experiment showed no reaction of FDPS with excess TF, even after 48 h under the reaction conditions.

$$\text{(structure)} + \text{Ph}_3\text{CBF}_4 \xrightarrow[23°]{\text{CH}_2\text{Cl}_2} \text{(structure)} + \text{Ph}_3\text{CH} + \text{BF}_3 \qquad (1)$$

Kinetically, the reaction is second-order overall with a rate constant at 23° of 2.21 X 10^{-3} mol^{-1} sec^{-1} With a large excess of TF a pseudo-first-order rate constant of 1.19 X 10^{-3} sec^{-1} was found.

Control experiments showed no reaction between DMSCH and 48% fluoroboric acid, or triphenylmethyl chloride, or triphenylmethyl bromide, and no reaction between cyclohexane and TF.

Discussion

The rate constant for reaction of DMSCH with TF falls between those found [5] for reaction of Et$_4$Si and Et$_4$Sn with TF, albeit within an order of magnitude of the rate for the tin compound (Table 1). confirming the reactivity sequence observed by Seyferth and coworkers[4] for dichlorocarbene insertion into similar substrates: CH$_2$Sn > CH$_2$(ring)Si > CH$_2$Si. It is noteworthy that the latter workers found no reaction at methyl groups, i.e. EtSnMe$_3$ was inert to mercurial-derived dichlorocarbene Apparently the dehydrosilylation of DMSCH is mechanistically related to these reactions.

Although the primary dehydrometallation product FDPS contains a β-CH$_2$, its failure to react implies a significantly (orders of magnitude) slower rate per hydrogen. Although trityl bromide has been reported to cleave butyl groups from tetraalkyl tins, this reagent did not react with DMSCH. Apparently trityl bromide is sufficiently ionized to react with a CH$_2$ group β to tin [11], but not with the less-reactive DMSCH, in accord with the reactivity series proposed [4].

TABLE 1

RELATIVE RATES PER H ATOM FOR DEHYDROMETALLATION

Compound	Rate per hydrogen	Ref
Et$_3$Si	1.0	5
DMSCH	5 2 X 10^3	this work
Et$_4$Sn	1 5 X 10^4	5

Mechanistically, the enhanced reactivity of DMSCH is well-explained by σ—π conjugation or vertical stabilization [8]. Geometrically, the β-equatorial hydrogens of DMSCH are *trans* to the silicon—α-carbon bond, the optimum position for abstraction [8], and the resultant ion A unstrained, at least on the basis of current theory [12,13] These factors probably account for the greater part of the rate enhancement of DMSCH over Et_4Si. A cyclopropenium ion B, such as that proposed by Jarvie et al [14] to explain the stereochemical result of solvolysis of *erythro*-1,2-dibromopropyltrimethylsilane, seems to be unlikely, since it would be isostructural with the bicyclo[3 1.0]-2-silacyclohexane system, known to be strained [15]. Vertical stabilization predicts replacement of alkyl
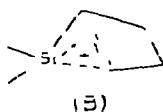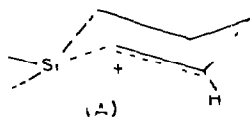
with fluoride at silicon will lead to lessened reactivity at the β carbon, in accord with our observation for FDPS. A mechanism involving direct fragmentation, via a 4- or 6-center transition state, seems unlikely in view of the strain involved.

In certain of its reactions, TF can act as a one-electron acceptor, but a radical mechanism seems unlikely in the present case in view of the observation [1] that tetrabutylammonium bromide decreased, by a common ion effect, the rate of reaction of triphenylmethyl bromide with tetraalkyl tins. Also, ion A was implicated in, and similar ring cleavage observed in, the acetolysis of 4-tosyl-1,1-dimethyl-1-silacyclohexane [16], and the non-radical nature of tosylate solvolysis is part of the dogma of organic chemistry

The convenient rate of this silicon—carbon bond cleavage holds forth the promise of synthetic utility for a hydrosilylation—dehydrosilylation sequence in the protection of a double bond during synthetic transformations. Studies on this topic are under investigation.

Experimental

DMSCH, prepared by the procedure of West [17], was purified by distillation through a 10-ball Snyder column. The center fraction was more than 99.9% pure by GLPC (15% SF-96/Chromasorb PAW/140—210°), b.p. 127—130°; mass spectrum, *m/e* (rel. intensity)· 128 (25), 113 (100), 100 (7), 85 (98), 86 (10), 72 (17), 71 (6), 59 (78), 43 (44).

TF, prepared by the method of Dauben et al. [18] in 79—94% yield, was stored in a desiccator over $CaSO_4$ and protected from light. NMR (CDCl₃): δ 6 83 ppm, $\lambda_{max}(CCl_4)$ 412, 438 nm

Dichloromethane, of ACS reagent grade, was distilled through a 20-ball Snyder column. The fraction with b.p. 39.5—40.4° was more than 99 9% pure by GLPC.

Reaction of DMSCH with TF To a deep yellow solution of 6.6 g (0.02 mol) of TF in 50 ml of CH_2Cl_2 was added 2.6 g (0.02 mol) of DMSCH in one portion, producing a brown solution which steadily evolved a gas identified as BF_3 by condensation temperature and chemical behavior. After 16 h the black solution was trap-to-trap distilled, affording a colorless distillate and a black residue.

GLPC analysis of the distillate showed only one product peak, which was collected on a preparative column (20% SE-30). The isolated material, 4-pentenyldimethylfluorosilane (FDPS) exhibited NMR (CCl$_4$): δ 0 22 (d, 6), 0.73 (m, 2), 1.5 (m, 2), 2.2 (m, 2), and 5.3 (m, 3) ppm; mass spectrum: 146 (25), 131 (72), 127 (5), 105 (67) 77 (100) in accord with the proposed structure. (Found: C, 57.11; H, 10.62; F, 12.06. C$_7$H$_{15}$FSi calcd.: C, 57.48; H, 10.34; F, 12.99%.) Sublimation at 60°/0.05 mm of the black residue afforded colorless crystals, m.p. 93.8—94.6°, identified by mixed m.p. and mass spectrum as triphenylmethane.

Control Reactions (a) TF with cyclohexane. A mixture of 2.48 g (0.0075 mol) of TF, 0.42 g (0.005 mol) of cyclohexane, and 12 ml of CH$_2$Cl$_2$, stirred at room temperature, and monitored by GLPC, showed no change in cyclohexane concentration over a 27 day period (b) DMSCH with 48% HBF$_4$ A mixture of 0.64 g (0.005 mol) of DMSCH, 0.24 ml (0.0075 mol) of ACS reagent fluoroboric acid, and 5 ml of CH$_2$Cl$_2$ was stirred. GLPC curves of the organic layer, taken after $\frac{1}{2}$ and 48 h, were identical, showing only the starting reagents (c) DMSCH with triphenylmethyl halides. GLPC analysis showed no reaction when DMSCH and Ph$_3$CBr were stirred (ca. 0.5 M solution) for 10 days in CH$_2$Cl$_2$ or heated at reflux (ca. 0.6 M solution) in dichloroethane for 30 days or when DMSCH and Ph$_3$CCl were heated at reflux (ca. 1.0 M solution) for 3 days in CH$_2$Cl$_2$.

Kinetic studies. By determination of the disappearance of DMSCH by GLPC (15% SF-96, 140°) and standard treatment of the data [19] second-order and pseudo-first-order rate constants were determined Heptane was used as internal standard for all runs. The relative response factor was observed to vary from 0.98 at equal concentrations of heptane and DMSCH to 1.12 at dilute concentrations of DMSCH. The second-order run, followed for one half-life at 21.8°, with initial concentrations of 0.0513 M DMSCH and 0.0501 M TF, gave k_2 = 2 21 × 10^{-3} mol^{-1} sec^{-1} The pseudo-first-order run, followed for three half-lives at 22.8°, with initial concentrations of 0.0513 M DMSCH and 0.425 M TF, gave k = 1.18 × 10^{-3} sec^{-1}.

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