Oxidative Desilylation of Alkylsilanes with Triphenylcarbenium Ion. **Control of Transition-State Geometry**

Stephen S. Washburne* and Robert Szendroi

Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122

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Ten acylic, cyclic, and aralkyl-type silanes were treated with triphenylcarbenium tetrafluoroborate in dichloromethane to measure rates of oxidative desilylation: $RCH_2CH_2SiR_3 + Ph_3C^+BF_4^- \rightarrow Ph_3CH + RCH=CH_2$ + R₃SiF + BF₃. The divergence of rates, from Ph₂CHCH₂SiMe₃, which was inert, through dimethylsilacyclopentane $(k_2 = 4 \times 10^{-6})$, to dimethylsilacyclohexane $(k_2 = 2.2 \times 10^{-3})$, can not be rationalized on purely electronic grounds. A transition state requiring anticoplanar arrangement of the silicon moiety and β -hydrogen to be extruded is proposed. Dimethylsilacyclobutane, which reacts extremely rapidly $(k_2 \approx 2 \times 10^{-2})$, suffers allylic cleavage of the initially formed fluoro(2-propenyl)dimethylsilane. As the olefin products suffer decomposition or polymerization under the reaction conditions, this desilylation is of minimal preparative value.

It is by now well-known that β -metalloalkyl compounds are markedly more reactive toward acids, bases, heat, and solvolytic reagents than their α and γ analogues.¹ Although silicon is barely a metal in terms of activating positions β to it,² such activation can be turned to synthetic advantage, as in the oxidation of trimethylsilyl ethers (readily derivable from alcohols) with triphenylcarbenium (trityl) tetrafluoroborate, as pioneered by the Jung group,³ or with nitrosonium fluoroborate.⁴ In the related alkylsilane case, oxidation with trityl ion (eq 1, $An = BF_4$) is slow⁵ unless the silane is particularly activated, as, for example, silacyclohexane.⁶

$$HC - C - Si + Ph_{3}C^{+}An^{-} - C = C + Ph_{3}CH + An - Si$$

Since cis-(4-tert-butylcyclohexyl)trimethyltin is destannylated by trityl ion three times faster than the trans isomer, implying that an anti conformation is favored for elimination of the elements of Me₃SnH, we considered it of value to determine the geometrical and structural factors governing elimination in the alkylsilane series and to probe the potential utility of oxidative desilylation, coupled with hydrosilylation, as a method of protecting the alkene function during synthetic transformations.

Results

As suspected earlier.⁶ dimethylsilacyclohexane is one of the most reactive silanes toward triphenylcarbenium ion, but the nature of the counterion is also crucial, as bromide and chloride (eq 1, An = Br, Cl), which are certainly nucleophilic toward silicon, failed to react with this substrate. Although $An = PF_6$ gave successful reaction, we used fluoborate in this study exclusively. A variety of acyclic tetraalkylsilanes were treated with triphenylcarbenium tetrafluoroborate (TTFB) in methylene chloride solution at room temperature (\sim 22 °C), Table I. Substrate and

TTFB concentrations were about 0.05 and 0.06 M, respectively. Second-order rates were measured qualitatively by gas chromatographic measurement of the disappearance of silane. Only reaction 3 was sufficiently rapid to allow quantitative estimation of the rate (more than 30% completion after 1 week), and only in reaction 6 could the product olefin be isolated. Styrene (reaction 3) and butene (reaction 2) disappeared from the gas chromatogram with time after they had reached a maximum concentration, probably through polymerization, although volatilization may be a factor in reaction 2. The concentration of (5hexenyl)trimethylsilane (reaction 6) was at a maximum after 90 h and decreased thereafter, either through polymerization or through further desilylation to 1,6-hexadiene. In a control experiment, 1,6-hexadiene was totally consumed after 48 h of treatment under the reaction conditions.

Dimethylsilacycloalkanes proved more amenable to study. Rate constants are collected in Table II. Dimethylsilacyclobutane reacted so rapidly (90% completion in 30 min) that accurate kinetics were impossible with our method. As a further complication, the initial desilylation product, H₂C=CHCH₂SiMe₂F, being an allylsilane, was cleaved by TTFB about as rapidly as starting material, giving Me₂SiF₂ as the principal silicon-containing material isolated (together with Ph₃CCH₂CH=CH₂, not isolated).

In an attempt to study the effect of other carbocations as oxidizing agents, tropylium (cycloheptatrienyl) tetrafluoroborate was reacted with 1.1-dimethyl-1-silacyclobutane. While commercial carbocation material gave rapid reaction, the product (propyldimethylfluorosilane) was that of simple HF cleavage of the reactive silacyclobutane ring. Freshly purified tropylium tetrafluoroborate did not react with dimethylsilacyclobutane.

Discussion

The hope that oxidative desilvlation coupled with hydrosilvlation would be a means to protect olefins certainly remains unrealized, as most alkylsilanes are only sluggishly reactive toward trityl tetrafluoroborate, and for those that are, the product olefin suffers rapid cationic polymerization. Nevertheless, the great spread in reactivity among the ten silanes studied here requires comment.

The mechanism invoked earlier,⁶ involving an intermediate carbonium ion stabilized by a β -metal substitutent, makes sense in rationalizing reactions 1-3 and 6, where the rate per hydrogen is in qualitative accord with what is expected for carbonium ion processes, i.e., benzyl > secondary > primary. The enhanced reactivity of dimethylsilacyclobutane is compatible with known properties

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Table I. Reaction of Acyclic Tetraalkylsilanes with Trityl Tetrafiuoroborate at 22 °C

rxn	silane	olefin product	rate const, ^c $M^{-1} s^{-1}$	rate const per H, ^c M ⁻¹ s ⁻¹	
1	$(CH_{2}CH_{2})_{4}Si^{a}$	CH ₂ =CH ₂	6.8 ^{<i>a</i>}	0.57	_
2	CH,CH,CH,CH,Si(CH,),	$CH_{CH}CH_{C}H=CH_{b}$	~ 50	~ 25	
3	PhCH, CH, SiMe,	PhCH=CH, b	5300	2700	
4	Ph.CHCH_SiMe	2	nil	nil	
5	Ph.CHCH.SiMeEt	$CH_{a} = CH_{a}$	~ 3	~0.5	
6	Me ₃ Si(CH ₂) ₆ SiMe ₃	CH ₂ =CH(CH ₂) ₄ SiMe ₃	~ 300	~ 75	
^a Reference 5a	a. ^b Not isolated, detected by gas	chromatography. ^c Times 10 ⁷			

Table II. Reaction of Dimethylsilacycloalkanes with Trityl Tetrafluoroborate at 22 °C

$(CH_2)_n Si(CH_3)_2$			rate const. ^b	rate const per H ^b	
no.	n	product	$M^{-1} s^{-1}$	$M^{-1} s^{-1}$	
7 8 9 10	3 4 5 ^a 6	$SiMe_2F_2 + CH_2=CHCH_2SiMe_2F$ $CH_2=CHCH_1CH_2SiMe_2F$ $CH_2=CH(CH_2)_3SiMe_2F$ $CH_2=CH(CH_2)_4SiMe_2F$	~ 200 0.04 22^{a} 15.8	100 0.01 5.5 4.0	

^a Reference 6. ^b Times 10⁴.

of this compound⁷ and attributable more to relief of ring strain than any other factor. But transition state A and



intermediate B fail to explain the nonreactivity of the 2,2-diphenylethyl group (reactions 4 and 5) and the fact that in reaction 5 ethyl is cleaved in preference to 2,2diphenylethyl, which could form a stable ion of the benzhydryl type.

The answer lies most probably in a strong preference for an anticoplanar orientation of hydrogen and silicon in the transition state. The elegant study of stereochemistry of elimination of Me₃SiBr from erythro-(1,2-dibromopropyl)trimethylsilane by Jarvie, Holt, and Thompson⁸ showed better than 97% antarafacial elimination in 95% ethanol. If an antarafacial relationship of R_3Si and H is similarly required in the present system, the transition state for (2-phenylethyl)trimethylsilane C has a gauche



relationship of Ph and Me₃Si; (2,2-diphenylethyl)trimethylsilane is obliged to adopt the unfavorable congested state D. The second phenyl group, rather than providing extra stabilization to the developing positive center, prevents the molecule from adopting a conformation compatible with desilylation.

Results in the cyclic series confirm this hypothesis. While dimethylsilacyclopentane is of the same order of reactivity as n-butyltrimethylsilane (reactions 2 and 8), dimethylsilacyclohexane and cycloheptane (reactions 9 and 10) are about 500 times as reactive and nearly as reactive as tetraethyltin (rate constant of $8.3 \times 10^{-3}/H$).⁵

The calculated ground-state conformations of silacyclopentane⁹ and silacyclohexane¹⁰ rings are instructive.

While the latter has two β -C-H bonds within 5° of anticoplanarity with the Si- C_{α} bond (E, n = 3), in silacyclopentane (E, n = 2) the most favorably located β -C-H makes a dihedral angle of 35° with the Si- C_{α} bond. Examination of models of the more flexible silacycloheptane system shows at least one anticoplanar β -C–H in the most reasonable conformations. While full potential surfaces for these compounds are not known, our admittedly crude model explains the reactivity pattern shown. Such behavior is not without precedent. For insertion of dichlorocarbene into β -C-H bonds of tetraalkylsilanes,¹¹ which involves development of partial positive charge at the carbon β to silicon, dimethylsilacyclohexane was 2 orders of magnitude more reactive than dimethylsilacyclopentane.

In summary, geometrical factors appear to control elimination reactions in silicon systems at least as importantly as in the carbon series. The recent report of nonreactivity of steroidal tert-butyldimethylsilyl ethers toward trityl tetrafluoroborate oxidation¹² (i.e., t-BuMe₂Si-testosterone was cleaved to testosterone rather than being oxidized to androst-4-ene-3,17-dione) can be explained with our geometrical argument. If oxidation of H-C-O-Si requires anticoplanar H and Si, that conformation (F) will be difficult to obtain when both carbon and



silicon bear bulky groups, and the preferred conformation (G) will suffer the observed result of direct Si-O cleavage by fluoride ion attack.

Experimental Section

The silane starting materials were prepared by literature methods with the following exceptions.

(2,2-Diphenylethyl)trimethylsilane. A mixture of 18 g (0.1 mol) of 1,1-diphenylethane, 16.25 g (0.15 mol) of dimethyl-

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chlorosilane, and 3 drops of 5% aqueous H2PtCls6H2O was stirred at reflux for 24 h. Excess (CH₃)₂SiHCl was removed by evaporation at reduced pressure and the residue treated with 0.3 mol of ethereal methylmagnesium iodide solution and then heated at reflux 48 h. Hydrolysis (saturated NH₄Cl solution), extraction with petroleum ether of the aqueous layer, drying (Na₂SO₄), and concentration of the combined organic layers gave an oil which was fractionated to afford 20.4 g (80%) of silane product: bp 81-82 °C (0.05 mm); NMR (CDCl₃) δ 7.1–7.5 (10 H, m), 4.0–4.3 (1 H, m), 2.4 (2 H, d), 0.17 (9 H, s). Anal. Calcd for C₁₆H₂₂Si: C, 80.25; H, 8.72. Found: C, 80.30; H, 8.99. Crystallization of the distillation residue from MeOH afforded 2.5 g (14%) of 1-methyl-1,3,3-triphenylindane, mp 141.5-142.5 °C (lit.¹³ mp 143.5 °C).

Diethyl(2,2-diphenylethyl)methylsilane. Treatment of the crude hydrosilylation residue prepared as above (0.1-mol scale) with 0.3 mol of ethereal ethylmagnesium bromide and a similar workup afforded 12.7 g (45%) of silane product as a heavy oil. Anal. Calcd for C₁₈H₂₆Si: C, 80.77; H, 9.26. Found: C, 80.73; H, 9.25. IR and NMR spectra are in good accord with the assigned structure. Workup of the distillation residue as above gave 3.5 g (20%) of 1-methyl-1,3,3-triphenylindane.

1,1-Dimethylsilacycloheptane. The general procedure of Nametkin¹⁴ was used. Since the Lewis acid-catalyzed rearrangement of 1-(chloromethyl)-1-chlorosilacyclohexane is violently exothermic and in some runs exploded, the following modification was employed. Behind an efficient shield, 13 g (0.08 mol) of 1-(chloromethyl)-1-methylsilacyclohexane¹⁴ was treated with a small spatulaful of $AlCl_3$ (~10 mg). The mixture was heated with stirring to 70 °C. A vigorous reaction ensued which moderated within a few minutes. Direct distillation of the reaction mixture afforded 9.7 g (75%) of 1-chloro-1-methylsilacycloheptane, bp 92-94 °C (20 mm).

Triphenylcarbenium Tetrafluoroborate (TPMTFB). As commercial material gave erratic results, the dry salt, prepared by the Dauben procedure¹⁵ was stored in a desiccator over CaSO₄ and used within 1 week, preferably sooner.

General Procedure for Oxidation with TPMTFB. A flame-dried, 100-mL, three-necked flask, equipped with a condenser, gas inlet, and serum cap, was swept with a strong stream of dry nitrogen and charged with 0.005 mol of silane in 50 mL of dichloromethane (freshly distilled from CaH₂) and $\sim 2 \text{ g}$ (0.006 mole) of TPMTFB in dichloromethane. The mixture was stirred at 22 ± 0.4 °C, and samples were periodically withdrawn by syringe for GLC analysis. A 0.006 × 11 m column of 15% SF-96 silicone oil on 60/80-mesh Chromosorb PAW was used for all analyses. During the reaction course, the mixture gradually turned from orange to black. Boron trifluoride was detected fuming from the gas exit and was analyzed for as previously.⁶

For acyclic silanes, trimethylfluorosilane was detected by GLC or better by condensation of vapors from a nitrogen purge of the reaction mixture: bp 15 °C; NMR (CDCl₃) δ 0.07 (d, J = 7.5 Hz). For cyclic silanes, alkenylfluorodimethylsilanes were characterized by GLC and NMR or in the case of reaction 7 by fractional distillation (20-cm, helix-packed column) of the reaction mixture and by NMR. Reactions carried out in 1.2-dichloroethane solvent showed no substantial differences with respect to rate or product distribution.

In preparative runs, the reaction mixture was washed with saturated sodium bicarbonate solution, dried (Na_2SO_4) , and concentrated to one-third of the original volume. Solids were removed by filtration, and the product was collected from the filtrate by preparative GLC. (5-Hexenyl)trimethylsilane¹⁶ (reaction 6) and (5-hexenyl)dimethylfluorosilane (reaction 10) were characterized by comparison with authentic samples. Sublimation (60 °C, 0.075 mm) of the solids afforded pure triphenylmethane.

Kinetic Measurements. The disappearance of silane substrate was determined by GLC, using an appropriate C_7 to C_{12} hydrocarbon, for which a response factor curve had been prepared. as internal standard. The laboratory temperature, determined by a recording thermograph, was 22 ± 0.4 °C. Second-order rate constants were calculated from the integrated form of the second-order rate equation by assuming $[TPMTFB] = [TPMTFB]_0$ ([silane]₀ - [silane]).

(5-Hexenyl)dimethylfluorosilane. A mixture of 8.25 g (0.1 mol) of 1,5-hexadiene, 9.4 g (0.8 mol) of dichloromethylsilane, and 2 drops of 5% aqueous H2PtCl6 solution was stirred 16 h and then treated with 18 g (0.9 mol) of silver fluoroborate in 50 mL of anhydrous acetone. After being stirred for 45 min, the mixture was filtered and the filtrate fractionally distilled to afford 10.7 g (62%) of fluorosilane: bp 68-71 °C (20 mm); NMR (CDCl₃) δ 5.68 (1 H, m), 4.84 (2 H, m), 1.94 (2 H, m), 1.34 (4 H, m), 0.56 (2 H, m), 0.07 (6 H, d, J = 8 Hz).

Registry No. (CH₃CH₂)₄Si, 631-36-7; CH₃CH₂CH₂CH₂Si(CH₃)₃, 1000-49-3; PhCH₂CH₂SiMe₃, 772-64-5; Ph₂CHCH₂SiMe₃, 75961-63-6; Ph₂CHCH₂SiMeEt₂, 75961-64-7; Me₃Si(CH₂)₆SiMe₃, 13083-96-0; (CH₂)₃Si(CH₃)₂, 2295-12-7; (CH₂)₄Si(CH₃)₂, 1072-54-4; (CH₂)₅Si(C-H₃)₂, 4040-74-8; (CH₂)₆Si(CH₃)₂, 15896-02-3; 1,1-diphenylethene, 530-48-3; dimethylchlorosilane, 1066-35-9; 1-methyl-1,3,3-triphenylindane, 19303-32-3; 1-(chloromethyl)-1-methylsilacyclohexane, 15303-37-4; TPMTFB, 341-02-6; (5-hexenyl)dimethylfluorosilane, 75961-65-8; 1,5-hexadiene, 592-42-7.

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Regiospecific Synthesis of Allylic Dimethylmethoxysilanes

Dongjaw Tzeng and William P. Weber*

Department of Chemistry, University of Southern California, Los Angeles, California 90007

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Photochemically generated dimethylsilylene reacts regiospecifically with allylic methyl ethers to yield allylic dimethylmethoxysilanes. Reaction of allylic methyl ethers with dimethyldichlorosilane and sodium metal likewise gives allylic dimethylmethoxysilanes in preparatively useful yields. Regiospecificity, however, is not always observed in this latter reaction. Such allylic dimethylmethoxysilanes can be converted to allylic trimethylsilanes easily by reaction with methyllithium.

Allylic trimethylsilanes have been shown to be versatile intermediates in organic synthesis.¹ They react regiospecifically with a wide range of electrophilic reagents to give substitution with allylic rearrangement in the sense shown (eq 1).²⁻¹⁴ In addition, allylic trimethylsilanes can

E Si(CH3)3	 E > ~	(1)
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