

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

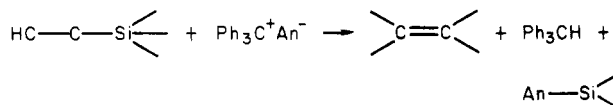
Stephen S. Washburne* and Robert Szendroi

Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122

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Ten acyclic, cyclic, and aralkyl-type silanes were treated with triphenylcarbenium tetrafluoroborate in dichloromethane to measure rates of oxidative desilylation: $RCH_2CH_2SiR_3 + Ph_3C^+ BF_4^- \rightarrow Ph_3CH + RCH=CH_2 + R_3SiF + BF_3$. The divergence of rates, from $Ph_3C^+ BF_4^-$, which was inert, through dimethylsilacyclopentane ($k_2 = 4 \times 10^{-6}$), to dimethylsilacyclohexane ($k_2 = 2.2 \times 10^{-8}$), 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



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 Me_3SnH , 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 ($\sim 22^\circ C$), 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 (5-hexenyl)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, $H_2C=CHCH_2SiMe_2F$, being an allylsilane, was cleaved by TTFB about as rapidly as starting material, giving Me_2SiF_2 as the principal silicon-containing material isolated (together with $Ph_3CCH_2CH=CH_2$, 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 desilylation coupled with hydrosilylation 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 substituent, 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

(1) For leading references see T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Am. Chem. Soc.*, **93**, 5715 (1971).

(2) As shown by, for example, charge-transfer studies: (a) W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Am. Chem. Soc.*, **92**, 829 (1970). (b) See also I. Fleming in "Comprehensive Organic Chemistry", Vol. 3, D. Barton and W. D. Ollis, Eds., Pergamon Press, Oxford, 1979, p 542.

(3) M. E. Jung and L. M. Speltz, *J. Am. Chem. Soc.*, **98**, 7882 (1976).

(4) G. A. Olah and T. Ho, *Synthesis*, 609 (1976).

(5) (a) J. Jerkunica and T. G. Traylor, *J. Am. Chem. Soc.*, **93**, 6278 (1971); (b) T. G. Traylor, H. J. Berwin, J. Jerkunica, and M. L. Hall, *Pure Appl. Chem.*, **30**, 599 (1972).

(6) S. S. Washburne and J. Simolike, *J. Organomet. Chem.*, **81**, 41 (1974).

Table I. Reaction of Acyclic Tetraalkylsilanes with Trityl Tetrafluoroborate 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 ₃ CH ₂) ₄ Si ^a	CH ₂ =CH ₂	6.8 ^a	0.57
2	CH ₃ CH ₂ CH ₂ CH ₂ Si(CH ₃) ₃	CH ₃ CH ₂ CH=CH ₂ ^b	~50	~25
3	PhCH ₂ CH ₂ SiMe ₃	PhCH=CH ₂ ^b	5300	2700
4	Ph ₂ CHCH ₂ SiMe ₃	nil	nil	nil
5	Ph ₂ CHCH ₂ SiMeEt ₂	CH ₂ =CH ₂	~3	~0.5
6	Me ₃ Si(CH ₂) ₆ SiMe ₃	CH ₂ =CH(CH ₂) ₄ SiMe ₃	~300	~75

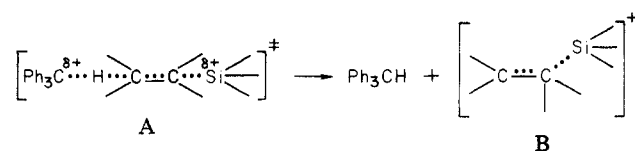
^a Reference 5a. ^b Not isolated, detected by gas chromatography. ^c Times 10⁷.

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

no.	(CH ₂) _n Si(CH ₃) ₂ n	product	rate const, ^b M ⁻¹ s ⁻¹	rate const per H, ^b M ⁻¹ s ⁻¹
7	3	SiMe ₂ F ₂ + CH ₂ =CHCH ₂ SiMe ₂ F	~200	100
8	4	CH ₂ =CHCH ₂ CH ₂ SiMe ₂ F	0.04	0.01
9	5 ^a	CH ₂ =CH(CH ₂) ₃ SiMe ₂ F	22 ^a	5.5
10	6	CH ₂ =CH(CH ₂) ₄ SiMe ₂ F	15.8	4.0

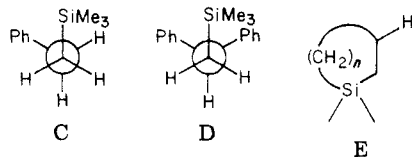
^a Reference 6. ^b Times 10⁴.

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 2,2-diphenylethyl, 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 R₃Si and H is similarly required in the present system, the transition state for (2-phenylethyl)trimethylsilane C has a *gauche*



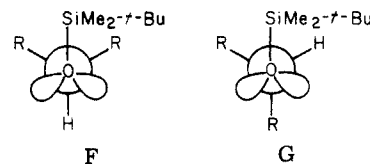
relationship of Ph and Me₃Si; (2,2-diphenylethyl)trimethylsilane is obliged to adopt the unfavorable congested state D. The second phenyl group, rather than providing extra stabilization to the developing positive center, prevents the molecule from adopting a conformation compatible with desilylation.

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 × 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-

(9) R. Ouellette, *J. Am. Chem. Soc.*, **96**, 2421 (1974).

(10) J. R. Doring, W. J. Lafferty, and V. Kalasinsky, *J. Phys. Chem.*, **80**, 1199 (1976).

(11) D. Seyferth, S. S. Washburne, C. S. Attridge, and K. Yamamoto, *J. Am. Chem. Soc.*, **98**, 1629 (1976).

(12) B. W. Metcalf, J. P. Burkhart, and K. Jund, *Tetrahedron Lett.*, **21**, 35 (1980).

(7) R. Damrauer, *Organomet. Chem. Rev., Sect. A*, **8**, 67 (1972).

(8) A. W. Jarvie, A. Holt, and J. Thompson, *J. Chem. Soc. B*, 852 (1969).

