Acknowledgment. This research was supported by the National Cancer Institute DHEW (CA 13689-06).

References and Notes

(1) K. C. Nicolaou, *Tetrahedron*, **33**, 683 (1977).

(2) Recent reports in the literature have described the synthesis of selenol esters by reaction of (a) carboxylic acid–imidazoles with aliphatic and aromatic selenols,[3,4] (b) carboxylic acid–1,2,4-triazoles with selenols,[3] (c) cyclohexanecarboxylic acid diethylphosphoric anhydride, acid chloride, or imidazole with the Tl(I) salt of benzeneselenol,[5] and (d) cyclohexanecarboxylic acid with benzeneselenenyl chloride or diphenyl diselenide in the presence of tri-*n*-octylphosphine.[5]

(3) H.-J. Gais, *Angew. Chem., Int. Ed. Engl.*, **16**, 244 (1977).

(4) G. S. Bates, J. Diakur, and S. Masamune, *Tetrahedron Lett.*, 4423 (1977).

(5) See footnotes 3 and 17 in ref 6i.

(6) For recent reports describing the synthesis of thiol esters see: (a) E. J. Corey and D. J. Beames, *J. Am. Chem. Soc.*, **95**, 5829 (1973); (b) T. Mukaiyama, T. Takeda, and K. Atsumi, *Chem. Lett.*, 187 (1974); (c) S. Masamune, S. Kamata, J. Diakur, Y. Sugihara, and G. S. Bates, *Can. J. Chem.*, **53**, 3693 (1975); (d) T. Mukaiyama, *Angew. Chem., Int. Ed. Engl.*, **15**, 94 (1976); (e) F. Souto-Bachiller, G. S. Bates, and S. Masamune, *J. Chem. Soc., Chem. Commun.*, 719 (1976); (f) R. P. Hatch and S. M. Weinreb, *J. Org. Chem.*, **42**, 3960 (1977); (g) S. Masamune, S. Kamata, and W. Schilling, *J. Am. Chem. Soc.*, **97**, 3515 (1975); (h) H.-J. Gais, *Angew. Chem., Int. E. Engl.*, **16**, 244 (1977); (i) S. Masamune, Y. Hayase, W. Schilling, W. K. Chan, and G. S. Bates, *J. Am. Chem. Soc.*, **99**, 6756 (1977); (j) S. Yamada, Y. Yokoyama, and T. Shioiri, *J. Org. Chem.*, **39**, 3302 (1974).

(7) P. A. Grieco, S. Gilman, and M. Nishizawa, *J. Org. Chem.*, **41**, 1485 (1976).

(8) P. A. Grieco and Y. Yokoyama, *J. Am. Chem. Soc.*, **99**, 5210 (1977).

(9) O. Behaghel and H. Seibert, *Ber.*, **65**, 812 (1932).

(10) K. Kottke, F. Friedrich, and R. Pohloudek-Fabini, *Arch. Pharm.*, **300**, 583 (1967).

(11) F. Challenger, C. Higginbottom, and A. Huntington, *J. Chem. Soc.*, 26 (1930).

(12) Fellow of the Alfred P. Sloan Foundation.

Paul A. Grieco,*[12] Yuusaku Yokoyama
Eric Williams

Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

Received December 20, 1977

Favored Reduction of α-Chlorosilanes vs. α-Chloroalkanes with Tri-*n*-butyltin Hydride

Summary: The reduction of 1-chloro-2,2-dimethyl-2-silapropane, neopentyl chloride, and 1,6-dichloro-2,2,5,5-tetramethyl-2-silahexane with tri-*n*-butyltin hydride under free-radical conditions is described.

Sir: In 1965 it was suggested that α-silyl radicals may be specially stabilized compared to their all-carbon analogues, possibly by vicinal (d-p) π overlap.[1] Such stabilization was invoked to explain the absence of rearrangement in α-silyl radicals.[2] Although ESR studies appear to confirm this stabilization,[3] it seemed desirable to investigate it further. We describe here external and internal competition studies that show the heretofore unreported *preferential reduction of certain α-chlorosilanes over their all-carbon analogues* with tri-*n*-butyltin hydride. These results strongly suggest that some α-silyl radicals are indeed more stable than their all-carbon congeners.

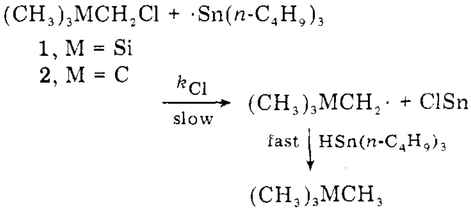
In the external competition, mixtures of 1-chloro-2,2-dimethyl-2-silapropane ("silaneopentyl chloride", **1**) and neopentyl chloride (**2**) were dissolved in dry benzene, sealed in ampules after degassing, and reduced with tri-*n*-butyltin hydride,[4] using di-*tert*-butyl peroxide as the free-radical initiator. The results are given in Table I.

Table I. Competitive Reduction of 1 and 2[a]

Ratio 1/2, mM	$k_{\mathrm{Si}}/k_{\mathrm{C}}$[b,c]
1:2[d]	78
1:1.5[d]	81

[a] On a 10–20 mmol scale. In benzene at 151–152 °C for 20 h. Ratio of materials (**1** + **2**)/tri-*n*-butyltin hydride/di-*tert*-butyl peroxide = 10:3:1. [b] Competitive rate ratio, calculated from calibrated initial and final ^{1}H NMR spectra by a standard method (M. J. Hutchinson and M. W. Mosher, *J. Chem. Educ.*, **48**, 629 (1971)). The results are for several runs and are ±3%. [c] The reductions afforded tetramethylsilane from **1** and neopentane from **2**, each in >90% yield. [d] Excess **2** was employed to increase the precision of the results.

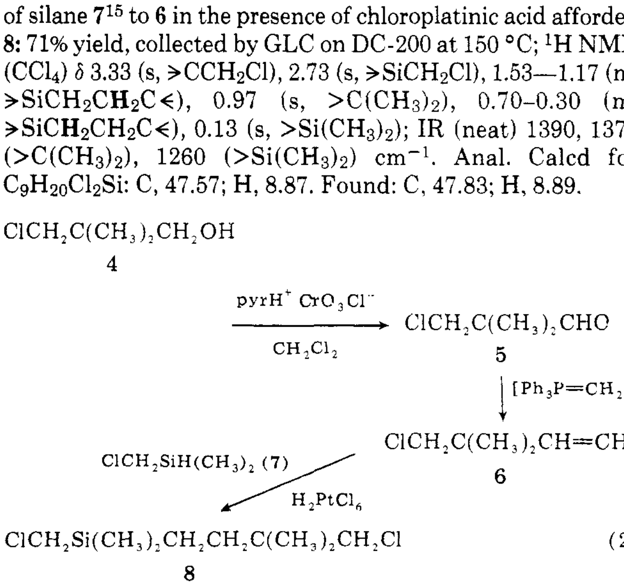
It may be seen that **1** is nearly two orders of magnitude faster in this reduction than is **2**. Because the chlorine abstraction step (eq 1) determines the rate of these reductions,[5] it would appear that $(CH_3)_3SiCH_2\cdot$ (**1·**) is more easily formed than $(CH_3)_3CCH_2\cdot$ (**2·**) and therefore that **1·** might be more stable than **2·**. External competition experiments can be misleading, however. The competitive rate ratio, which only measures the relative activation barriers, might actually reflect a less stable reactant (i.e., **1**) rather than a more stable intermediate (i.e., **1·**).



$$(CH_3)_3MCH_2Cl + \cdot Sn(n\text{-}C_4H_9)_3 \qquad 1,\ M = Si \quad 2,\ M = C$$

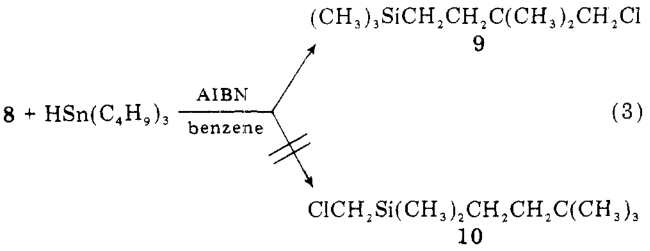
$$\xrightarrow[\text{slow}]{k_{Cl}} (CH_3)_3MCH_2\cdot + ClSn(n\text{-}C_4H_9)_3 \xrightarrow[\text{fast}]{HSn(n\text{-}C_4H_9)_3} (CH_3)_3MCH_3 \qquad (1)$$

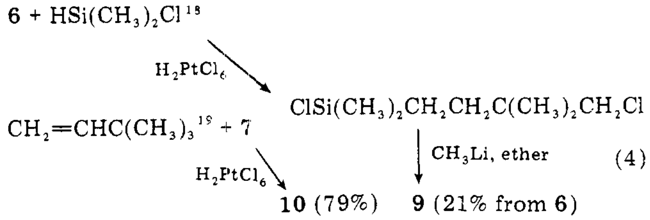
Because literature data applicable to the free-energy content of **1** appear to vary significantly,[6] another approach to the selectivity in eq 1 was used, viz., internal competition. Here the problem of possible ground-state-energy differences between reactants disappears. The model chosen was 1,6-dichloro-2,2,5,5-tetramethyl-2-silahexane (**8**). Its synthesis (eq 2) commenced with the oxidation of the chloro alcohol **4** (Aldrich) to the chloro aldehyde **5**: pyridinium chlorochromate in methylene chloride;[12] 80% yield; bp ~100 °C (150 mm) (Kugelrohr); 2,4-DNP, mp 137–138 °C. Anal. Calcd for $C_{11}H_{13}ClN_4O_4$: N, 18.63. Found: N, 18.69. Conversion of aldehyde **5** to olefin **6** was accomplished via the Wittig reaction: dimsyl sodium;[13] methyltriphenylphosphonium bromide (or tosylate[14]); 30% yield; bp 108–109 °C (atm); ^{1}H NMR (CCl_4) δ 5.83, 5.12, 4.90 ($-CH{=}CH_2$) (ABX, $J_{\mathrm{trans}} = 18$, $J_{\mathrm{cis}} = 9$, $J_{\mathrm{gem}} = 3$ Hz), 3.30 (s, $-CH_2Cl$), 1.10 (s, $-CH_3$); IR (neat) 3110, 1642, 928 ($-CH{=}CH_2$), 1382, 1368 (CH_3) cm^{-1}. Anal. Calcd for $C_6H_{11}Cl$: C, 60.76; H, 9.35. Found: C, 61.08; H, 9.50. Addition of silane **7**[15] to **6** in the presence of chloroplatinic acid afforded **8**: 71% yield, collected by GLC on DC-200 at 150 °C; ^{1}H NMR (CCl_4) δ 3.33 (s, $\geqslant CCH_2Cl$), 2.73 (s, $\geqslant SiCH_2Cl$), 1.53—1.17 (m, $\geqslant SiCH_2\mathbf{CH_2}C\leqslant$), 0.97 (s, $>C(CH_3)_2$), 0.70–0.30 (m, $\geqslant Si\mathbf{CH_2}CH_2C\leqslant$), 0.13 (s, $>Si(CH_3)_2$); IR (neat) 1390, 1370 ($>C(CH_3)_2$), 1260 ($>Si(CH_3)_2$) cm^{-1}. Anal. Calcd for $C_9H_{20}Cl_2Si$: C, 47.57; H, 8.87. Found: C, 47.83; H, 8.89.



$$\underset{4}{ClCH_2C(CH_3)_2CH_2OH} \xrightarrow[CH_2Cl_2]{pyrH^+\,CrO_3Cl^-} \underset{5}{ClCH_2C(CH_3)_2CHO} \xrightarrow{[Ph_3P{=}CH_2]} \underset{6}{ClCH_2C(CH_3)_2CH{=}CH_2} \xrightarrow[H_2PtCl_6]{ClCH_2SiH(CH_3)_2\ (7)} \underset{8}{ClCH_2Si(CH_3)_2CH_2CH_2C(CH_3)_2CH_2Cl} \qquad (2)$$

A sample reduction of **8** is described. In an NMR tube were placed **8** (45 mg, 0.198 mmol), tri-*n*-butyltin hydride (freshly prepared,[16] 61 mg, 0.209 mmol), azobisisobutyronitrile (Aldrich, 10 mg), and benzene (distilled Spectrograde material, 300 μL). Nitrogen was bubbled through the material briefly and the tube was capped. The solution was then irradiated in a small irradiation apparatus (Bradford Scientific Co.) at 366 nm and 37 °C (ambient) for 6.5 h. Processing the mixture directly by GLC (DC-200, 150 °C) afforded **9** in essentially quantitative yield based upon consumed reactants (94% reaction), with <5% (if any) of **10,** along with benzene and tri-*n*-butyltin chloride (eq 3).[17] For confirmation of their structures, chlorosilanes **9** and **10** were synthesized by the routes shown in eq 4. Chloro silane **9** was identical (spectra, GLC) with the reduction product: ^{1}H NMR (CCl_4) δ 3.30 (s, $-CH_2Cl$), 1.53–1.17 (m, $>SiCH_2CH_2C<$), 1.0 (s, $>C(CH_3)_2$), 0.67–0.23 (m, $>SiCH_2CH_2C<$), 0.07 (s, $>Si(CH_3)_3$); IR (neat) 1383, 1367 ($>C(CH_3)_2$), 1252, 840–870 ($>Si(CH_3)_3$) cm^{-1}. Anal. Calcd for $C_9H_{21}ClSi$: C, 56.06; H, 10.98, Found: C, 55.72; H, 10.96. Chlorosilane **10** was distinguished from its isomer **9** most readily by its NMR spectrum: ^{1}H NMR (CCl_4) δ 2.73 (s, $-CH_2Cl$), 1.40–1.03 (m, $>SiCH_2CH_2C<$), 0.90 (s, $-C(CH_3)_3$), 0.77–0.32 (m, $>SiCH_2CH_2C<$), 0.12 (s, $>Si(CH_3)_2$); IR (neat) 1392, 1362 ($-C(CH_3)_3$), 1252 ($>Si(CH_3)_2$) cm^{-1}. Anal. Calcd for $C_9H_{21}ClSi$: C, 56.06; H, 10.98. Found: C, 55.67; H, 10.74.





Work is in progress on the reduction of other α-chlorosilanes and α-chloroalkanes, both by external and internal competition techniques, to establish the generality of the present findings.

References and Notes

(1) J. W. Wilt and O. Kolewe, *J. Am. Chem. Soc.*, **87**, 2071 (1965).
(2) J. W. Wilt, O. Kolewe, and J. F. Kraemer, *J. Am. Chem. Soc.*, **91**, 2624 (1969).
(3) P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, **91**, 6161 (1969).
(4) H. G. Kuivila, *Acc. Chem. Res.*, **1**, 299 (1968).
(5) D. J. Carlsson and K. U. Ingold, *J. Am. Chem. Soc.*, **90**, 7047 (1968).
(6) E.g., the standard heat of formation of tetramethylsilane (a value needed to calculate the energy content of **1** by the method of O'Neal and Ring[7]) has literature values of: −26,[8] −33,[9] −68,[10] −69,[11] and −73[7] kcal mol^{-1}.
(7) H. O'Neal and M. Ring, *Inorg. Chem.*, **5**, 435 (1966).
(8) M. Tribble and N. Allinger, *Tetrahedron*, **28**, 2147 (1972).
(9) P. Potzinger and F. Lampe, *J. Phys. Chem.*, **74**, 719 (1970).
(10) S. Band, I. Davidson, and C. Lambert, *J. Chem. Soc. A*, 2068 (1968).
(11) S. Tannenbaum, *J. Am. Chem. Soc.*, **76**, 1027 (1954).
(12) E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, 2647 (1975).
(13) R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).
(14) D. Klamann and P. Weyerstahl, *Angew, Chem.*, **75**, 89 (1963).
(15) D. Seyferth and E. G. Rochow, *J. Am. Chem. Soc.*, **77**, 907 (1955).
(16) H. G. Kuivila and O. F. Beumel, Jr., *J. Am. Chem. Soc.*, **83**, 1246 (1961).
(17) Control experiments showed that 5% of **10** in **9** could be easily observed by ^{1}H NMR analysis. Analysis by IR or GLC was less useful. Work in progress on larger scale reactions will establish the extent of formation of **10.**
(18) Obtained from Silar Laboratories.
(19) Obtained from Aldrich Chemical Co.
(20) A portion of this work comes from the M. S. Thesis of P.M.A., Loyola University of Chicago, 1974.

James W. Wilt,* Peter M. Aznavoorian[20]
Department of Chemistry
Loyola University of Chicago
Chicago, Illinois 60626

Received January 6, 1978