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REACTION OF CHLOROMETHYLTRIMETHYLSILANE AND CHLOROMETHYLTRIMETHYLSTANNANE WITH LITHIUM 2,2,6,6-TETRAMETHYLPIPERIDIDE

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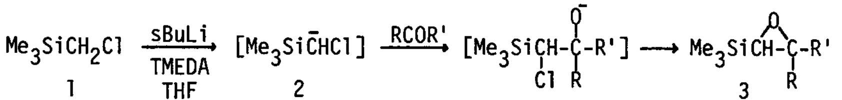
Recently Magnus and coworkers reported the selective deprotonation of chloromethyltrimethylsilane (1) to the carbanion (2) with sec-butyllithium-TMEDA.[1] In the presence of aldehydes and ketones, 2 reacted to give α,β-epoxysilanes (3), compounds of substantial preparative value.[1]



$$\underset{1}{Me_3SiCH_2Cl} \xrightarrow[\text{TMEDA}\atop\text{THF}]{sBuLi} \underset{2}{[Me_3Si\bar{C}HCl]} \xrightarrow{RCOR'} [Me_3Si\underset{Cl}{CH}-\overset{O^-}{\underset{R}{C}}-R'] \longrightarrow \underset{3}{Me_3SiCH\overset{O}{-}\underset{R}{C}-R'}$$

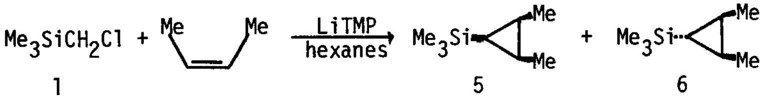
1 2 3

$$\underset{4}{[Me_3Si\ddot{C}H]}$$

Otherwise 2 was comparatively stable to -40°C and then decomposed only slowly by pathways which did not include fragmentation to trimethylsilylcarbene (4).[2] Failure to generate 4 by the α-elimination of HCl from 1 with various bases also has been noted in earlier literature.[3] Some of the alternate processes favored instead are illustrated by the reaction of 1 with nBuLi where the products include $nAmSiMe_3$ (from displacement of Cl^-), $nBuSiMe_3$ (from attack at Si), and $Me_3SiCH{=}CHSiMe_3$ (from 2 + 1).[3,4] Though compounds derived from 4 or the analogous carbenoid[5] have been obtained by the thermal, photochemical, and CuCl-induced decomposition of Me_3SiCHN_2, these methods[3,6,7] have little practical use because the potentially dangerous diazo precursor is itself the endproduct of a multistep sequence.

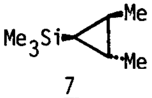
The multiplicity of reaction sites in 1 toward bases together with the surprising prejudice of 2 against losing chloride would seem to promise failure for any new attempt to convert 1 to 4 with a base. Despite this prognosis, methodology for accomplishing this transformation has been developed and is introduced here. Moreover, abetted by the ready availability of 1,[8] the new procedure provides a useful new source of silyl substituted cyclopropanes. The key to success is utilization of the $\overset{+}{\mathrm{H}}$arpoon base, lithium 2,2,6,6-tetramethylpiperidide (LiTMP), a proton-selective reagent developed in this laboratory[9] which has in the past proved particularly effective in promoting α-eliminations.[9-11]

The process is exemplified by the formation of the silylcyclopropanes (5 and 6,[12] 23% yield, ratio: 1:12[13]) on treatment of 1 with a hexanes solution of LiTMP containing a severalfold excess of cis-butene.



1 5 6

(bp 61-63° at 82 torr)



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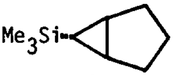
The reaction was completely stereospecific: Though searched for, none of the trans-dimethylcyclopropane (7) was found. This indication of the intermediacy of a singlet carbene[5] was confirmed by the isolation of 7 and no 5 or 6 on treatment of 1 with LiTMP and trans-butene.

Silylcyclopropanes including those depicted below were also prepared from 1, LiTMP, and cycloalkenes or cycloalkadienes (e.g. 11 from 1,5-cyclooctadiene).



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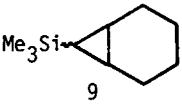

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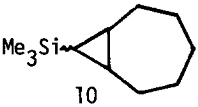

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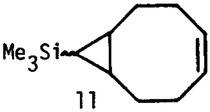


11

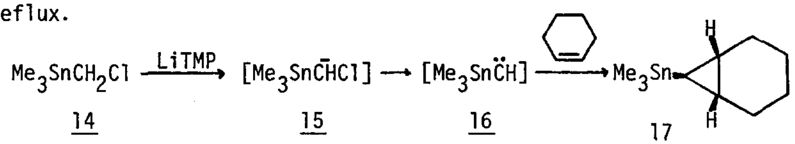
	8	9	10	11
Yield:	28%	33%	30%	30%
Bp at (torr):	81-85°(78)	69-71° (5)	79-83° (6)	70-73° (2)
Syn:anti:	No syn found	1:9	Little syn[14]	1:13

In the optimum procedure, first the alkene and then the chloromethylsilane were added to the LiTMP in hexanes. The mixture then was heated at reflux (or in an oil bath set at 85°C[15]) overnight before a workup which included extraction of the salts and HTMP into aqueous citric acid before distillation. Under these conditions, the only other volatile product was a trace of the disilylethylenes (13) formed by displacement of chloride from 1 by the carbanion (2) followed by β-elimination of HCl from the intermediate (12) with a second mole of base.

$$\underset{1}{\mathrm{Me_3SiCH_2Cl}} + \underset{2}{\mathrm{Me_3Si\bar{C}HCl}} \longrightarrow \underset{12}{\mathrm{Me_3SiCH_2CHClSiMe_3}} \xrightarrow[\text{or } 2]{\text{LiTMP}} \underset{13}{\mathrm{Me_3SiCH{=}CHSiMe_3}}$$

After distillation, the still pot contained a substantial amount of an unidentified $\mathrm{Me_3Si}$-bearing residue. When ether was used in place of hexanes as the cosolvent, the yield of 13 went up to 3%, and with THF as the cosolvent, 13 became a major product (22%). It would seem that in more polar, ion-stabilizing solvents, the driving force for the salt (2) to fragment to the neutral carbene[5] is reduced thus increasing the yield of 13 at the expense of carbene-derived products. The ethylenes (13, cis:trans 1:6) could be prepared in 42% yield just by adding ethereal LiTMP to a refluxing THF solution of 1. In the past, these alkenes were available only by less efficient multistep procedures[16] (or as by-products). In another experiment, the predicted epoxysilane was isolated when benzaldehyde was heated with 1 and LiTMP in THF. However, the process was inferior to that of Magnus (see above).

The generation of trimethylstannylcarbene (16) has not been reported before. Even the diazo compound, Me_3SnCHN_2, has failed as a carbene source[17] although the carbethoxy stabilized species, $[Ph_3Sn\ddot{C}CO_2Et]$, the only previously described tin substituted carbene, has been produced from the diazoacetate and trapped with isobutene.[18] In an attempt to extend the new methodology outlined here, chloromethyltrimethyltin (14) was made[19] and reacted with LiTMP in cyclohexene-ether at reflux.



14 15 16 17

$Me_3SnCH{=}CHSnMe_3$

18

The only product identified was anti-7-trimethylstannylnorcarane (17) which was isolated in 21% yield; bp 67-68°C at 2 torr; NMR (δ) in CCl_4: -0.44 (1H, t, J=6.5 Hz), -0.02 (9H, s; also: d, $J_{^{117}Sn-H}$=51 Hz; d, $J_{^{119}Sn-H}$=53 Hz), 0.55-1.0 (2H, m), 1.0-1.5 (4H, m), 1.5-2.2 (4H, m); anal. calc. for $C_{10}H_{20}Sn$: C,46.38%; H,7.79%; found: C,46.20%; H,7.65%. Some 14 (15%) also was recovered. Though searched for, the syn isomer of 17 and the cis- and trans-alkenes (18) were not found. The latter also were absent when the reaction was performed in THF under conditions which would have yielded the disilylalkenes (13) as the major product. Efforts are underway to explain why the tin stabilized anion (15) should be much more susceptible to fragmentation to the carbene than the silyl analogue (2).

Also, ready access to silylcyclopropanes is the prelude to the development of preparative uses of these species based on their predicted high and selective reactivity.[20]

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2) See ref. 1, footnote 3.

3) For example: D. Seyferth, A. W. Dow, H. Menzel, and T. C. Flood, J. Amer. Chem. Soc., 90, 1080 (1968); J. Organometal. Chem., 44, 279 (1972); also see: I. A. D'yakonov, I. B. Repinskaya, and G. V. Golodnikov, J. Gen. Chem. USSR (Engl.), 35, 203 (1965).

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5) The terms "carbene" and "carbenoid" are used almost interchangeably here; for differentiation see: W. Kirmse, "Carbene Chemistry", 2nd Edit., Academic Press, 1971. Though no definitive experiments have been performed, the new chemistry described here probably best fits the intermediacy of a carbenoid species.

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7) The precursors, $(Me_3SiCHX)_2Hg$ (X=Br,I), are much poorer carbene sources; ref. 3 and D. Seyferth and E. M. Hanson, J. Organometal. Chem., 27, 19 (1971); D. Seyferth, S. B. Andrews, and R. L. Lambert, ibid., 37, 69 (1972). For some complex reactions which may involve 4 as an intermediate see: P. S. Skell and E. J. Goldstein, J. Amer. Chem. Soc., 86, 1442 (1964); J. W. Connolly and G. Urry, J. Org. Chem., 29, 619 (1964).

8) Commercially available from several sources; many syntheses including chlorination of Me_4Si.

9) R. A. Olofson and C. M. Dougherty, J. Amer. Chem. Soc., 95, 581, 582 (1973).

10) α-Elimination instead of β-elimination even occurs with $ClCH_2OCH_2CH_2Cl$: G. N. Barber and R. A. Olofson, Tetrahedron Lett., 3783 (1976).

11) R. A. Olofson, K. D. Lotts, and G. N. Barber, Tetrahedron Lett., 3381, 3779 (1976).

12) All silyl- and stannylcyclopropanes except 7 and 9 are new. Spectral and analytical data including IR, NMR, and high resolution mass spectra are in accord with the assigned structures.

13) Ratios were determined by GC separation and independent NMR analysis. Syn-anti isomer assignments are based on analogy and on the discovery by L. M. Jackman and S. Sternhell ("Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd Edit., Pergamon Press, Oxford, 1969) that the cis vicinal NMR coupling constants of the cyclopropyl protons in any isomer pair are always larger than the corresponding trans J values.

14) Incomplete resolution of NMR and GC-MS.

15) The butene experiments were carried out in stirred pressure bottles in an oil bath set at 70°C.

16) See for example: J. Cudlin, J. Schraml, and V. Chvalovsky, Coll. Czech. Chem. Comm., 29, 1476 (1964).

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18) U. Schöllkopf and N. Rieber, Angew. Chem. Internat. Edit., 6, 884 (1967).

19) D. Seyferth and S. B. Andrews, J. Organometal. Chem., 30, 151 (1971).

20) Note effect of an adjacent Me_3Si or Me_3Sn on cyclopropyl CH acidity. For predictions concerning ring reactivity toward electrophiles see: T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, J. Amer. Chem. Soc., 93, 5715 (1971); A. Hosomi and T. G. Traylor, ibid., 97, 3682 (1975), and refs. therein.