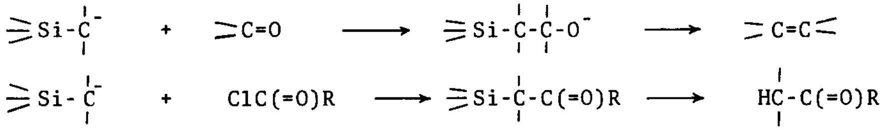
Tetrahedron Letters No. 42, pp 4193 - 4196, 1973. Pergamon Press. Printed in Great Britain.

NEW METHOD OF PREPARING SILYL SUBSTITUTED CARBANIONS BY BASE CATALYZED CLEAVAGE OF CARBON SILICON BONDS. APPLICATION TO SYNTHESES OF OLEFINS[1]

Hideki Sakurai,* Ken-ichiro Nishiwaki and Mitsuo Kira
(Department of Chemistry, Faculty of Science,
Tohoku University, Aobayama, Sendai, Japan)

(Received in Japan 24 July 1973; received in UK for publication 11 September 1973)

Silyl-substituted organometallic compounds of a general formula of $R_3SiC^- - R^1R^2M^+$ have been recognized to be effective intermediates in the conversion of carbonyl compounds and acid chlorides to olefins[2] and ketones,[3] respectively.



$$\geqq Si-\overset{|}{\underset{|}{C}}{}^- + \;>C{=}O \longrightarrow \;\geqq Si-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-O^- \longrightarrow \;>C{=}C<$$

$$\geqq Si-\overset{|}{\underset{|}{C}}{}^- + ClC({=}O)R \longrightarrow \;\geqq Si-\overset{|}{\underset{|}{C}}-C({=}O)R \longrightarrow H\overset{|}{\underset{|}{C}}-C({=}O)R$$

These carbanions α to silicon have been prepared by halogen-metal exchange, metalation with alkyllithium,[2-6] and addition of alkyllithium to vinylsilane.[3] The usefulness of these reagents is, however, limited more or less by the availability of the precursory (haloalkyl)silanes or by the limited reactivity of metalation. For example, it is rather difficult to prepare disilylalkyl anions which can be led to vinylsilanes, useful intermediates in syntheses.[7]

On the other hand, numerous examples show that cleavage of alkyl groups substituted by electronegative atoms or groups from the silicon atom occurs readily.[8] Simple alkyl groups such as methyl are also cleaved from the silicon atom by strong bases.[9] However, no example of synthetic application of these carbanions thus formed has been reported, since these carbanions undergo proton-abstraction from the solvent very readily under the experimental conditions.

Recent success of preparing trimethylsilylsodium[10] from hexamethyldisilane by nucleophilic attack on silicon by alkoxide anion in hexamethylphosphoramide

(HMPA) prompted us to examine the reaction of various alkylsilanes with alkoxide anions in HMPA. In this paper we show that these reactions turned out a new method of preparing carbanions.

$$\mathrm{Me_3Si\text{-}SiMe_3 \quad + \quad MeO^-Na^+ \quad \longrightarrow \quad Me_3SiOMe \quad + \quad Me_3Si^-Na^+}$$

$$\mathrm{R_3Si\text{-}R \quad + \quad MeO^-M^+ \quad \longrightarrow \quad R_3SiOMe \quad + \quad R^-M^+ \quad (M{=}Li,\ Na)}$$

To a stirred suspension of 1.62 g (30 mmol) of sodium methoxide in 18 ml of HMPA was added 3.04 g (10 mmol) of tetrakis(trimethylsilyl)methane at 60° under an atmosphere of argon. The resulting yellow solution was stirred for 2 h and then treated with 2.15 g (15 mmol) of methyl iodide. The mixture was allowed to stand for 12 h and treated with water. Extraction with ether followed by distillation under reduced pressure gave 0.43 g (17.5% yield) of 1,1,1-tris(trimethylsilyl)ethane.[6]

$$\mathrm{(Me_3Si)_4C \quad + \quad NaOMe \quad \longrightarrow \quad (Me_3Si)_3C^-Na^+ \quad + \quad Me_3SiOMe}$$

$$\mathrm{(Me_3Si)_3C^-Na^+ \quad + \quad MeI \quad \longrightarrow \quad (Me_3Si)_3CCH_3 \quad + \quad NaI}$$

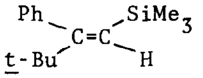
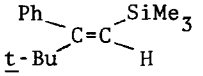
Tris(trimethylsilyl)methane and sodium methoxide in HMPA also gave, after aqueous work-up, expected $\mathrm{(Me_3Si)_2CH_2}$ in 82.8% yield.

These facts indicate that carbanions $\mathrm{(Me_3Si)_nH_{3-n}C^-}$ can be prepared by cleavage of a trimethylsilyl group from the compound, $\mathrm{(Me_3Si)_{n+1}H_{3-n}C}$. Cook, Eaborn, Jukes, and Walton[6] obtained $\mathrm{(Me_3Si)_3CLi}$ by metalation of $\mathrm{(Me_3Si)_3CH}$ with methyllithium in tetrahydrofuran. However, the trimethylsilyl group was not cleaved from $\mathrm{(Me_3Si)_4C}$ by methyllithium in spite of the ease of metalation of $\mathrm{(Me_3Si)_3CH}$.[6] Therefore, one of the important driving force of the present reaction is apparently the formation of a thermodynamically favored silicon-oxygen bond. The resulting carbanions $\mathrm{(Me_3Si)_nH_{3-n}C^-}$ are stabilized by delocalization of a negative charge involving interaction of the non-bonding electrons with the vacant d-orbitals of silicon.[6]

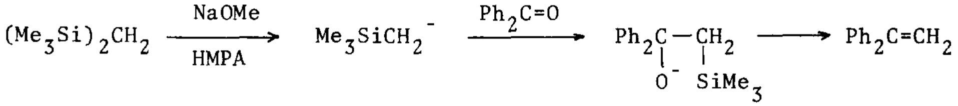
These carbanions were then subjected to the reaction with carbonyl compounds. For example, in the presence of benzophenone, the carbanion derived from bis(trimethylsilyl)methane gave 1,1-diphenylethylene in 53% yield.

Table 1

Preparation of Olefins by the Reaction of the
Silyl-Substituted Anions and Ketones

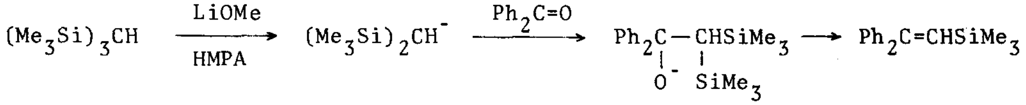
Starting Silane	Base	Ketone	Product (% yield)[a]	
$(Me_3Si)_2CH_2$	NaOMe	$Ph_2C=O$	$Ph_2C=CH_2$	(53)
$(Me_3Si)_2CH_2$	NaOMe	*t*-Bu·PhC=O	*t*-Bu·PhC=CH_2	(—)[b]
$(Me_3Si)_3CH$	LiOMe	$Ph_2C=O$	$Ph_2C=CHSiMe_3$	(51)
$(Me_3Si)_3CH$	LiOMe	*t*-Bu·PhC=O		(12.6)
$(Me_3Si)_4C$	NaOMe	*t*-Bu·PhC=O		(28.5)
$PhCH(SiMe_3)_2$	NaOMe	$Ph_2C=O$	$Ph_2C=CHPh$	(79)
$PhCH(SiMe_3)_2$	NaOMe	*t*-Bu·PhC=O	*t*-Bu·PhC=CPhH	(26)[c]

[a] Yields of the isolated product based on the starting ketone are indicated.
[b] Yield was not determined. [c] This is a mixture of cis and trans olefins(5.7/1).



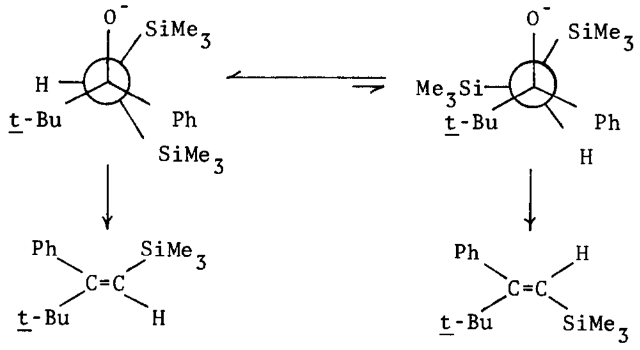
$$(Me_3Si)_2CH_2 \xrightarrow[\text{HMPA}]{\text{NaOMe}} Me_3SiCH_2^- \xrightarrow{Ph_2C=O} \underset{O^-}{Ph_2C}-\underset{SiMe_3}{CH_2} \longrightarrow Ph_2C=CH_2$$

Similar reaction of tris(trimethylsilyl)methane with benzophenone afforded dimethyl(2,2-diphenylvinyl)silane in 51% yield.



$$(Me_3Si)_3CH \xrightarrow[\text{HMPA}]{\text{LiOMe}} (Me_3Si)_2CH^- \xrightarrow{Ph_2C=O} \underset{O^-}{Ph_2C}-\underset{SiMe_3}{CHSiMe_3} \longrightarrow Ph_2C=CHSiMe_3$$

Other examples are summarized in Table 1. It is of interest to note that, from the reaction of $(Me_3Si)_2CH^-Na^+$ with pivalophenone in which geometrical isomerism was possible, only single isomer (A) was obtained.[11] The stereoselectivity can be rationalized in terms of cis elimination in the olefin-forming process as shown in the following scheme. Examination of a molecular model indicates readily that the *t*-butyl group cannot eclipse the trimethylsilyl group in an intermediate which could lead to (B).



(A) (B)

REFERENCES

1. Presented in part at the Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1973; Abstracts III, p.1480.
2. D. J. Peterson, J. Org. Chem., **33**, 780 (1968).
3. T. H. Chan, E. Chang, and E. Vinokur, Tetrahedron Lett., 1137 (1970).
4. D. J. Peterson, J. Organometal. Chem., **9**, 373 (1967).
5. G. A. Gornowicz and R. West, J. Amer. Chem. Soc., **90**, 4478 (1968).
6. M. A. Cook, C. Eaborn, A. E. Jukes, and D. R. M. Walton, J. Organometal. Chem., **24**, 529 (1970).
7. G. Strok and E. Colvin, J. Amer. Chem. Soc., **95**, 2080 (1971).
8. V. Chvalovský, in "Organometallic Reactions," vol.3, E. I. Becker and M. Tsutsui ed., Wiley-Interscience, New York, 1972, p.198.
9. C. C. Price and J. R. Sowa, J. Org. Chem., **32**, 4126 (1967).
10. H. Sakurai, A. Okada, M. Kira, and K. Yonezawa, Tetrahedron Lett., 1511 (1971).
11. The structure of (A) was substantiated by the NOE measurements. Thus, while irradiation of the Me_3Si signal at δ-1.20 ppm increased the integrated intensity of the signal due to olefinic proton at 5.72 ppm only in the extent of 3%, irradiation of the *t*-Bu signal at 1.20 ppm caused an enhanced increase (17%) in the intensity of the same olefinic proton.