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1,1-BIS(TRIMETHYLSILYL)-1-ALKANOLS AS SILYLCARBENE EQUIVALENT

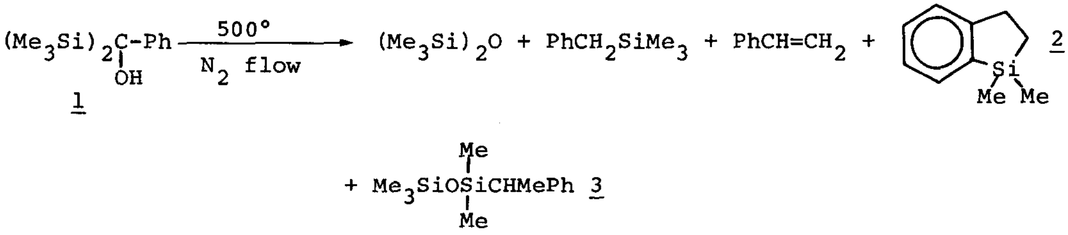
Akira Sekiguchi and Wataru Ando*
Department of Chemistry, The University of Tsukuba,
Niiharigun, Ibaraki 300-31, Japan

Summary: Silylcarbenes are generated by the pyrolysis of 1,1-bis(trimethylsilyl)-1-alkanols with elimination of trimethylsilanol.

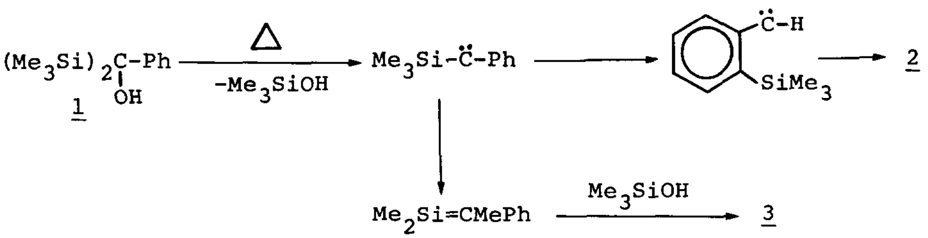
In recent years, interests in the chemistry of α-silylcarbenes have been extensively increased.[1] Attractive reactions of silylcarbenes are intramolecular ones in which silene (Si=C double bond intermediate) and silirane (silacyclopropane) intermediates are formed. Silylcarbenes are generally produced by the decomposition of silyl diazo compounds[1] or organomercury reagents such as $(Me_3SiCCl_2)_2Hg$,[2] a base induced α-elimination of halomethylsilane,[3] and an insertion of atomic carbon into silicon-hydrogen bond.[4] We are interested in alternative routes of the generation of silylcarbenes concerned with our chemistry of silyl diazo compounds.[1] We demonstrate here a very simple method of the generation of silylcarbenes in the pyrolyses of 1,1-bis(trimethylsilyl)-1-alkanols

The reaction was carried out by passing of bis(trimethylsilyl)phenyl methanol 1 (1.93 mmol) through a vertical Pyrex tube heated at ca. 500°C (nitrogen flow; ca. 11 ml/min), and then the pyrolysates were trapped in a receiver cooled by dry ice-acetone. Analysis of the pyrolysates by GLC showed the presence of five products. They were collected by praparative GLC and identified as hexamethyl siloxane, benzyltrimethylsilane (2%), styrene (10%), 1,1-dimethyl-2,3-benzo-1-silacyclopent-2-ene 2 (27%), and siloxane 3 (29%).

The yields were determined by GLC on addition of an internal standard to the reaction mixture. The structures of 2 and the siloxane 3 were confirmed by nmr, ir, and mass spectra.[1g,5]

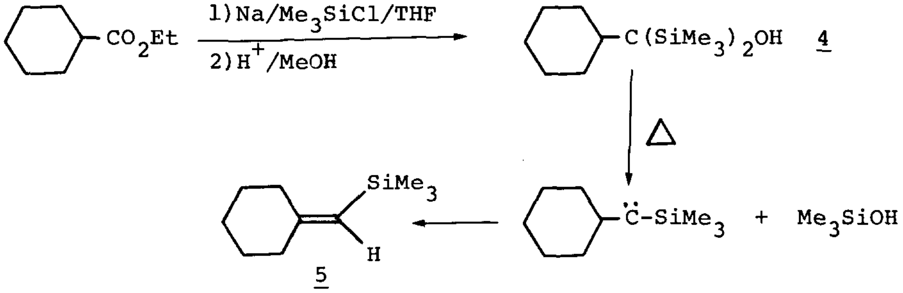


The above results were compared with those of the pyrolysis of phenyltrimethylsilyldiazomethane which gave four products, ditrimethylsilylstilbene (13%), benzyltrimethylsilane (2%), styrene (2%), and the silacyclopentene 2 (15%).[1g] Copyrolysis of the silyldiazomethane with alcohols produced alkoxysilanes, $ROSi(Me_2)CHMePh$ (16%), together with the above products.[1g] It was found that the reaction products from the silylated alcohol 1 are quite similar to those of the silyldiazomethane.



Benzyltrimethylsilane is a hydrogen abstraction product by phenyltrimethylsilylcarbene and is a typical minor product of carbene reactions. The silacylopentene 2 arises from o-trimethylsilyl phenylcarbene via a carbene-carbene rearrangement of the silylcarbene.[1g,6] The styrene is probably formed by the decomposition of 1,1-dimethyl-2-phenylsilirane produced by intramolecular C-H insertion of the silylcarbene and hexamethyl siloxane from dehydration of trimethylsilanols.[1g] The siloxane is the addition product of trimethylsilanol to 1,2,2,-trimethyl-1-phenylsilene.[1g] These results clearly indicate that 1,1-bis-(trimethylsilyl)-1-alkanols are convenient sources of silylcarbenes.

Pyrolysis of 1,1-bis(trimethylsilyl)cyclohexyl alcohol 4 gave cyclohexylidene trimethylsilane 5 in 90% yield along with hexamethyl siloxane.



The nmr spectrum (CCl_4, δ) of the vinylsilane 5 had peaks at 0.07(s,9H,$SiMe_3$), 1.40-1.85(m,6H,$-CH_2CH_2CH_2-$), 1.93-2.43(m,4H,$-CH_2C(=)CH_2-$), and 5.05(s,1H,SiCH=C) and identified by comparison with the reported spectral data.[7]

Table I. Pyrolysis of 1,1-Bis(trimethylsilyl)-1-alkanols.[a]

Alkanol	Product[b]	Yield (%)	Isomer ratio (cis/trans)	J(CH=CH)[c] cis(Hz)	trans(Hz)
$Me(CH_2)_6C(SiMe_3)_2OH$	$Me(CH_2)_5CH=CHSiMe_3$	98	1.0	14	19
$Me(CH_2)_8C(SiMe_3)_2OH$	$Me(CH_2)_7CH=CHSiMe_3$	93	1.0	14	19
$PhCH_2CH_2C(SiMe_3)_2OH$	$PhCH_2CH=CHSiMe_3$	94	1.3	15	18

a. Pyrolysis temperature, ca. 500°C.

b. Products were collected by bulb-to-bulb distillation. Products are a mixture of two isomers (cis and trans) and the ratio is determined by GLC. The structures of products were determined by nmr, ir, and mass spectra. Each isomers were separated by preparative GLC.

c. Nmr coupling constant in carbon tetrachloride.

This provides a new method for the synthesis of vinylsilanes via silylcarbene intermediates. Although the reaction conditions are relatively drastic, this seems to be a very convenient method for the praparation of vinylsilanes, because 1,1-bis(trimethylsilyl)-1-alkanols are easily prepared from ester and trimethylchlorosilane.[8] Some vinylsilanes were prepared by the pyrolyses of the silylated alcohols. The results are summarized in Table I. Two stereo isomeric vinylsilanes were produced.

References and Notes

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