

CYCLO-HYDROSILYLATION: A NOVEL ROUTE TO SILOXETANES AND SILANONES

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Summary

A novel and convenient method for the apparent liquid phase generation of dimethylsilanone, $\text{Me}_2\text{Si}=\text{O}$ (D_1), based on readily obtainable reactants and employing conventional temperatures (50-150°) is reported herein. Platinum catalyzed hydrosilylation of vinyl dimethylcarbinoxydimethylsilane (I) appears to proceed by an exclusively intramolecular path to produce not only the expected 5-membered heterocyclic, 1,1,3,3-tetramethyl-2-oxa-1-silacyclopentane (V), but also the isomeric and highly unstable 4-membered siloxetane, 1,1,3,3,4-pentamethyl-2-oxa-1-silacyclobutane (IV). The intermediacy of IV is suggested by the products: i.e., 2-methyl-2-butene which is believed to arise along with $\text{Me}_2\text{Si}=\text{O}$ from fragmentation of IV; D_3 and D_4 from D_1 self-coupling; a 6-membered cyclic derived from insertion of D_1 into the Si-O bond of IV, i.e., 1,1,3,3,5,5,6-heptamethyl-2,4-dioxa-1,3,-disilacyclohexane (VI); a polymer which upon alkaline cracking produces more 6-ring (VI) but little or no 5-ring (V) suggesting that the polymer arose from copolymerization of D_1 , D_2 , and siloxetane (IV). Compound I is also an excellent thermolytic source of D_1 as evidenced by the formation of the expected derivatives upon heating in the presence of known silanone traps.

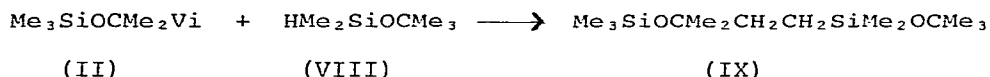
Introduction

Highly reactive unsaturated silicon intermediates such as $\text{Me}_2\text{Si}=\text{O}$ and $\text{Me}_2\text{Si}=\text{CH}_2$ have been the subject of much study during the past few years[1]. Their transient presence has been inferred from the nature of the products which arise when suitable trapping agents are employed. Unfortunately, their formation has generally required rather exotic precursors as well as the use of very high temperatures or high energy ultra-violet irradiation ($\lambda < 254 \text{ nm}$). We report herein evidence for the apparent generation of $\text{Me}_2\text{Si}=\text{O}$ under relatively ordinary conditions, i.e., without resorting to extremely elevated temperatures or high energy radiation.

Furthermore our method employs precursors which are easily prepared from more readily available starting materials.

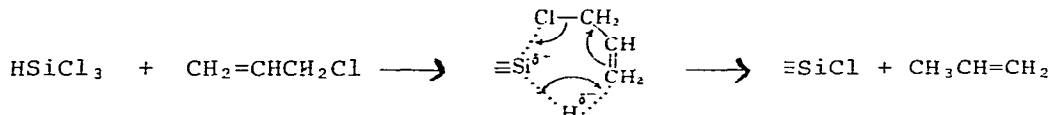
acid catalyzed ring closure did indeed result in the formation of minor amounts of the expected V, it soon became apparent that the hydrosilylation reaction was producing substantial quantities of other products which were strongly suggestive of a dimethylsilanone (D_1) reaction intermediate. Thus, as shown in Scheme 1, reaction of I yielded not only V, but also hexamethylcyclotrisiloxane (D_3), octamethylcyclotetrasiloxane (D_4), 2-methyl-butene-2 (III), a 6 membered cyclic (VI), and a 7-membered cyclic (VII) as well as varying amounts of polymeric materials. We believe that all products other than V have arisen from the transient formation of a 4-membered siloxetane [2] intermediate, IV, resulting from non-terminal addition of the silicon-hydride. Although intermolecular hydrosilylation reactions generally lead to products in which the silicon has added to the terminal site of the olefin, there is ample evidence that intra-molecular hydrosilylation can lead to the formation of major amounts of "non-terminal" adduct [3]. If the highly strained siloxetane (IV) fragments to yield 2-methylbutene-2 and dimethylsilanone (i.e., D_1) then VI can arise from insertion of D_1 into additional siloxetane, VII can arise from the similar reaction of D_1 and V, while D_3 and D_4 are the expected self-addition products of D_1 .

The polymer might have been attributed to a competing intermolecular hydrosilylation, however, this possibility seems to be excluded by our observation that alkaline depolymerization affords additional VI rather than V or VII, hence we conclude that the polymer has arisen from copolymerization of the highly reactive species IV along with its decomposition products D_1 and D_2 as suggested in Scheme 1. To exclude still further the possibility that the polymeric material might have arisen from an intermolecular reaction proceeding in a "non-terminal" fashion, we examined the following inter-molecular hydrosilylation of mono-functional reactants:

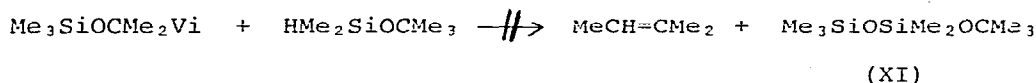


We observed no olefin and no $\text{Me}_3\text{SiOCMe}_2\text{CHMeSiMe}_2\text{OCMe}_3$ (X) thus providing additional evidence that the polymeric material did not arise from inter-molecular hydrosilylation.

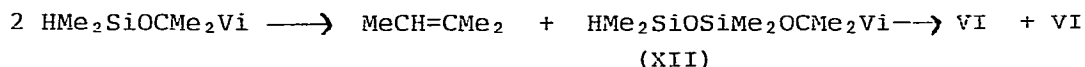
The above reaction with mono-functional model reactants also excludes another possible explanation for the formation of olefin during compound I hydrosilylation; i.e., Speier, et. al. [4] observed the formation of propylene during the reaction of Cl_3SiH with allyl chloride. This was attributed to a concerted bimolecular process of the following type:



In the above model compound reaction, not only did we not find olefin produced, but there was also none of the alkoxysiloxane (XI) which should have resulted from that type of bimolecular condensation process; i.e.,

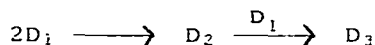


Nevertheless, despite all of the above contrary evidence, the bimolecular condensation rationale was considered still further because it offered an alternative explanation for the formation of the 6- and 7-membered cyclics (VI & VII) which could conceivably have arisen from ring closure of XII; i.e.,



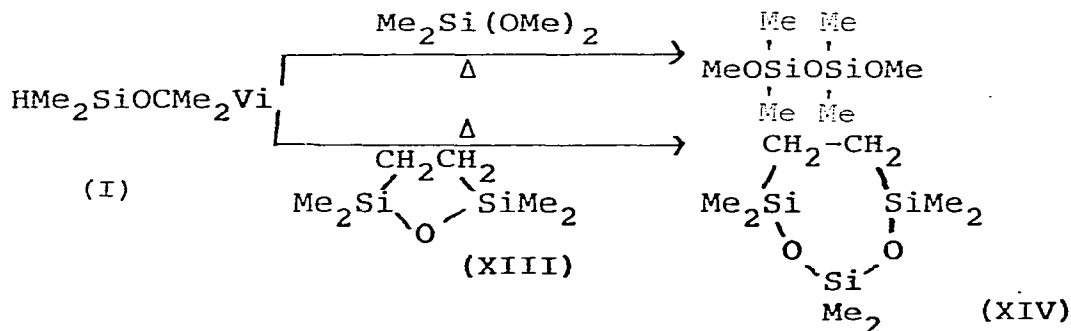
However, this possibility was convincingly ruled out by the following finding. XII was synthesized and shown to react in an almost exclusively inter-molecular fashion to yield a polymer which upon alkaline cracking afforded cyclic dimethylsiloxanes and compound V but no VI or VII. Thus the siloxetane/silanone mechanism appears to offer the only consistent rationale for our experimental observations.

In order to simplify the above discussion we have thus far omitted any mention of the function of the platinum catalyst in regard to the suggested reaction intermediates. For instance, it is possible that the postulated siloxetane might better be formulated as a 5-membered platinum metallocycle or that the silanone is present as a platinum π -complex. However, the reported [5] stability of even 4-membered metallocycles of rather similar structures suggests we are dealing with something far more reactive. In any event, since we are not yet in a position to make such distinctions, we have chosen the least complicated hypothetical intermediates to provide a mechanistic rationale for our observations to date. The key importance of the platinum catalyst is underscored by our observation that the relative amounts of D_3 and VI are inversely related to one another, but determined by the platinum level; i.e., higher catalyst loadings favor D_3 formation at the expense of VI, (see Experimental Section). This observation could mean that the platinum is in some way increasing the transient concentration of D_2 so that its conversion to D_3 is facilitated; i.e.,



Alternatively, one could argue that the platinum is simply catalyzing the more immediate fragmentation of the siloxetane so that it does not accumulate sufficiently to serve as a trap for dimethylsilanone which consequently has a better chance for self-addition to yield D_3 .

Compound I is also a useful precursor for the thermolytic generation of D_1 . Thus when I passed through a "ketene lamp" in the presence of the known silanone traps i.e., dimethyldimethoxysilane [6] and 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane [7] (XIII) the expected D_1 insertion products resulted; i.e



In the absence of such traps, compound I degraded to yield 2-methylbutene-2 and D₃ as well as higher boilers. Little degradation occurred when the compounds Me₂Si(OMe)₂, XIII, or V were individually passed through the ketene lamp.

Additional studies aimed at determining the utility of cyclohydrosilylation for generating other reactive intermediates are in progress with structures such as H(Ar)₂SiOCMe₂Vi, HMe₂SiOSiMe₂Vi, HMe₂SiCH₂CH=CH₂, HMe₂SiOCMe₂C≡CH, HMe₂Si-N(R)CH₂CH=CH₂, etc., as well as other catalysts.

Experimental

General comments

Gas liquid chromatograms were obtained with an Infotronics Model 2400 gas chromatograph equipped with a Model 68 linear temperature programmer and a 6' x 1/8" SP-2401 column. Infrared spectra were obtained on a Beckmann 4240 grating spectrometer. ¹H-NMR spectra were recorded on either a Varian Associates Model A-60 or a Varian Associates Model EM 390 spectrometer using CCl₄ as solvent and tetramethylsilane as internal standard. 15 MHz ¹³C NMR spectra were obtained on a JEOL FX-60 spectrometer using pulse Fourier transform technique. The 100 MHz spectra and integrals were scanned on a Varian XL-100 spectrometer in the CW mode. Both the ¹³C and 100 MHz NMR spectra were provided by Dr. J. P. Heeschen of the Dow Chemical Company, Midland, Michigan. All mass spectra were recorded with an AEI MS-30 dual beam mass spectrometer interfaced to an AEI-DX-50 data system.

Dimethylchlorosilane, dimethyldichlorosilane, and sym-tetramethyldisiloxane were technical grade materials manufactured by Dow Corning Corporation and not further purified; these materials are also available from Petrarch Systems, Inc. The 2-methyl-3-buten-2-ol was purchased from Aldrich Chemical Co. and dried over 4A° Molecular Sieves. The catalyst, H₂PtCl₆·6H₂O, was dissolved in sufficient reagent grade tetrahydrofuran to give solutions which were 0.10, 0.05, 0.005, and 0.0005 M. These solutions were stored in dark bottles. This range of catalyst solutions allowed the platinum level to be widely varied without changing reactant concentrations.

Preparation of vinyl dimethylcarbinoxy dimethylsilane (I)

Sym-tetramethyldisiloxane [368 g (2.75 mol)], 2-methyl-3-buten-2-ol [171 g (2.0 mol)], and one pellet of KOH were added to a 1 liter flask fitted with a thermometer, magnetic stirring bar, and a reflux condenser topped with a Dri-Ice/acetone cold-finger. The cold-finger helped to retain the dimethylsilane while allowing hydrogen to be vented from the system. After maintaining the temperature at 80° for three hours, the crude reaction product was strip-distilled away from the alkaline catalyst at reduced pressure and then fractionally distilled on a 2' spinning band column giving 208 g (1.44 mol) of pure I (72% yield); bp 109°; NMR (90 MHz) (δ, ppm) 0.14 and 0.16 (d, 6H, SiCH₃), 1.3 (s, 6H, C-CH₃) 4.75 (m, 1H, SiH) 5.9 (m, 3H, CH₂=CH). IR and GC-MS data were also consistent with the proposed structure. Note: Heating I at higher temperatures (i.e., 110°) in the presence of the alkaline catalyst causes disproportionation to yield dimethylsilane and bis-(vinyl dimethylcarbinoxy) dimethylsilane. It is therefore desirable to free the crude product from base before fractionating at atmospheric pressure. It can also be prepared from the reaction of HMe₂SiCl with the 2-methyl-3-buten-2-ol in the presence of dimethylaniline as an HCl-acceptor [8].

Preparation of 1-vinyl-1,1,3,3-tetramethyl-2-oxa-1-silacyclopentane (XII)

Triethylamine [202 g (2.0 mol)] and 2-methyl-3-buten-2-ol [43.3 g (0.5 mol)] were placed in a 2-liter flask fitted with a reflux condenser and an air-driven stirrer paddle. Dimethylchlorosilane [64.5 g (0.5 mol)] was added drop-wise to the stirred contents where it reacted exothermally. Water [9.0 g (0.5 mol)] was then added (all at once) to the ice-bath cooled slurry to convert the alkoxychlorodimethylsilane intermediate to the alkoxydimethylsilanol. Two hours later, dimethylchlorosilane [47.3 g (0.50 mol)] was introduced. A little pentane was used to thin out the slurry whenever it was too thick for efficient mixing. The resulting product was washed with water to remove the salt, dried over 4A° Molecular Sieves, and fractionally distilled to give XII in 40% yield [44 g (0.21 mole)]; bp 58° @ 20 mm Hg; NMR (90 MHz) (δ , ppm) 0.18 and 0.19 (d, 6H, SiMe₂H), 0.079 (s, 6H SiMe₂-O), 1.34 (s, 6H, CMe), 4.75 (m, 1H, SiH), 4.90 (m, 2H, CH₂=CH), and 5.9 (m, 1H, -CH=CH₂). GC-MS and IR also confirm the proposed structure.

Cyclohydrosilylation Reactions of I [9]

Reaction flasks were fitted with a reflux condenser, thermometer, and a rubber septum for syringe sampling and introduction of reactants. Entry of atmospheric moisture was prevented by the use of Dri-Ice/acetone cold traps and a nitrogen sweep. After adding I, solvent or trapping agent, and platinum catalyst, the flask was heated to the desired temperature (within the range of 50-150°) and the course of the reaction was followed by periodic glc assay. The resulting reaction product mixture was then fractionally distilled on a 2' spinning band column without prior removal of platinum. The various fractionated materials were then subjected to appropriate analyses (i.e., GLC, NMR, IR, mass spectroscopy). Dilution of the reactants with xylene, THF, or diphenylether as much as ten-fold had little or no effect upon the course of these hydrosilylations; i.e., polymer yield was about the same (~40%) and the distribution of the volatile components showed little variation. The polymeric residue remaining after removal of volatile components afforded additional substantial quantities of VI when heated at reduced pressure in the presence of catalytic potassium hydroxide.

The data tabulated below shows the marked effect of increased Pt level on the yields of D₃ and VI.

Pt / Si	GLC PEAK AREAS (%)					
	I	III	V	D ₃	VI	VII
10 ⁻³	0	19.6	48.7	25.7	1.4	3.2
10 ⁻⁴	9.06	14.3	37.1	1.56	21.1	3.4
10 ⁻⁵	9.01	13.2	25.4	0.42	30.7	1.7

The reaction products, some of which were new compounds, were characterized as follows:

1,1,3,3-Tetramethyl-2-oxa-1-silacyclopentane (V). NMR (90 MHz) (δ , ppm) 0.14 (s, 6H, SiMe), 0.77 (t, 2H, SiCH₂), 1.16 (s, 6H, CMe), 1.58 (t, 2H, CCH₂). Structure was confirmed by GC-MS and IR. Probably because of substantial ring-strain, V undergoes facile hydrolysis upon exposure to atmospheric moisture

to yield 4{hydroxydimethylsilyl}-2-methyl-2-butanol; mp 78-79°. NMR (90 MHz) (δ , ppm) 0.05 (s, 6H, SiMe), 0.57 (m, 2H, SiCH₂), 1.13 (s, 6H, CMe), 1.49 (m, 2H, CCH₂), 3.08 (s, 1H, COH), 4.25 (s, 1H, SiOH). The IR spectrum was consistent with the structure. This compound eliminates water, reforming V, during glc analysis of its solutions.

1,1,3,3,5,5,6-Heptamethyl-2,4-dioxo-1,3-disilacyclohexane (VI). NMR (60 MHz) (δ , ppm) 0.15, 0.10, 0.76, 0.058 (complex, 12H, SiMe), 1.26 and 0.96 (complex, 10H, CMe, CHMe); (100 MHz) (δ , ppm) 0-0.2 (complex, 12H, SiMe), 0.9 (distorted doublet, 2H, CHCH₃), 1.1-1.3, 1.3-1.8, and 2.2, 4.0, 4.8, 7.1 (complex, 7H, CH, CH₃). ¹³C-NMR (15 MHz) spectra clearly show three non-equivalent CH₃ groups attached to carbon, plus one CH and one quaternary carbon, in addition to four SiMe groups. GC-MS and IR spectra were also consistent with the proposed structure.

2,2,4,4,7,7-Hexamethyl-1,3-dioxo-2,4-disilacycloheptane (VII). Identified by GC-MS only; not isolated. D₃, D₄, and III are well known and were identified by comparison with authentic materials.

Inter-molecular Hydrosilylation with Monofunctional Reactants II and VIII.

This reaction was performed in the same fashion as the above described cyclohydrosilylations. A reactant mixture of II, [2.1 g (13 mmol)], VIII [1.48 g (10 mmol)], and platinum catalyst [2 μ l of 0.1M H₂PtCl₆·6H₂O in THF] was heated at re-flux for 90 minutes. Vacuum flash distillation and subsequent fractional distillation afforded unreacted II and VIII and 1.5 g of the "terminal" addition product IX [i.e., (3-trimethylsiloxy-3,3-dimethylpropyl) t-butoxydimethylsilane.] NMR (90 MHz) (δ , ppm) 1.4 (complex, 17H, OCMe₂CH₂ and t-Bu-O) 0.53 (complex, 2H, SiCH₂) and 0.13 and 0.046 (s, 15H, SiMe₂ and SiMe₃). No olefin was detected, and there appeared to be no other products from this sluggish, but apparently cleanly terminal, addition reaction. II and VII were prepared conventionally [8] by simple metathesis of the appropriate chlorosilanes and tertiary alcohols in the presence of a tertiary amine HCl-acceptor and purified by distillation:

Vinyltrimethylcarbinoxytrimethylsilane (II). bp, 118°; NMR (90 MHz) (δ , ppm) 4.7-6.2 (complex, 3H, CH=CH₂), 1.27 (s, 6H, C-CH₃), and 0.046 (s, 9H, Si-CH₃). t-Butoxydimethylsilane (VIII). bp, 78° (δ , ppm) 4.66 (complex 1H, SiH), 1.24 (s, 9H, C-CH₃), and 0.13 (d, 6H, SiCH₃).

Attempted Cyclohydrosilylation of XII

These reactions were performed in the same way as was described above for I. When neat XII [14.0 g (64 mmol)] was catalyzed (H₂PtCl₆) and heated to about 95°, an exotherm resulted and carried the temperature to about 200°. Evacuation produced less than 0.2 g of volatile material (attesting to the absence of significant olefin formation). The polymeric product (13.8 g) was then catalyzed with KOH (1 pellet) and heated at reduced pressure to yield 13.2 g volatiles which consisted of D₃, D₄, D₅, and V; no VI was present. Solution of these volatiles in acetone containing enough water to hydrolyze the alkoxysilane (V) followed by the addition of hexane led to the deposition of 4{hydroxydimethylsilyl}-2-methyl-2-butanol [4.9 g (30 mmol)] in a yield of 47% based on starting XII.

Thermolyses of I

A ketene generator (Ace Glass, Inc.) was used as a flow-pyrolysis reactor. The boil-up flask was charged with I [9.0 g (62 mmol)] and maintained at reflux while using a N₂ purge to sweep the vapors past the heated Chromel A coils (T 700°C) and into a series of cold traps. Examination of the trap contents revealed 2-methyl-2-butene, D₃, and unreacted I; no V was observed. Under similar conditions V did not degrade when swept past the hot coils. When the boil-up flask was charged with I [5.0 g (35 mmol)] and 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane (XIII) [2.5 g (17 mmol)], analysis of the resulting cold trap contents revealed a major new component shown to be 1,1,3,3,6,6-hexamethyl-2,7-dioxa-1,3,6-trisilacycloheptane (XIV) [7]. Similar thermolysis of I [5.0 g (35 mmol)] and dimethyldimethoxysilane [4.2 g (35 mmol)] resulted in the formation of substantial amounts of the expected trapping product, sym-tetramethyldimethoxydisiloxane [6]. In control experiments, XII and dimethyldimethoxysilane showed little or no degradation when individually swept past the hot coils.

Acknowledgements

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