

## Conclusion

Many experiments reported that the addition of O<sub>2</sub> for H<sub>2</sub>/F<sub>2</sub> chemical laser system makes the performance of chemical laser improved. In this paper, we calculated theoretically the illustration of this phenomena. The effects of the concentration of HF and other products and the output power were demonstrated. The added O<sub>2</sub> reacts with H and F, which makes the reaction explosive, and reduces the formation rate of HF. The dominating chain inhibition step is the production of HO<sub>2</sub>, whereas the production of FO<sub>2</sub> is unimportant. As the concentration of O<sub>2</sub> in the reaction mixture increases, the pulse power and temperature of the system becomes low, while the total energy does not change significantly. But the addition of O<sub>2</sub> makes the system easily controlled and the concentration of H<sub>2</sub>+F<sub>2</sub> could be high without changing total pressure. In the case of our calculation condition, as the addition of O<sub>2</sub> increases to 0.1, 0.2 and 0.4%, the sum of H<sub>2</sub>+F<sub>2</sub> can be as high as 41.04+20.52 torr, 60.80+30.40 torr and 77.52+38.76 torr respectively without explosion at total pressure (H<sub>2</sub>+F<sub>2</sub>+O<sub>2</sub>+He) of 760 torr. Since the increment of reactant, H<sub>2</sub>+F<sub>2</sub>, means the increment of product, HF, the output power of laser would be high. By the addition of 0.4% O<sub>2</sub>, the maximum output power increases about twice (1.8). This ratio varies depending upon the condition of initial mixture. Unfortunately the choice of initial calculation condition is not diverse enough due to the limited number of experimental data and due to the barriers in numerical analysis at abrupt change of concentration. However, we have shown a possible way to achieve higher output energy than that from oxygen free system.

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15. This computer code is programmed by FORTRAN using Runge-Kutta and/or GEAR Method, and executed in IBM PC 386 series.
16. This figure is adapted from ref. 12 and modified.

## Acid-Promoted Ring Cleavage Reactions of Silacyclohex-3-ene Derivatives

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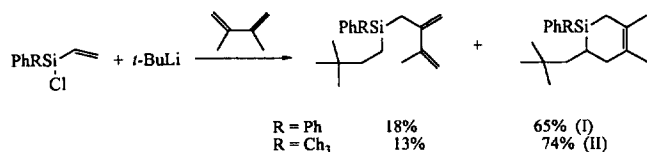
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The acid-promoted cleavage of the *E*- and *Z*-isomers of 1-phenyl-6-neopentyl-1,3,4-trimethyl-1-silacyclohex-3-ene(II) under various conditions gave clean and nearly quantitative formation of the ring-opened 2,3,7,7-tetramethyl-5-(X)silyl-1-octene products (X=OMe, Cl, OH). The possible mechanism for the formation of the ring-opened products was suggested that the initial protonation of II at C-4 would give a carbocation oriented so that they are  $\beta$  to the silicon atom, and the subsequent nucleophilic attack at silicon would give rise to the observed products (VI, VII, VIII).

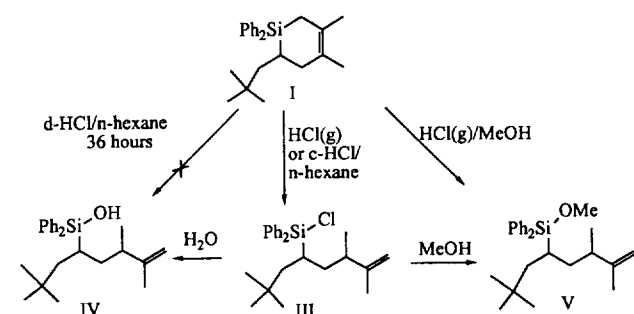
## Introduction

Unsaturated organosilanes often exhibit unusual reactivity towards electrophiles in comparison to their carbon analogues.

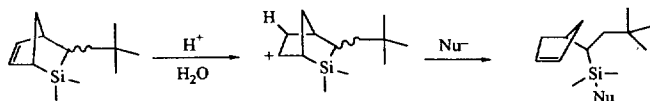
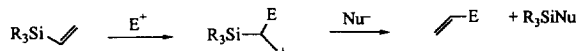
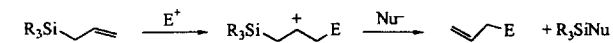
One important characteristic of their unusual reactivity is that a silicon-carbon  $\sigma$  bond exerts a greater stabilizing effect on a carbocation ion  $\beta$  to the silicon than does a carbon-carbon or carbon-hydrogen bond.<sup>1</sup> In all of the above



Scheme 1.



Scheme 2.



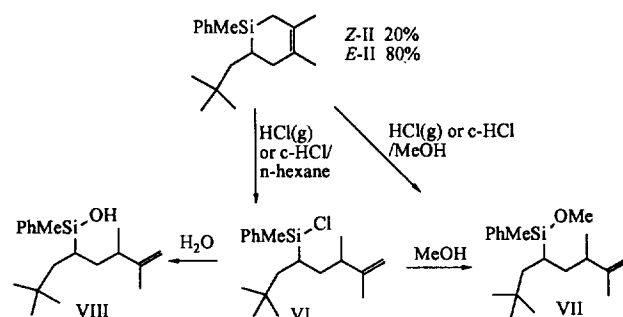
electrophilic reactions of organosilanes, the main products are presumably formed from pathways which involve intermediates, carbocations oriented so that they are  $\beta$  to the silicon atom.<sup>2,3,4,5</sup>

However, there is little evidence for the delocalized carbocation as an intermediate. We report here our studies of a related system, the acid-promoted ring cleavage reactions of the *E*- and *Z*-isomers of 1-phenyl-6-neopentyl-1,3,4-trimethyl-1-silacyclohex-3-ene(II).

## Results and Discussion

When 1,1-diphenyl-2-neopentylsilene was generated by the reaction of *tert*-butyllithium with chlorodiphenylvinylsilane in hexane at low temperature in the presence of 2,3-dimethyl-1,3-butadiene, there was obtained 65% yield of the cycloadduct(I) and 18% yield of the intermolecular "ene" product between silene and 2,3-dimethyl-1,3-butadiene. The *E*- and *Z*-isomers of 1-phenyl-6-neopentyl-1,3,4-trimethyl-1-silacyclohex-3-ene(II) were prepared using a known method (Scheme 1).<sup>6,7</sup> Products are separated and purified by column chromatography with *n*-hexane/chloroform as an eluent.

The acid-promoted cleavage of compound I under various experimental conditions gave clean and nearly quantitative formation of the ring-opened, 2,3,7,7-tetramethyl-5-silyl-1-octene, product except when diluted HCl was used as shown in Scheme 2. These results indicate that initial protonation of the carbon-carbon  $\pi$ -bond at C-4 to give a carbocation in which could be stabilized by the  $\beta$  silyl substituent. Subsequent nucleophilic attack at silicon would give rise to the



Scheme 3.

observed products(III, IV, V). None of the products formed from cation at C-4 which would result from protonation at C-3 were observed. These results are consistent with the formation of a carbocation  $\beta$  to the silicon.

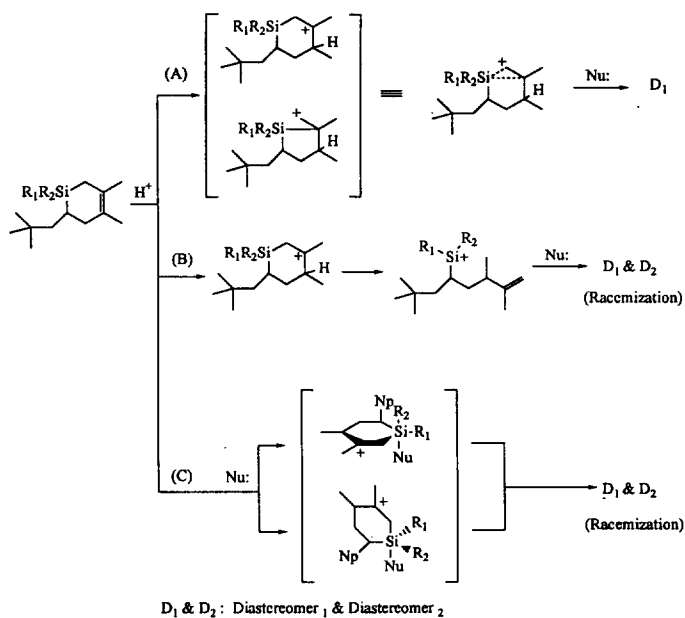
In extension of this work, the acid-promoted ring cleavage of the compound II was carried out under various conditions to study the stereochemistry. A few drops of concentrated HCl added to a mixture of 20% *Z*-II and 80% *E*-II in dry methanol gave two diastereomeric ring opened products(VII) in 50 to 50 ratio, while the acid-promoted ring cleavage of 2-silanorborn-3-ene derivatives gave stereospecifically only one diastereomer.<sup>5</sup> Two diastereomers in 50 to 50 ratio were also formed in quantitative yield by bubbling of dry HCl gas through a mixture of 20% *Z*-II and 80% of *E*-II in dry methanol. The acid-promoted cleavage of a mixture of 20% *Z*-II and 80% *E*-II with concentrated HCl or dry HCl gas in hexane was monitored by GC/MS. The only one peak on GC chromatogram observed was identified as a ring opened chlorosilane, (VI), using MS data. Subsequent addition of methanol or H<sub>2</sub>O gave the 50 to 50 ratio of two diastereomeric methoxysilanes, (VII), and hydroxysilane, (VIII), respectively.

The latter result indicates that although only one peak was shown in GC chromatogram, the chlorosilane, (VI) formed would be a mixture of 50 to 50 ratio of two diastereomers. This suggestion could be supported by an analogy that displacement of Cl in chlorosilanes occurs only with inversion, whatever the nucleophile is.<sup>8</sup>

Three possible mechanisms for the racemization of ring opened products, (VI, VII, VIII), might be conceivable as shown in Scheme 4.

The pathway(A) involves a pentacoordinate silicon intermediate (or transition state), which could lead to give only one diastereomer.<sup>5,8</sup> Therefore it seems not likely to explain the racemization. The pathway(B) could explain the formation of racemization by direct nucleophilic attack to the either side of silylenium ion. This suggestion can be supported by the clear evidence for the solvolytic generation of tricoordinated silylenium ion.<sup>9,10</sup> A cyclic strained geometry might influence the stereochemistry for endocyclic leaving groups.<sup>8</sup>

Therefore, pathway(C) might also be a possible mechanism. In this case, the six-membered ring would be able to occupy the diequatorial position and the apical-equatorial position of a trigonal bipyramidal intermediate, which implies an attack of the nucleophile at 90° and 180° angle to the leaving group. These lead to retention and inversion stereochemistry, respectively.<sup>11</sup>



Scheme 4.

## Experimental Section

**General Consideration.** All reactions were performed in flame-dried glassware under a nitrogen atmosphere, except where specified. Solvents were dried using standard techniques. All air-sensitive liquids and the dried solvents were transferred by standard syringe or double needle techniques.

<sup>1</sup>H-NMR spectra were obtained with a Varian EM-360L operating at 60 MHz and a Bruker WP-80SY FT operating at 80 MHz spectrometer and <sup>13</sup>C-NMR spectra with a Bruker WP-80SY FT operating at 80 MHz. Gas chromatography mass (GC-MS) spectra were recorded on a GC/MS spectrometer with Hewlett-packard GC 5890 and MSD 5970B. A Hitachi model 163 gas chromatograph with a flame ionization detector and a 3 ft × 1/8" *o.d.* stainless steel column packed with 5% SE-30 adsorbed on chromosorb-w (60-80 mesh) was used for analytical gas chromatography. The reactants and products were separated and purified by preparative GC using a Hitachi model GC equipped with thermal conductivity detector and 4 ft × 1/4" stainless steel packed with 5% SE-30 and column chromatography. Yields were determined by quantitative GLC analysis using hexadecane as the external standard.

**Materials.** Diphenylvinylchlorosilane and methylphenylvinylchlorosilane were purchased from Hüls America, Inc.. *Tert*-butyllithium and 2,3-dimethyl-1,3-butadiene were purchased from Aldrich Chemicals, and absolute methanol was prepared as described in literature.<sup>1</sup> All reagents were used as received without further purification.

**1,1-Diphenyl-3,4-dimethyl-6-neopentyl-1-silacyclohex-3-ene, I.** To a solution of 8.6 g (35 mmole) of chlorodiphenylvinylsilane and 3.3 g (40 mmol) of 2,3-dimethyl-1,3-butadiene in 300 mL of dry hexane cooled to -78°C was slowly added 17 mL (35 mmol) of *tert*-butyllithium (2.0 M in pentane). The mixture was allowed to warm slowly to room temperature and was stirred for 18 hrs. After quenching with saturated ammonium chloride solution, the orga-

nic layer was separated, combined with hexane-extracts of the aqueous layer, and dried with anhydrous sodium sulfate. After evaporation of the solvents using a rotary evaporator, GLC analysis of the residue gave in order of elution: 2,8,8-trimethyl-3-methylenyl-5,5-diphenyl-5-silanon-1-ene (IX) and title compound, I in 18% and 65% yields, respectively. The compounds, when purified by preparative GC for characterization, were colorless oils. The compound I; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) 0.84 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 1.04 (m, 2H, C<sub>2</sub>-H<sub>2</sub>), 1.45-1.57 (m, 2H, C<sub>5</sub>-H<sub>2</sub>), 1.76 (s, 3H, C<sub>3</sub>-CH<sub>3</sub>), 1.95 (s, 3H, C<sub>4</sub>-CH<sub>3</sub>), 7.25-7.65 (m, 10H, 2Ph) <sup>13</sup>C-NMR (CDCl<sub>3</sub>) 127.5-136.8, 2Ph; 128.7, C<sub>4</sub>; 124.7, C<sub>3</sub>; 17.2, C<sub>2</sub>; 19.5, C<sub>3</sub>-CH<sub>3</sub>; 23.5, C<sub>4</sub>-CH<sub>3</sub>; 40.3, C<sub>5</sub>; 21.8, C<sub>6</sub>; 44.0, CH<sub>2</sub>-C(CH<sub>3</sub>)<sub>3</sub>; 32.1, C(CH<sub>3</sub>)<sub>3</sub>; 29.8 C(CH<sub>3</sub>)<sub>3</sub> MS (EI, 70 eV) *m/z* (relative intensity) 348 (M<sup>+</sup>, 9), 279 (11), 209 (59), 183 ([Ph<sub>2</sub>SiH]<sup>+</sup>, 100), 105 (42), 57 (26).

The compound IX, MS (EI, 70 eV) *m/z* (relative intensity), 348 (M<sup>+</sup>, 5), 267 (5), 183 ([Ph<sub>2</sub>SiH]<sup>+</sup>, 100), 145 (3), 105 (17), 57 (6).

***E*- and *Z*-1-phenyl-6-neopentyl-1,3,4-trimethyl-1-silacyclohex-3-ene, II.** A mixture of *Z*-II (16% yield) and *E*-II (67% yield) was obtained using a known method<sup>7</sup>. These were separated and purified by column chromatography with *n*-hexane/chloroform as an eluent.

**Preparation of 2,3,7,7-tetramethyl-5-(diphenylchlorosilyl)-1-octene, III.** 1. An one-necked 10 mL flask was charged with 0.12 g (0.3 mmol) of the compound I diluted in 2 mL of hexane and then a few drops of concentrated HCl. After stirring for 0.5 hour GC chromatogram showed the formation of product, III. Further stirring for 12 hours, the reaction was completed to give only one peak, III, on GC chromatogram. MS (EI, 70 eV) *m/z* (relative intensity) 384 (M<sup>+</sup>, 1), 293 (3), 219 (35), 217 ([Ph<sub>2</sub>SiCl]<sup>+</sup>, 100), 57 (10).

2. In a dry 25 mL three-necked flask equipped with a gas inlet and septum was placed 0.12 g (0.3 mmol) of I diluted in 3 mL of dried hexane under nitrogen atmosphere. When dry HCl gas was then bubbled for 15 min. the solution became brown. GC/MS analysis showed the formation of product, III in quantitative yield.

**Preparation of 2,3,7,7-tetramethyl-5-(diphenylhydroxosilyl)-1-octene, IV.** The product IV was prepared in experiments 1 and 2 by quenching with 1-2 mL of distilled water. After stirring for 2 hours the reaction was completed in 95% conversion of the chlorosilane to the hydroxosilane, which was identified using GC/MS data. MS (EI, 70 eV) *m/z* (relative intensity) 366 (M<sup>+</sup>, 1), 309 (15), 199 ([Ph<sub>2</sub>SiOH]<sup>+</sup>, 100), 183 (16), 57 (12).

**Preparation of 2,3,7,7-tetramethyl-5-(diphenylmethoxosilyl)-1-octene, V.** The product V was also prepared in experiments 1 and 2 by quenching with 1-2 mL of absolute methanol as a quenching reagent. After stirring for 2 hours the reaction went to completion giving 95% conversion of III to V, which was identified using GC/MS data. MS (EI, 70 eV) *m/z* (relative intensity) 380 (M<sup>+</sup>, 1), 214 (20), 213 ([Ph<sub>2</sub>SiOMe]<sup>+</sup>, 100), 183 (22), 57 (7).

3. In a dry 10 mL three-necked flask equipped with a reflux condenser/ gas inlet and septum was placed 0.12 g (0.3 mmol) of I and 2 mL of dry methanol. A few drops of *c.*-HCl was added. After stirring vigorously for 5 hours the reaction was completed to give a 95% of V.

4. A 25 mL three-necked flask was fitted with a gas inlet and septum. Then, 3 mL of freshly distilled methanol and

0.12 g (0.3 mmol) of I was added. Dry HCl gas was then bubbled. Bubbling for 15 min. of the solution resulted in brown. GC analysis showed the formation of V.

**Preparation of 2,3,7,7-tetramethyl-5-(phenylmethyl-chlorosilyl)-1-octene, VI.** 5. An one-necked 10 mL flask was charged with 0.14 g (0.5 mmol) of a mixture of II diluted in 2 mL of hexane and then few drops of c.-HCl. After vigorous stirring for 12 hours the ring cleavage product, VI, was obtained in quantitative yield. MS (EI, 70 eV) *m/z* (relative intensity) 322 ( $M^+$ , 1), 157 (35), 155 ([PhMeSiCl]<sup>+</sup>, 100), 57 (33).

6. In the same conditions as experiment 5, dry HCl gas instead of c.-HCl was bubbled until pH paper showed the solution to be acidic. After bubbling of HCl gas for 15 min. the product, VI was obtained in quantitative yield.

**Preparation of 2,3,7,7-tetramethyl-5-(phenylmethyl-methoxysilyl)-1-octene, VII.** 7. In a dry 10 mL one-necked flask was placed 0.14 g (0.5 mmol) of a mixture of 20% *Z*-II and 80% of *E*-II and 2 mL of absolute methanol and then few drops of c.-HCl. The mixture was vigorously stirred for 10 hours. A GC/MS analysis of reaction mixture showed a quantitative yields of the two diastereomeric ring opened products, VII in 50 to 50 ratio. MS (EI, 70 eV) *m/z* (relative intensity) 318 ( $M^+$ , 1), 261 (3), 151 ([PhMeSiOMe]<sup>+</sup>, 100), 121 (19), 57 (9).

8. In a dry 25 mL three-necked flask equipped with a reflux condensor/gas inlet and septum was placed 0.14 g (0.5 mmol) of a mixture of 20% *Z*-II and 80% of *E*-II and 3 mL of absolute methanol. After bubbling of dry HCl gas for 15 min. the diastereomeric mixture of VII in 50 to 50 ratio was also obtained in experiments, 5, 6 by quenching with 2 mL of absolute methanol.

**Preparation of 2,3,7,7-tetramethyl-5-(phenylmethyl-hydroxysilyl)-1-octene, VIII.** 9. The diastereomeric mixture of VIII was prepared in experiments, 7, 8 by quenching

with 1-2 mL of distilled water. After stirring vigorously for 2 hours, the reaction went to completion giving the diastereomeric mixture of VIII in 50 to 50 ratio. MS (EI, 70 eV) *m/z* (relative intensity) 304 (parent, 1), 247 (4), 137 ([PhMeSiOH]<sup>+</sup>, 100), 57 (22).

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## Asymmetric [2,3]-Wittig Rearrangements in the Presence of Sparteine Derivatives

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Asymmetric [2,3]-Wittig rearrangements of allyl propargyl ethers in hexane were performed in the presence of *s*-butyllithium and (–)- $\alpha$ -isosparteine which is a C<sub>2</sub>-symmetric chiral ligand for the alkyllithium reagent. The reactions of (*Z*)- or (*E*)-allyl 3-trimethylsilylpropargyl ethers at –78°C showed good diastereoselectivities (74-100%) and moderate enantioselectivities (29-71%). The absolute configurations of the rearrangement products were determined by the corresponding Mosher's esters. It was found that (–)- $\alpha$ -isosparteine induced (*R*) configuration at the hydroxy carbon and *syn* stereochemistry more favorably. The possible transition state is discussed.

### Introduction

Considerable efforts have been directed toward the development of the stereoselective [2,3]-Wittig sigmatropic rearrangement of allyl ethers as a basic strategy for acyclic stereocontrol.<sup>1</sup> This [2,3]-Wittig rearrangement possesses several valuable features<sup>2</sup>: the regiospecific carbon-carbon bond formation with the allylic transposition of oxygen function, the

ngement of allyl ethers as a basic strategy for acyclic stereocontrol.<sup>1</sup> This [2,3]-Wittig rearrangement possesses several valuable features<sup>2</sup>: the regiospecific carbon-carbon bond formation with the allylic transposition of oxygen function, the