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# SILICON-DIRECTED BECKMANN FRAGMENTATION

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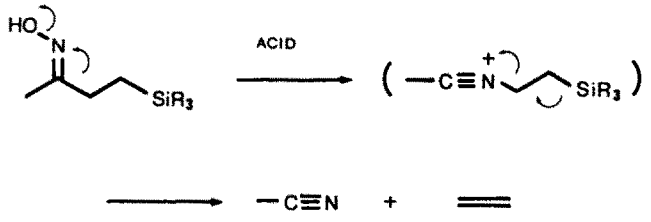
**Abstract:** The selective fragmentation reactions of β-trimethylsilylketoximes have been proved to proceed effectively with acid catalysts giving the corresponding nitriles. Cyclic silylketoximes gave unsaturated nitriles. The fragmentation in the Beckmann rearrangement is completely controlled and directed by a trimethylsilyl group to lead the regio- and stereo-specific formation of the double bond. The catalytic fragmentation proceeds with the combination of trimethylsilyl ketoxime acetates and trimethylsilyl trifluoromethanesulfonate giving nitriles in high yields. Excellent stereospecificity of the fragmentation based on the stereochemical outcome was discussed. Simple stereo-controlled synthetic approach to some insect pheromones is also described.

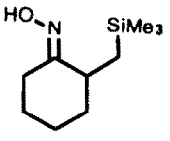
The Beckmann reaction has been intensively studied and developed to a new synthetic methodology.[1] In numerous cases of the reaction, especially, the fragmentation has been observed for ketoximes having α-substituents including hetero atoms, which can stabilize the intermediary carbocations.[2] The formation of nitriles is an important aspect for the fragmentation. In particular, cyclic ketoximes are more attractive because of the fragmentation of ω-functionalized nitriles. However, the control of the regio- and stereo-chemistry of the forming double bonds has been difficult, because random deprotonation undergoes acidic media adopted.

In order to attain the regio- and stereo-specific formation of alkenyl function, it is necessary to recognize one specific proton out of others. For that purpose, trimethylsilyl group seems to be the most attractive candidate for a proton equivalent or a so-called "super proton"[3]. Recent interest in the utilization of the trialkylsilyl group as a leaving group lies in highly selective formation of target olefins.[4] In the present problem, if one can place a trimethylsilyl group at the β-carbon atom of the ketoximes, the Beckmann fragmentation may take place efficiently to give the desired double bond derived from the selective Si-C bond cleavage without the competing deprotonation.[5]



**Fragmentation of (E)-β-Trimethylsilylketoximes with Common Acid Catalysts.**

The cyclic (E)-β-trimethylsilylketoximes **1** and **2** gave the desired unsaturated nitriles **3** and **4**, respectively, by the reactions with common acid catalysts for the Beckmann rearrangement in $CH_2Cl_2$ at room temperature for 1 day; catalyst ( yield of the olefin, %); for **1**, $PCl_5$ (28%), $P_2O_5$ (73%), $POCl_3$ (48%), MsCl-Pyridine (52%); for **2**, $P_2O_5$ (51%). The corresponding lactams, **5** and **6**, were obtained in 5-35% yields. It is important to note that the Beckmann fragmentation took place successfully under mild condition without formation of any other olefin isomers, since it has been well known that the frag-

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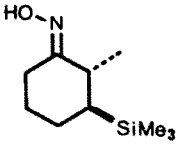


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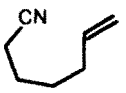


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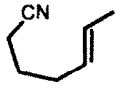


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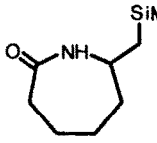


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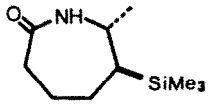
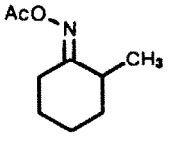



**6**

mentation via deprotonation is limited to the case of oximes having three alkyl groups or one aryl group on the α-carbon of the (E)-chain.[6] Recently, Hudrlik independently reported the effect of the trimethylsilyl group on the Beckmann rearrangement and fragmentation, which is closely related to our work.[7]

We, therefore, examined the reaction of the non-silylated oxime acetate **7**, 2-methylcyclohexanone oxime acetate, and the silylketoxime **8**, respectively. Both of the oximes **7** and **8** were treated with $BF_3 \cdot Et_2O$. The oxime **7** gave only the lactam **9** (59%) at room temperature for 16 h. Whereas the oxime **8** was converted selectively to the nitrile **3** (80%) at 0°C for 4 h. By the treatment with $P_2O_5$, **7** was recovered in 71% and the (Z)-oxime isomer was obtained in 16% in $CH_2Cl_2$ at room temperature for 7 h. In contrast, the reaction of **8** with $P_2O_5$ gave the nitrile **3** (66%) and the lactam **5** (21%) even at 0°C for 2 h.[8] The clear difference in the reaction was thus observed. Consequently, we think that the initial migration of the (E)-side chain should be accelerated and induced by the silyl group at the β-position. It would also imply that the elimination of the leaving group (OAc) and subsequent alkyl

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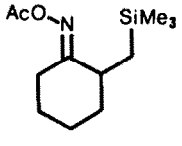


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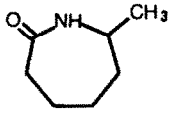
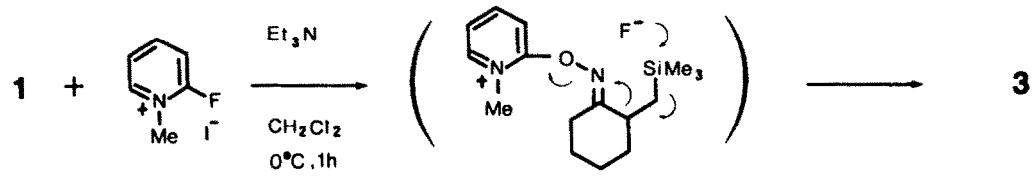



**9**

migration are enhanced by electron donating nature of the silyl group toward the back lobe (σ*) of the cleaving C-C bond.

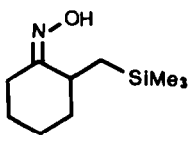
This silicon-enhanced fragmentation can be modified when N-methyl-2-fluoropyridinium salt[9] was employed. Treatment of **1** with the pyridinium salt in $CH_2Cl_2$ at 0°C for 1 h gave the desired nitrile **3** in good to excellent yield (71%). Fluoride ion including the intermediary pyridinium salt **10** could effectively attack on the silyl group. Under the same condition the silylketoxime **2** gave only trans-




**10**

5-hexenonitrile **4** in 84%. Stereoselective formation of the olefin was also observed in the mild condition.

Under the same reaction conditions employed for the (E)-isomers above descirbed, the corresponding (Z)-isomers **11** and **12** did not react in $CH_2Cl_2$ at 20°C with $BF_3 \cdot Et_2O$ and $P_2O_5$. Although the acetate **13** did not react with $BF_3 \cdot Et_2O$ at 0°C, treatment of **13** at refluxing temperature in $CH_2Cl_2$ for 5 h gave the nitrile **14** in 95% yield. The fragmentation from the (Z)-oxime isomer was thus observed under more drastic conditions. In contrast, the (E)-isomer **15** induced the same fragmentation even at 0°C for only 20 min.

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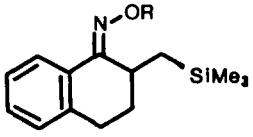
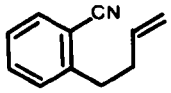



**12** R = H
**13** R = Ac

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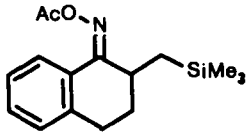
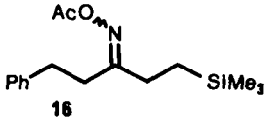
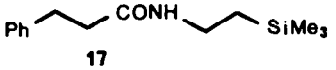



**15**

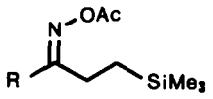
We examined the behavior of the linear oxime acetate **16** [a mixture of (E) and (Z), 55:45]. When the mixture with $BF_3 \cdot Et_2O$ in refluxing $CH_2Cl_2$ for 2h, β-phenylpropionitrile (67%) and the amide **17** (21%) were obtained. Thus the fragmentation from the (Z)-isomer was also observed. However the linear oximes **18** and **19** gave 3-trimethylsilylpropanamides **20** (75%) and **21** (74%), respectively, which are normal Beckmann products.[10] These observation can be accounted for the migratory aptitude of anti-alkyl or aryl groups being present to the acetoxy group. The facile anti-migration of a phenyl and a t-butyl group gave the corresponding amides **20** and **21** with neither syn-migration or desilylative fragmentation. However, because of the low migratory aptitude of the phenethyl group in **16**, upon heating (Z)-(E)-isomerization would occur prior to the migration and then the 2-trimethylsilylethyl group could migrate.[11]




**16**




**17**




**18** R = Ph
**19** R = $^t$Bu


**20** R = Ph
**21** R = $^t$Bu

**Catalytic Design**

We reasoned that as a special design of the silicon-directed fragmentation, the combination of the silylketoxime acetate and trimethylsilyl trifluoromethanesulfonate (TMSOTf)[12] makes the reaction catalytic to afford the desired unsaturated nitriles. The reaction was carried out with 10 mol% of TMSOTf in $CH_2Cl_2$ at 0°C to room temperature for several hours. The obvious advantages of the results lead the specific formation of the nitriles in high yields (Table 1). The stereospecificity of the reaction was also clarified.

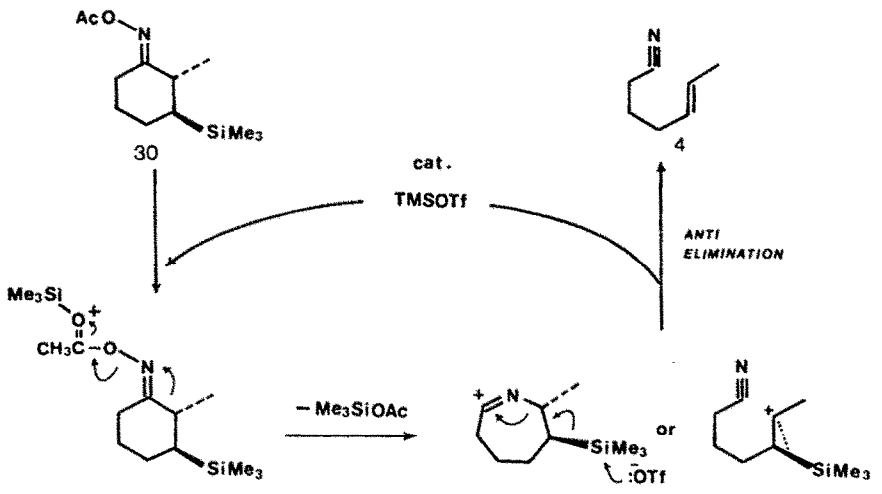
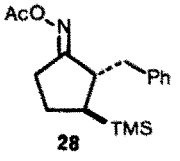
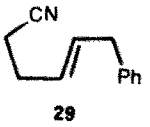
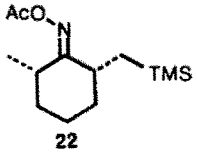
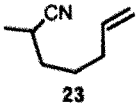
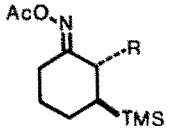
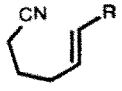
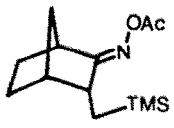
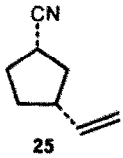
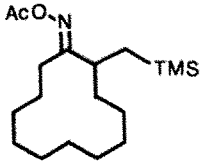
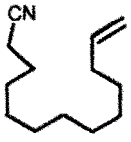
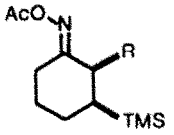
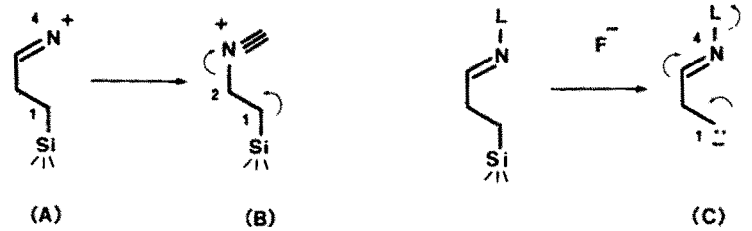



Table 1. Catalytic Fragmentation of Silylketoxime Acetates with TMSOTf.

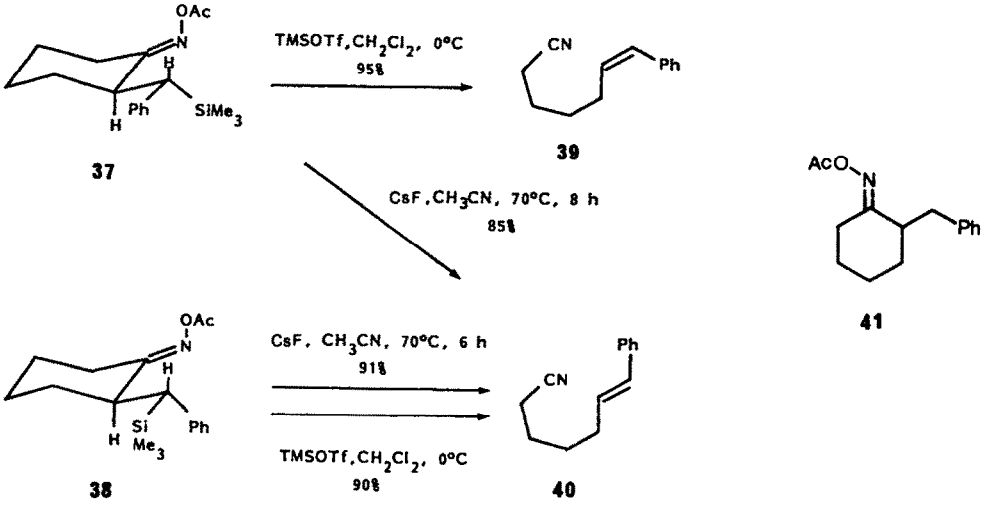
| Substrate | Product | (Yield,%) | Substrate | Product | (Yield,%) |
|---|---|---|---|---|---|
| **8** | **3** | (89) |  **28** |  **29** | (93) |
|  **22** |  **23** | (95) |  **30** R=Me<br>**31** R=$C_5H_{11}$ |  **4** R=Me (94)<br>**32** R=$C_5H_{11}$ (93) | |
|  **24** |  **25** | (94) | | | |
|  **26** |  **27** | (81) |  **33** R=Me<br>**34** R=$C_5H_{11}$ |  **35** R=Me (90)<br>**36** R=$C_5H_{11}$ (88) | |

**Fluoride-Induced Reaction: Anionic Fragmentation?**

The acid-catalyzed Beckmann fragmentation as mentioned above could be formally a cationic 1,4-heterolysis (A), or the reaction would actually be reduced to 1,2-heterolysis in stepwise mechanism (B). In contrast, we are interested in the possibility of an anionic-heterolysis induced by fluoride ion (C).



However, we could find no fragmentation of **1** and **8** by treatment with an excess of CsF in $CH_3CN$ at refluxing temperature. Therefore we have tried the two oxime isomers **37** and **38** having the silyl group at the benzylic position.[13] Treatment of the both isomers with an excess of CsF in $CH_3CN$ at refluxing temperature gave only the trans-isomer **40** as a fragmentation product (85% from **37** and 91% from **38**, respectively) and 2-benzylcyclohexanone oxime acetate **41** (8-10%) as a minor product. As we have found, use of TMSOTf gave stereospecifically the corresponding olefins, the cis-olefin from **37** and the trans-olefin from **38**, respectively. Accordingly, the fragmentation with CsF can be accounted for the facile inversion of the transient carbanion species, which were partly protonated in the reaction media.

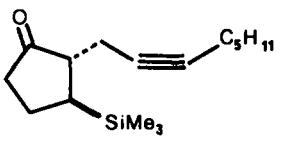



**Synthetic Application**

On the basis of the regio- and stereo-specificity of the silicon-directed Beckmann fragmentation, new synthetic approach for some insect pheromones is demonstrated. Synthesis of **46**, a component of the sex pheromone of potatotuberworm moth (phthorimaea operculella)[14], was started from the preparation of the trimethylsilyl ketone **42**. Addition of 2-cyclopentenone to an excess (1.5 eq) of trimethylsilyllithium[15] in THF-HMPA at -78°C followed by treatment with 1.5 eq of tri-n-butyltin chloride and 1-bromo-2-octyne at -50°C to -40°C for 1 h to give the silylketone **42** in 67%. The trapping of the enolate intermediate as the stannyl enolate (or stannyl ketone) is thought to lead good to excellent yield for the α-alkylation in the sequencial vicinal double alkylation.[16] Hydrogenation of **42** with Pd-$BaSO_4$ and quinoline in methanol gave the cis-olefinic ketone **43** (84%). Oximation and subsequent acetylation of **43** gave the oxime acetate **44** (74%). Treatment of **44** with 10 mol% of TMSOTf at 0°C for 2.5 h afforded the nitrile **45** in 79% yield as a single product. Reduction of **45** with diisobutylaluminum hydride at -78°C and then with sodium borohydride at 0°C followed by acetylation gave the desired compound **46**.

By utilization of the nitriles **32** and **36** (in Table 1), a couple of the sex pheromones of Douglas fir tussock moth (orgyia psedotsugata)[17] could be synthesized. Alkylation of each unsaturated nitrile with n-decanyl Grignard reagent in ether followed by hydrolysis with hydrochloric acid gave the target ketones **47** (77%) and **48** (71%), respectively.

These sequences thus allow a unique approach to internal olefin synthesis with high stereospecificity via the silicon-directed fragmentation.



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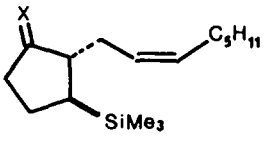
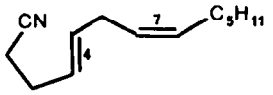


43 X = O
44 X = NOAc



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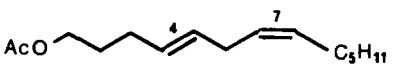
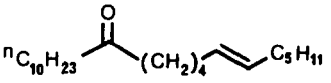
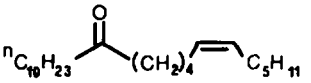


46



47



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**Experimental Section.**

**General:** $^{1}H$ NMR spectra were recorded on JEOL JNM-FX90Q and JEOL JMR-PMX60 spectrometers using tetramethylsilane as the internal reference. $^{13}C$ NMR spectra were obtained on a JEOL JNM-FX90Q. High and low resolution mass spectra were determined with a JEOL JMS D-300 spectrometer. Infrared spectra were recorded on a JASCO A-3 spectrometer. GLC analyses were performed with a Shimadzu GC-3BT using a 2 m x 3 mm column (PEG 20M, 10%) and helium as carrier gas. Microanalyses were accomplished at the Microanalysis Center of Kyoto University. Analytical TLC was performed on Merck precoated silica gel plates (0.25 mm). Column chromatography was performed with silica gel (Merck Art 7734 and 9385).

All reactions were run under an inert atmosphere of Ar or $N_2$. Dichloromethane was dried by distillation under argon from $CaCl_2$ and phosphorus pentoxide. Ether and tetrahydrofuran were distilled from sodium and lithium aluminum hydride. Other chemicals used were purchased.

**Preparation of Silylketoxime 1 and its Acetate 8.**

Alkylation of 2.5 mL (25.0 mmol) of cyclohexene oxide with trimethylsilylmethyl magnesium chloride (33.0 mmol) in 60 mL of THF in the presence of 350 mg of CuI at -20°C for 2 h gave 3.98 g of trans-2-trimethylsilylmethylcyclohexanol in 80% yield. The alcohol was purified by silica gel column chromatography and then was subjected to treatment with 4.5 g of $CrO_3$ in 9 mL of pyridine and 60 mL of $CH_2Cl_2$ at room temperature for 1 h gave 2.19 g of 2-trimethylsilylmethylcyclohexanone in 69% yield. Treatment of 1.5 g (8.1 mmol) of the ketone with 7.0 g of $HONH_2 \cdot HCl$ and 1.4 g of NaOAc in 20 mL of ethanol at 0°C for 1h gave 1.26 g (6.3 mmol) of (E)-2-trimethylsilylmethylcyclohexanone oxime 1 (78 %) and 0.27 g (1.35 mmol) of the (Z)-isomer (17%); Rf, 0.55 for 1 and 0.40 for (Z)-isomer (hexane-ether = 1:1). 1: mp 42.0-43.0 °C; $^{1}H$ NMR ($CDCl_3$, 90 MHz) -0.02 (s, 9H), 0.56 (dd, J = 8.1 and 15.0 Hz, 1 H, $CH_2Si$), 0.96 (dd, J = 4.2 and 15.0 Hz, 1 H, $CH_2Si$), 1.3-1.9 (m, 6 H), 2.3-2.6 (m, 3 H, $H_2C(6)$ and HC(2)); $^{13}C$ NMR ($CDCl_3$, 22.4 MHz) -0.74 (q), 18.96 (t, $CH_2Si$), 22.76 (t), 23.05 (t), 26.36(t), 35.66 (t), 38.19 (d,

HC(2) ), 163.94 (s, C=N); IR (film) 3500-3000, 1640, 1238, 840 $cm^{-1}$; Anal. Calcd for $C_{10}H_{21}NOSi$: C, 60.25 ; H, 10.62; N, 7.03. Found: C, 59.74; H, 10.94: N, 6.98. The (Z)-isomer **11**: $^1H$ NMR ($CDCl_3$, 90 MHz) -0.01 (s, 9 H), 0.75 (dq, 2 H, $CH_2Si$), 1.3-2.0 (m, 6 H), 2.1-2.3 (m, 2 H, $H_2C(5)$ ), 3.6 (m, 1 H. HC(2) ).

Treatment of 199 mg (1.0 mmol) of **1** with 0.15 mL of acetic anhydride and 0.5 mL of pyridine at 0°C for 5 h gave 231 mg (0.96 mmol) of **8** (96%), which was purified by silica gel chromatography. Rf, 0.30 for **8** and 0.40 for **1** (hexane:ether = 1:4). **8**: a colorless oil; $^1H$ NMR ($CDCl_3$, 90 MHz) -0.02 (s, 9 H), 0.71 (dd, J = 8.5 and 14.8 Hz, 1 H, $H_2CSi$), 1.00 (dd, J = 6.8 and 14.8 Hz, 1 H, $H_2CSi$), 1.4-1.9 (m, 6 H), 2.12 (s, 3 H, $CH_3CO$), 2.35-2.70 (m, 3 H); IR (film) 1755, 1636, 1245, 1200, 850 $cm^{-1}$; Anal. Calcd for $C_{12}H_{23}NO_2Si$: C, 59.71; H, 9.60; N, 5.80. Found: C, 59.73; H, 9.60:, N, 5.92.

**Preparation of Silylketoxime 2 and its Acetate 30.**

Starting trans-2-methyl-3-trimethylsilylcyclohexanone was prepared from 2-cyclohexenone by Still's procedure.[15] Treatment of 350 mg (1.90 mmol) of the silylketone with an excess of $HONH_2 \cdot HCl$ (3 mmol) and NaOAc (4 mmol) in EtOH as above mentioned gave 375 mg (1.88 mmol) of (E)-trans-2-methyl-3-(trimethylsilyl)cyclohexanone oxime **2** in 98% yiled. **2**: mp 53.0-54.0 °C; $^1H$ NMR ($CDCl_3$, 90 MHz) 0.0 (s, 9 H), 0.80-1.90 (m, 5 H), 1.13 (d, J = 7.0 Hz, $H_3C(2)$ ), 2.28 (dq, $J_{HC(2)-HC(3)}$ = 8.5 Hz, J = 7.0 Hz, 1 H), 3.0 (m, 1 H, HC(6) ), 9.6 (b, 1 H); $^{13}C$ NMR ($CDCl_3$, 22.5 MHz) -1.33 (q), 17.83 (q), 24.32 (t), 26.70 (t), 27.34 (t), 34.07 (d, C(3) ), 38.94 (d, C(2) ), 164.05 (s); IR (film) 3600-3000, 1660, 1250, 840 $cm^{-1}$; Anal. Calcd for $C_{10}H_{21}NOSi$: C, 60.25; H, 10.62; N, 7.03. Found: C, 60.05; H, 10.26; N, 6.77.

Treatment of 260 mg (1.30 mmol) of **2** with 0.45 mL of acetic anhydride and 0.75 mL of pyridine at 0°C for 2 h gave 308 mg (1.28 mmol) of **30** in 98% yield. **30** was purified by silica gel column chromatography. **30**: a colorless oil; $^1H$ NMR ($CDCl_3$, 90 MHz) 0.01 (s, 9 H), 0.80 (m, 1 H, HCSi), 1.22 (d, 3 H), 1.40-1.90 (m, 4 H), 2.13 (s, 3 H, $CH_3CO$), 2.45 (dq, 1 H, $HCCH_3$), 2.60-2.80 (m, 2 H, $H_2C(6)$ ); $^{13}C$ NMR ($CDCl_3$, 22.5 MHz), -1.43 (q), 18.51 (q, $CH_3$), 20.02 (q, $CH_3CO$), 25.53 (t), 26.87 (t), 27.85 (t), 33.63 (d, C (3) ), 38.69 (d, C(2) ), 168.90 (s, C=N), 172.14 (s, CO); IR (film) 1765, 1630, 1250, 840 $cm^{-1}$; Anal. Calcd for $C_{12}H_{23}NO_2Si$: C, 59.71; H, 9.60; N, 5.80. Found: C, 60.03; H, 9.77; N, 6.07.

**Preparation of Silylketoximes 12, 13, and 15.**

Starting 2-methylene-1-tetralone[18] was prepared by the method according to the literature. Transformation of the tetralone to the corresponding silylketone was carried out by Still's procedure. The silylketone (424 mg, 1.82 mmol) was treated with $HONH_2 \cdot HCl$ (255 mg, 3.70 mmol) and NaOAc (430 mg, 5.20 mmol) in ethanol at room temperature for 40 h. Concentration of the reaction mixture under reduced pressure and extraction of the residue with ether gave a colorless oil, which was treated with 0.21 mL of acetic anhydride and 0.74 mL of pyridine in 1 mL of $CH_2Cl_2$ at room temperature for 1.5 h. The reaction mixture was concentrated, and the residual oil was purified by silica gel column to give 463 mg (1.60 mmol) of **13** and **15**; Rf, 0.45 for **13** and 0.40 for **15** (ether:hexane = 1:4, two developments). **13**: mp 46.0-46.5 °C; $^1H$ NMR ($CDCl_3$, 90 MHz) 0.0 (s, 9 H), 0.71 (m, $H_2CSi$), 1.55-2.00 (m, 2 H, HC-C=N), 2.18 (s, 3 H, $H_3CC=O$), 2.70 (t ,1 H), 2.88 (t, 1 H), 7.0-7.35 (m, 3 H, aromatic), 8.00 (dd, 1 H, aromatic); $^{13}C$ NMR ($CDCl_3$, 22.5 MHz) -0.98, 17.7, 20.8, 24.4, 27.8, 29.4, 126.4 (two carbons), 128.7, 130.5, 139.4, 166.3, 168.8; IR (film) 1770, 1362, 1250 $cm^{-1}$; Anal. Calcd for $C_{16}H_{23}NO_2Si$: C, 66.39; H, 8.01; N, 4.84. Found: C, 66.17; H, 7.91; N, 4.78.

**Preparation of Silylketoxime Acetate 33.**

According to Still's procedure, the starting cis-2-methyl-3-(trimethylsilyl)cyclohexanone was prepared from 2-methyl-2-cyclohexenone[19]. To a solution of 2.2 mL (10.5 mmol) of hexamethyldisilane and 9 mL of HMPA at 0°C was added a ether solution of methyllithium (9.5 mmol). The mixture was stirred for 20 min, diluted 10 mL of THF, and then was cooled to -78°C. A solution of 2-methyl-2-cyclohexenone (698 mg, 6.34 mmol) in 2 mL of THF was added. The mixture was stirred for 30 min and 5 mL of water was added. The mixture was extracted with a mixture of ether and hexane (1:1). The organic layer was washed with water, dried over anhydrous $MgSO_4$, and concentrated. The residual oil was purified by silica gel column to give 644 mg (3.50 mmol) of cis-2-methyl-3-(trimethylsilyl)cyclohexanone as colorless oil: IR

(film) 1700, 1250 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 60 MHz) 0.11 (s, 9 H), 1.23 (d, 3 H), 1.53-2.17 (m, 5 H), 2.27-2.80 (m, 3 H). The ketone (447 mg, 2.43 mmol) was treated with $HONH_2 \cdot HCl$ (290 mg, 4.2 mmol) and NaOAc (570 mg, 7.0 mmol) in 15 mL of ethanol at 0°C for 1.5 h to give the (E)-oxime (151 mg, 0.76 mmol) and the (Z)-oxime (163 mg, 0.82 mmol); Rf, 0.42 for the (E)-oxime and 0.31 for the (Z)-oxime (ether:hexane = 1:3, two developments). The (E)-oxime: a colorless oil; $^1H$ NMR ($CDCl_3$, 90 MHz) 0.0 (s, 9 H), 1.10 (d, 3 H, J = 7.5 Hz, $H_3C$), 1.30-2.10 (m, 5 H), 2.50-2.85 (m, 2 H, HC(2), HC(6) ), 3.18 (broad, 1 H, HC(6) ); IR (film) 3300, 1660, 1375, 1250 $cm^{-1}$; Anal. Calcd for $C_{10}H_{21}NOSi$: C, 60.22; H, 10.62; N, 7.03. Found: C, 60.22; H, 10.82; N, 6.81. The (Z)-oxime: a colorless oil; $^1H$ NMR ($CDCl_3$, 90 MHz), 0.0 (s, 9 H), 1.05 (d, 3 H, $H_3C$), 1.40-2.10 (m,5 H), 2.10-2.35 (m, 2 H, $H_2C(6)$ ), 3.70 (dq, 1 H, J = 3.0 and 7.5 Hz, HC(2) ); IR (film) 3300, 1660, 1375, 1250 $cm^{-1}$.

The (E)-oxime (145 mg, 0.73 mmol) was treated with 0.1 mL of acetic anhydride and 0.18 mL of pyridine in $CH_2Cl_2$ (0.5 mL) at 0°C for 1 h to give 143 mg (0.59 mmol) of the acetate **33** (81%) as a colorless oil. **33**: $^1H$ NMR ($CDCl_3$, 60 MHz) 0.05 (s, 9 H), 1.20 (d, 3 H, $H_3C$), 1.40-2.40 (m, 6 H), 2.18 (s, 3 H, $H_3CCO$), 2.93-3.40 (m, 3 H); $^{13}C$ NMR ($CDCl_3$, 22.5 MHz) -2.0, 16.0, 19.9, 21.3, 23.0, 28.7, 32.2, 36.6, 165.7, 172.9; IR (film) 1765, 1650, 1250 $cm^{-1}$; Anal. Calcd for $C_{12}H_{23}NO_2Si$: C, 59.71; H, 9.60. Found: C, 59.26; H, 9.80.

**Preparation of Silylkeoxime Acetate 28.**

Starting 1-benzyl-2-(trimethylsilyl)-2-cyclopentanone, as described above, was prepared with 2-cyclopentenone, benzyl bromide, and trimethylsilyllithium. The ketone (310 mg, 1.26 mmol) was treated with $HONH_2 \cdot HCl$ (104 mg, 1.50 mmol) and NaOAc (204 mg, 2.50 mmol) in 3 mL of ethanol at 0°C for 1 h to give 257 mg (1.0 mmol) of the (E)-oxime and 64 mg (0.25 mmol) of the (Z)-oxime; the (E)-oxime: mp 68.0 -70.0 °C. The (E)-oxime (210 mg, 0.80 mmol) was treated with 0.1 mL of acetic anhydride and 0.18 mL of pyridine at 0°C for 3 h to give 218 mg (0.72 mmol) of the acetate **28**. **28**: a colorless oil: $^1H$ NMR ($CDCl_3$, 90 MHz) 0.02 (s, 9 H), 1.20 (m, 1 H, HCSi), 1.50-2.80 (m, 5 H), 2.20 (s, 3 H, $H_3C$), 3.05 (s, 2 H, $H_2CPh$), 7.30 (s, 5 H); IR (film) 1765, 1655, 1250, 835, 750, 700 $cm^{-1}$; Anal. Calcd for $C_{17}H_{25}NO_2Si$: C, 67.28; H, 8.30; N, 4.62. Found: C, 66.98; H, 8.16; N, 4.71.

**Preparation of Silylketoxime Acetate 16.**

Treatment of 4-phenyl-1-butene oxide with trimethylsilylmethyl Grignard reagent in ether in the presence of CuI (10 mol%) gave 5-phenyl-1-trimethylsilyl-3-pentanol in 95% yield as a colorless oil. Oxidation of the alcohol (0.67 g) with $CrO_3$ (1.7 g) and pyridine (3.2 mL) in $CH_2Cl_2$ (25 mL) for 1.5 h gave 0.50 g of 5-phenyl-1-trimethylsilyl-3-pentanone in 74% yield. The ketone (0.48 g, 2.07 mmol) was treated with $HONH_2 \cdot HCL$ (0.34 g) and NaOAc (1.1 g) in 10 mL of ethanol at 0°C for 1 h gave the oxime as a colorless oil. The crude product was directly acetylated. Treatment of the oxime with 0.6 mL of acetic anhydride and 0.8 mL of pyridine at room temperature for 1 day gave the silylketoxime acetate **16** (0.50 g, 1.72 mmol); a mixture of (E) and (Z)-isomers. The mixture: colorless oil; $^1H$ NMR ($CDCl_3$, 90 MHz) 0.0 (s), 0.03 (s), 0.43-0.99 (m, 2 H, $H_2CSi$), 2.08 (s, 3 H, $H_3CCO$), 2.53-3.11 (m, 4 H, $PhCH_2CH_2$), 7.31 (s, 5 H); IR (film) 1760, 1630, 1250, 840 $cm^{-1}$; Anal. Calcd for $C_{16}H_{25}NO_2Si$: C, 65.93; H, 8.65; N, 4.81. Found: C, 66.16; H, 8.53; N, 4.66.

**Preparation of Silylketoxime Acetate 18.**

To a solution of 945 mg (7.0 mmol) of acetophenone oxime in THF (15 mL) at 0°C was added n-butyllithium(1.5 N-hexane, 9.8 mL). The mixture was stirred for 1 h at 0°C. A solution of 1.56 g (7.3 mmol) of iodomethyltrimethylsilane in 3 mL of THF was added and the mixture was stirred for 2 h. After usual work-up, 522 mg of phenyl 2-trimethylsilylethyl ketoxime was obtained. Treatment of the oxime (278 mg, 1.26 mmol) with 0.24 mL of acetic anhydride and 0.61 mL of pyridine at 0°C for 2 h gave the silylketoxime acetate **18** (0.292 mg, 1.03 mmol). **18**: mp 69.5-70.5 °C; $^1H$ NMR ($CDCl_3$, 60 MHz) 0.04 (s, 9 H), 0.50-0.96 (m, 2 H, $H_2CSi$), 2.25 (s, 3 H, $H_3CCO$), 2.60-2.98 (m, 2 H, $H_2CCN$), 7.50 (m, 5 H); IR (film) 1770, 1613, 1575, 1250, 860, 840 $cm^{-1}$; Anal. Calcd for $C_{14}H_{21}NO_2Si$: C, 63.84; H, 8.04; N, 5.32. Found: C, 63.83; H, 7.93; N, 5.40.

**Preparation of Silylketoxime Acetate 19.**

As described for **18**, dilithiate of pinacolone oxime gave t-butyl a-trimethylsilylethyl ketoxime in a low yield. The oxime (347 mg, 1.72 mmol) was treated with 0.33 mL of acetic anhydride and 0.83 mL of pyridine at room temperature for 2 h gave the silylketoxime acetate **19** (417 mg, 1.72 mmol) as a colorless oil. **19**: $^1$H NMR ($CDCl_3$, 60 MHz) 0.10 (s, 9 H), 0.60-0.99 (m, 2 H, $\underline{H}_2CSi$), 1.33 (s, 9 H), 2.18 (s, 3 H, $\underline{H}_3CCO$), 2.20-2.43 (m, 2 H, $\underline{H}_2CCN$); IR (film) 1772, 1621, 1370, 1253, 865, 833 cm$^{-1}$; Anal. Calcd for $C_{12}H_{25}NO_2Si$: C, 59.21; H, 10.35; N, 5.75. Found: C, 59.41; H, 10.23; N, 5.87.

**Preparation of Silylketoxime Acetate 22.**

To a solution of 1 (199 mg, 1.0 mmol) in 3 mL of THF was added n-butyllithium (1.5 N in hexane, 1.4 mL). The mixture was stirred at room temperature for 1 h and iodomethane (280 mg) was added. After stirring for 1 h and usual work-up, cis-6-methyl oxime (191 mg, 0.90 mmol) was obtained; Anal. Calcd for $C_{11}H_{23}NOSi$: C, 61.91; H, 10.86; N, 6.56. Found: C, 61.90; H, 11.17; N, 6.34. The oxime (227 mg, 1.07 mmol) was treated with 0.3 mL of acetic anhydride and 1.0 mL of pyridine at 0°C for 1 h to give 215 mg (0.84 mmol) of **22** as a colorless oil. **22**: $^1$H NMR ($CDCl_3$, 90 MHz) -0.02 (s, 9 H), 0.45 (m, 1 H), 0.62 (m, 1 H), 1.10 (d, 3 H, $\underline{H}_3C$), 1.20-1.80 (m, 6 H), 2.14 (s, 3 H, $\underline{H}_3CCO$), 2.55 (m, 1 H, $\underline{H}CCSi$), 3.55 (m,1 H, $\underline{H}CCH_3$); IR (film) 1763, 1618, 1250, 840 cm$^{-1}$; MS, m/e 255 (2, M), 240 (50), 198 (100), 180 (90), 152 (35), 140 (30).

**Preparation of Silylketoxime Acetate 24.**

To a solution of trimethylsilylmethyl magnesium chloride (9.0 mmol) in 20 mL of THF was added norbornene oxide (584 mg, 5.31 mmol) and 257 mg of CuI. The mixture was stirred at room temperature for 16 h. After usual work-up, silylalcohol (458 mg, 2.31 mmol) was obtained. Subsequent oxidation of the alcohol (452 mg, 2.30 mmol) with $CrO_3$ (460 mg) and pyridine (0.74 mL) in $CH_2Cl_2$ (10 mL) at room temperature for 9 h to give the corresponding ketone (400 mg, 2.04 mmol) as a colorless oil; IR (film) 1740 cm$^{-1}$. The ketone (389 mg, 1.98 mmol) was treated with $HONH_2 \cdot HCl$ (165 mg) and NaOAc (325 mg) in 5 mL of ethanol to give the oxime (368 mg, 1.74 mmol). The oxime (266 mg, 1.26 mmol) was treated with 0.14 mL of acetic anhydride and 0.8 mL of pyridine to give the silylketoxime acetate **24** (304 mg, 1.20 mmol) as a colorless oil. **24**: $^1$H NMR ($CDCl_3$, 60 MHz) 0.0 (s, 9 H), 0.63 (dd, J = 10.0 and 15.0 Hz, 1 H, $\underline{H}CSi$), 1.06 (dd, J = 5.0 and 15.0 Hz, 1 H, $\underline{H}CSi$), 1.20-1.50 (m, 6 H), 2.10 (s, 3 H, $\underline{H}_3CCO$), 2.10-2.30 (m, 1 H), 2.55 (m, 1 H, $\underline{H}CCSi$), 3.35 (m, 1 H, $\underline{H}CCN$); IR (film) 1765, 1620, 1250, 840 cm$^{-1}$; Anal. Calcd for $C_{13}H_{23}NO_2Si$: C, 61.62; H, 9.15; N, 5.53. Found: C, 61.37; H, 9.24; N, 5.52.

**Preparation of Silylketoxime Acetate 26.**

Alkylation of 1.0 g of 2-carboethoxycyclododecanone with NaH (1.2 eq) and iodomethyl(trimethyl)-silane (2.0 eq) in 6 mL of benzene and 3 mL of DMF at 60°C for 2 days gave 390 mg of 2-carboethoxy-2-(trimethylsilylmethyl)cyclododecanone. Treatment of 333 mg of the ketone with excess $Ba(OH)_2$ in methanol at reflux temperature for 1 week gave 100 mg (0.30 mmol) of 2-(trimethylsilylmethyl)cyclo-dodecanone. The silylketone (61 mg, 0.23 mmol) was treated with $HONH_2 \cdot HCl$ (20 mg) and NaOAc (40 mg) in 1 mL of ethanol at 80°C for 1 h to give the oxime (60 mg). The crude oxime was treated with 0.05 mL of acetic anhydride and 0.1 mL of pyridine in $CH_2Cl_2$ (1 mL) to give the silylketoxime acetate **26** (59.5 mg, 0.18 mmol). **26**: $^1$H NMR ($CDCl_3$, 60 MHz) 0.0 (s, 9 H), 0.90 (m, 2 H, $\underline{H}_2CSi$), 1.0-2.0 (m, 18 H), 2.10 (s, 3 H, $\underline{H}_3CCO$), 2.20-2.80 (m, 3 H); IR (film) 1765, 1620, 1250, 840 cm$^{-1}$.

**Preparation of Silylketoxime Acetates 37 and 38.**

To a solution of 2.30 g (14.0 mmol) of benzyltrimethylsilane and N,N,N',N'-tetramethylethylenediamine (3mL) in 30 mL of THF at -78°C was added n-butyllithium (in hexane, 1.68 N, 8.33 mL). After stirring at 0°C for 30 min, the mixture was then cooled at -78°C. Cyclohexene oxide (0.98 g, 10.0 mmol) was added to the mixture. The temperature was then raised to -15°C. After stirring for 4 h, aqueous ammonium chloride was added and the mixture was extracted with ether. The organic layer was dried over anhydrous magnesium sulfate and concentrated to give the residual oil, which was purified by silica

gel column chromatography. 2-[(Trimethylsilyl)phenylmethyl]-cyclohexanol (2.03 g, 7.72 mmol) was obtained in 77% yield. The alcohol was treated with $CrO_3$ (2.0 g) and pyridine (5.0 mL) in 30 mL of $CH_2Cl_2$. The mixture was stirred for 4 h. Ether (50 mL) was added to the mixture. The extract was concentrated and purified by silica gel to give the two isomers of cyclohexanone derivatives (threo ketone, 795 mg; erythro ketone, 785 mg; total 82%; Rf, 0.63 and 0.56, respectively). Threo ketone: a colorless oil; $^1H$ NMR ($CDCl_3$, 90 MHz) -0.10 (s, 9 H), 1.01-2.11 (m, 6 H), 2.27-2.68 (m, 2 H, $H_2CCO$), 2.52 (d, 1 H, J = 10.6 Hz, HCSi), 2.75-3.10 (m, 1 H, HCCO), 6.81-7.37 (m, 5 H); IR (film) 1712, 1599, 1496, 1246, 738, 698 $cm^{-1}$; Anal. Calcd for $C_{16}H_{24}OSi$: C, 73.79; H, 0.29. Found: C, 73.93; H, 9.35. Erythro ketone: mp 38.0-39.0 °C; $^1H$ NMR ($CDCl_3$, 90 MHz) -0.03 (s, 9 H), 1.47-2.44 (m, 8 H), 2.55 (d, 1 H, J = 9.2 Hz, HC-Si), 2.69-3.18 (m, 1 H, HCCO), 6.85-7.33 (m, 5 H); Anal. Calcd for $C_{16}H_{24}OSi$: C, 73.79; H, 9.29. Found: C, 73.52; H, 9.36. As above described, the two isomers of the ketones were transformed to the oximes, which were subsequently acetylated: threo ketone (615 mg, 2.36 mmol), $HONH_2 \cdot HCl$ (197 mg), NaOAc (387 mg), EtOH (8.0 mL), at room temp., for 3 h, threo oxime (623 mg, 2.26 mmol, 96%); erythro ketone (604 mg, 2.32 mmol), $HONH_2 \cdot HCl$ (193 mg), NaOAc (381 mg), EtOH (8.0 mL), at room temp., for 3 h, erythro oxime (611 mg, 2.22 mmol0, 96%); threo oxime (300 mg, 1.09 mmol), acetic anhydride (0.22 mL), pyridine (0.43 mL), $CH_2Cl_2$ (2.0 mL), at 0°C, for 2 h, threo silylketoxime acetate **37** (335 mg, 1.06 mmol, 97%); erythro oxime (299 mg, 1.08 mmol), acetic anhydride (0.22 mL), pyridine (0.42 mL), $CH_2Cl_2$ (2.0 mL), at 0°C, for 2 h, erythro silylketoxime acetate **38** (337 mg, 1.06 mmol, 98%); Rf, 0.56 for **37** and 0.48 for **38**, ether:hexane = 1:1. **37**: mp 76.0-77.0 °C; $^1H$ NMR ($CDCl_3$, 90 MHz) -0.09 (s, 9 H), 1.06-2.31 (m, 7 H), 2.20 (s, 3 H, $H_3CCO$), 2.54 (d, 1 H, J = 12.5 Hz, HCSi), 2.93-3.41 (m, 2 H, $H_2CCN$), 6.80-7.41 (m, 5 H); IR (film) 1770, 1636, 1601, 1494, 1249, 741, 701 $cm^{-1}$; Anal. Calcd for $C_{18}H_{27}NO_2Si$: C, 68.09; H, 8.57; N, 4.41. Found: C, 68.87; H, 8.74; N, 4.36. **38**: mp 75.0-76.0 °C; $^1H$ NMR ($CDCl_3$, 90 MHz) -0.03 (s, 9 H), 1.08-2.30 (m, 7 H), 1.98 (s, 3 H, $H_3CCO$), 2.58 (d, 1 H, J = 11.9 Hz, HCSi), 2.71 (m, 1 H), 3.25 (m, 1 H), 6.87-7.30 (m, 5 H); IR (film) 1762, 1637, 1598, 1491, 1247, 720, 699 $cm^{-1}$; Anal. Calcd for $C_{18}H_{27}NO_2Si$: C, 68.09; H, 8.57; N, 4.41. Found: C, 67.87; H, 8.74; N, 4.36.

**Reaction of Silylketoxime 1 with $P_2O_5$.**

To a solution of 99 mg (0.50 mmol) of **1** in $CH_2Cl_2$ (2.0 mL) was added ca. 70 mg (0.5 mmol) of phosphorus pentoxide at 0°C. The mixture was stirred for 1 day at room temperature. Ether (2 mL) and triethylamine (0.2 mL) were added and the mixture was washed with brine and concentrated under reduced pressure by aspirator. The residual oil was diluted with $CDCl_3$ (0.3 mL) and benzene (0.030 mL) as an internal standard was added. Crude yield was calculated on the basis of integral value of olefinic protons by $^1H$ NMR analysis (82%). The crude oil was then passed through a short column of silica gel to give 43 mg (0.37 mmol) of **3** (73%). Further purification for identification was performed by preparative GLPC. **3**: $^1H$ NMR ($CDCl_3$, 60 MHz) 1.20-2.80 (m, 8 H), 4.90-5.20 (m, 2 H), 5.85 (m, 1 H); $^{13}C$ NMR ($CDCl_3$, 22.5 MHz) 17.17, 24.98, 27.97, 32.95, 115.52, 137.68; IR (film) 2250, 910 $cm^{-1}$; MS exact mass m/e 109.0873 (calcd for $C_7H_{11}N$, 109.0890); MS, m/e 109 (9, M), 73 (16).

**Reaction of Silylketoxime 2 with $P_2O_5$.**

The silylketoxime **2** (124 mg, 0.62 mmol) was treated, as described for **1**, with phosphorus pentoxide (90 mg) in $CH_2Cl_2$ (2.0 mL) at room temperature for 4 h to give **4** (35 mg, 0.32 mmol) in 51%. **4**: $^1H$ NMR ($CDCl_3$, 90 MHz) 1.50 (d, 3 H), 1.60 (m, 2 H), 2.0 (m, 4 H), 2.18 (t, 3 H, $H_2CCN$), 5.50 (m, 2 H); $^{13}C$ NMR ($CDCl_3$, 22.5 MHz) 16.45 (t, CCN), 17.96 (q), 127.47, 128.69 ; IR (film) 2250, 965 $cm^{-1}$; MS exact mass m/e 109.0858 (calcd for $C_7H_{11}N$, 109.0890); MS, m/e 109 (100, M), 83 (11), 81 (58), 69 (41), 67(54).

**Reaction of Silylketoxime Acetate 8 with $BF_3 \cdot Et_2O$.**

The acetate **8** (136 mg, 0.57 mmol) was treated with borontrifluoride etherate (0.077 mL) in $CH_2Cl_2$ (1 mL) at 0°C for 4 h to give **3** (50 mg, 0.46 mmol) in 80%.

**Reaction of 1 with N-Methyl-2-fluoropyridinium Iodide.**

To a solution of 199 mg (1.0 mmol) of **1** in $CH_2Cl_2$ (3.0 mL) was added 0.11 (1.1 mmol) of triethylamine and the pyridinium salt (263 mg, 1.10 mmol) at 0°C. The mixture was stirred for 1 h. After work-up as described above, 77 mg (0.71 mmol) of **3** was obtained.

**Reaction of Silylketoxime Acetate 13 with $BF_3 \cdot Et_2O$.**

The acetate **13** (132 mg, 0.35 mmol) was treated with borontrifluoride etherate (0.052 mL) in $CH_2Cl_2$ (2.0 mL) at refluxing temperature for 5 h. After extraction with ether, the crude oil was purified by silica gel column to give 56 mg (0.34 mmol) of the nitrile **14** as a colorless oil (97%). **14**: $^1H$ NMR ($CDCl_3$, 60 MHz) 2.34 (m, 2 H), 3.48 (m, 2 H), 4.70-5.24 (m, 2 H), 5.85 (m, 1 H), 7.0-7.7 (m, 4 H); IR (film) 2200, 1600,1585, 905, 758 $cm^{-1}$; MS m/e 158 (M), 117, 90, 40.

**Reaction of Silylketoxime Acetate 18 with $BF_3 \cdot Et_2O$.**

The acetate **18** (77.4 mg, 0.29 mmol) was treated with borontrifluoride etherate (0.044 mL) in $CH_2Cl_2$ (1.0 mL) at room temperature for 8 h. N-Phenyl-3-trimethylsilylpropanamide **20** (49 mg, 0.22 mmol) was obtained. **20**: a colorless oil; $^1H$ NMR ($CDCl_3$, 60 MHz) 0.04 (s, 9 H), 1.00 (m, 2 H, $\underline{H}_2CSi$), 2.39 (m, 2 H, $\underline{H}_2CCO$), 7.10-7.77 (m, 5 H); IR (film) 1660, 1600, 1550, 1500, 1255, 860, 833 $cm^{-1}$.

**General Procedure of Catalytic Fragmentation.**

To a solution of the silylketoxime acetate (0.5-1.0 mmol) in anhydrous $CH_2Cl_2$ (2-4 mL) was added dropwise TMSOTf (10 mol% equivalent) at 0°C. The mixture was stirred for 1-4 h (monitored by TLC), was treated with aqueous sodium bicarbonate and triethylamine (0.1 mL), and was quickly extracted with ether (10 mL). The extract was concentrated, and the residual oil was purified by silica gel column chromatography to give the corresponding nitrile.

**Reaction of Silylketoxime Acetate 8 with TMSOTf.**

The acetate **8** (121 mg, 0.50 mmol) was treated with TMSOTf (ca. 0.01 mL) in $CH_2Cl_2$ (2.0 mL) at 0°C for 4 h. After work-up, the crude oil was diluted in $CDCl_3$ and benzene (0.020 mL). Calculation on the basis of $^1H$ NMR analysis gave 89% yield of **3**.

**Reaction of Silylketoxime Acetate 24 with TMSOTf.**

The acetate **24** (134 mg, 0.53 mmol) was treated with TMSOTf (0.01 mL) in $CH_2Cl_2$ (2.0 mL) at 0°C for 1 h. After work-up and silica gel chromatography, the nitrile **25** (60.9 mg, 0.50 mmol) was obtained. **25**: a colorless oil; $^1H$ NMR ($CDCl_3$, 90 MHz) 1.40-2.10 (m, 6 H), 2.40 (m, 1 H, $\underline{H}CC{=}C$), 2.82 (m, 1 H, $\underline{H}CC{=}N$), 4.90-5.20 (m, 2 H), 5.80 (m, 1 H); IR (film) 2230, 1640, 990, 910 $cm^{-1}$; MS exact mass m/e 121.0889 (calcd for $C_8H_{11}N$, 121.0890).

The reaction of other silylketoxime acetate **22**, **26**, **28**, **30**, **31**, **33**, and **34** with TMSOTf were carried out in a manner similar to that described above. The reaction conditions and analytical data of the nitriles are listed below.

**22** (122 mg, 0.48 mmol), TMSOTf (0.01 mL), $CH_2Cl_2$ (2 .0 mL), 0°C, 2 h; **23** (48 mg, 0.39 mmol): a colorless oil; $^1H$ NMR ($CDCl_3$, 60 MHz) 1.30 (d, 3 H), 1.50-1.80 (m, 4 H), 2.10 (m, 2 H), 2.60 (m, 1 H), 4.80-5.20 (m, 2 H), 5.85 (m, 1 H); IR (film) 2220, 1640, 940, 910 $cm^{-1}$; MS exact mass m/e 123.1084 (calcd for $C_8H_{13}N$, 123.1048).

**26** (52 mg, 0.16 mmol), TMSOTf (0.005 mL), $CH_2Cl_2$ (0.8 mL), 0°C, 2 h; **27** (25 mg, 0.128 mmol): a colorless oil; $^1H$ NMR ($CDCl_3$, 60 MHz) 1.20-2.80 (m, 20 H), 4.80-5.20 (m,2 H), 5.80 (m, 1 H); IR (film) 2250, 1640, 990, 910 $cm^{-1}$; MS exact mass m/e 193.1837 (calcd for $C_{13}H_{23}N$, 193.1831).

**28** (147 mg, 0.48 mmol), TMSOTf (0.01 mL), $CH_2Cl_2$(2.0 mL), 0°C, 3 h; **29** (76.3 mg, 0.45 mmol): a colorless oil; $^1H$ NMR ($CDCl_3$, 60 MHz) 2.43 (broad s, 4 H), 3.44 (d, 2 H), 5.17-5.95 (m, 2 H), 7.21 (s, 5 H); IR (film) 2250, 964 $cm^{-1}$; MS exact mass m/e 171.1042 (calcd for $C_{12}H_{12}N$, 171.1037)

**30** (121 mg, 0.50 mmol), TMSOTf (0.01 mL), $CH_2Cl_2$ (2.0 mL), 0°C, 3 h; **4** (51 mg, 0.47 mmol). **31** (93 mg, 0.31 mmol), TMSOTf (0.006 mL), $CH_2Cl_2$ (1.0 mL), 0°C, 1 h; **32** (47.2 mg, 0.29 mmol): $^1H$ NMR ($CDCl_3$, 90 MHz) 0.89 (t, 3 H), 1.10-1.50 (m, 8 H), 1.70 (m, 2 H), 2.05 (m, 2 H), 2.32 (t, 2 H, $\underline{H}_2C$ CN), 5.10-5.70 (m, 2 H); $^{13}C$ NMR ($CDCl_3$, 22.5 MHz) 14.1, 16.3, 22.6, 25.3, 29.2, 31.3, 32.6, 119.0, 127.3, 133.3; IR (film) 2245, 965 $cm^{-1}$; MS m/e 166 (20, M+1), 165 (14, M), 137 (56), 136 (65), 122 (70), 108 (33), 95 (34), 80 (100), 67 (53), 55 (80); MS exact mass m/e 165.1516 (calcd for $C_{11}H_{19}N$, 165.1516). **33** (128 mg, 0.53 mmol), TMSOTf (0.01 mL), $CH_2Cl_2$ (2.0 mL), 0°C, 3 h; **35** (54.0 mg, 0.50 mmol): $^1H$ NMR ($CDCl_3$, 90 MHz) 1.50-1.90 (m,4 H), 2.35 (m, 2 H,$\underline{H}_2CC$=C), 2.40 (t, 2 H, $\underline{H}_2CCN$), 5.40 (m, 2 H); $^{13}C$ NMR ($CDCl_3$, 22.5 MHz) 12.86 (q, $\underline{C}H_3$, cis-methyl), 16.46 (t), 25.31 (t), 25.65 (t), 126.36, 128.04; IR (film) 2240, 1655, 910, 835 $cm^{-1}$; MS exact mass m/e 109.0898 (calcd for $C_{17}H_{11}N$, 109.0890). **34** (70.6 mg, 0.24 mmol), TMSOTf (0.005 mL), $CH_2Cl_2$ (1.0 mL), 0°C, 1 h; **36** (35.4 mg, 0.21 mmol): a colorless oil; $^1H$ NMR ($CDCl_3$, 90 MHz) 0.89 (t, 3 H), 1.10-1.95 (m, 8 H), 1.70 (m, 2 H), 2.10 (m, 2 H), 2.34 (t, 2 H), 5.10-5.70 (m, 2 H); $^{13}C$ NMR ($CDCl_3$, 22.5 MHz) 14.1, 16.5, 22.6, 25.5, 26.0, 27.2, 29.4, 31.5, 119.8, 126.7, 132.6; MS m/e 166 (8, M+1), 165 (10, M), 137 (64), 134 (75), 122 (66), 95 (64), 80 (100), 67 (80), 55 (100); MS exact mass m/e 165.1499 (calcd for $C_{11}H_{19}N$, 165.1516).

**Reaction of Silylketoxime Acetate 37 and 38 with CsF and TMSOTf.**

The acetate **37** (95.2 mg, 0.30 mmol) was treated with CsF (137 mg, 0.90 mmol) in acetonitrile (1.0 mL) at refluxing temperature for 8 h. After concentration and silica gel column chromatography, the nitrile **39** (49.2 mg, 0.266 mmol) and 2-benzylcyclohexanone oxime acetate **41** ( 8.8 mg, 0.036 mmol) were obtained. In the same manner, the acetate **38** (95.2 mg, 0.30 mmol) gave the nitrile **40** (45.7 mg, 0.247 mmol) and **41** ( 7.4 mg, 0.030 mmol).

The acetate **37** (63.5 mg, 0.20 mmol) was treated with TMSOTf (0.02 mL) in $CH_2Cl_2$ (0.6 mL) at 0°C for 3 h. After work-up, the nitrile **39** (36.3 mg, 0.18 mmol) was obtained. In the same manner, the acetate **38** (63.5 mg, 0.20 mmol) gave the nitrile **40** (33.3 mg, 0.19 mmol).
**39**: a colorless oil; $^1H$ NMR ($CDCl_3$, 60 MHz) 1.33-1.95 (m, 4 H), 1.95-2.78 (m, 4 H), 5.80-6.53 (broad, 2 H, $\underline{H}C$=C$\underline{H}$), 7.21 (broad s, 5 H); IR (film) 2260, 1601, 1498, 767, 700 $cm^{-1}$. **40**: a colorless oil; $^1H$ NMR ($CDCl_3$, 60 MHz) 1.05-1.95 (m, 4 H), 1.95-2.78 (m, 4 H), 5.56 (m, 1 H), 6.40 (m, 1 H), 7.22 (broad s, 5 H); IR (film) 2260, 1600, 1498, 962 (trans olefin), 742, 692 $cm^{-1}$.

**Synthesis of (4E), (7Z)-Tridecadienyl Acetate 46.**

To a solution of 0.44 mL (2.2 mmol) of hexamethyldisilane in 3.0 mL of HMPA was added a solution of methyllithium (2 mmol) at room temperature. After stirring for 30 min, 8 mL of THF was added. The mixture was cooled to -78°C and 123 mg (1.5 mmol) of 2-cyclopentenone was added slowly by microsyringe. Then tri-n-butyltin chloride (650 mg, 2.0 mmol) was added. The mixture was stirred for 10 min. 1-Bromo-2-octyne (370 mg, 2.0 mmol) was added. The temperature was raised to -40 °C and the mixture was stirred for 1h. The mixture was extracted with a mixture of ether and hexane (1:1) and the extract was washed with water and was concentrated. The residual oil was purified by silica gel column to give the silylketone **42** (264 mg, 1.0 mmol). **42**: a colorless oil; $^1H$ NMR ($CDCl_3$, 90 MHz) 0.03 (s, 9 H), 0.84 (t, 3 H), 1.10-1.50 (m, 9 H), 1.70-2.20 (m, 5 H), 2.30 (m, 1 H), 2.53 (m, 1 H), 2.80 (m, 1 H); IR (film) 1740, 1250, 835 $cm^{-1}$; MS m/e 265 (23, M+1), 264 (6, M), 207 (15), 183 (27), 173 (64), 164 (84), 156 (100).

Under atmospheric pressure of hydrogen, a solution of the silylketone **42** (136 mg, 0.51 mmol), Pd-$BaSO_4$ (30 mg), and quinoline (0.01 mL) in 1.5 mL of methanol was stirred for 10 h. After concentration the residual oil was purified by silica gel column to give the silylketone **43** (118 mg, 0.44 mmol). **43**: IR (film) 1738, 1250 $cm^{-1}$; MS m/e 267 (4, M+1), 177 (12), 156 (21), 155 (30), 119 (11), 73 (100).

The silylketone **43** (118 mg, 0.44 mmol) was treated with $HONH_2 \cdot HCl$ (37 mg) and NaOAc (72 mg) in ethanol (2.0 mL) to give the corresponding oxime. The crude oxime was treated with acetic anhydride (0.05 mL) and pyridine (0.11 mL) in dichloromethane (1.0 mL) at 0°C for 1h. After usual work-up and silica gel column chromatography, the silylketoxime acetate **44** (105 mg, 0.32 mmol) and the (Z)-isomer (35 mg, 0.08 mmol) were obtained; Rf, 0.50 for **44** and 0.39 for the isomer, ether:hexane = 1:1. **44**: a

colorless oil; $^1$H NMR ($CDCl_3$, 90 MHz) -0.06 (s, 9 H), 0.82 (t, 3 H), 2.05 (s, 3 H), 5.20-5.60 (m, 2 H); $^{13}$C NMR ($CDCl_3$, 22.5 MHz) -2.75, 13.9, 14.4, 19.6, 21.6, 22.5, 24.8, 27.3, 27.5, 29.3 (two carbons), 30.1, 30.5, 31.5, 44.7, 125.7, 132.2, 168.8, 177.5; IR (film) 1765, 1650, 1245, 835 cm$^{-1}$; MS m/e 264 (10, M-59), 190 (10), 170 (100), 154 (50), 113 (38), 73 (62); MS exact mass m/e 264.2147 (M-AcO) (calcd for $C_{18}H_{33}NO_2Si$-$C_2H_3O_2$, 264.2147).

The silylketoxime acetate **44** (109 mg, 0.34 mmol) was treated with TMSOTf (0.07 mL) in $CH_2Cl_2$ (1.0 mL) at 0°C for 1 h to give the nitrile **45** (51 mg, 0.27 mmol). **45**: a colorless oil; $^1$H NMR ($CDCl_3$, 90 MHz) 0.89 (t, 3 H), 1.10-1.50 (m, 6 H), 1.80-2.10 (m, 4 H), 2.34 (s, 1 H), 2.36 (s, 1 H), 2.75 (broad, 2 H), 5.20-5.80 (m, 4 H); $^{13}$C NMR ($CDCl_3$, 22.5 MHz) 14.0, 17.7, 22.6, 27.2, 28.4, 29.3, 30.2, 31.5, 119.3, 125.9, 126.6, 131.2, 132.2; IR (film) 2240, 965 cm$^{-1}$; MS m/e 191 (16, M), 163 (13), 121 (23), 111 (26), 108 (43), 80 (86), 68 (100); MS exact mass m/e 191.1647 (calcd for $C_{13}H_{21}N$, 191.1672).

To a solution of **45** (50 mg, 0.34 mmol) in hexane (1.0 mL) was added di-iso-butylaluminum hydride (0.08 mL) by micro-syringe at -78°C. After stirring for 30 min, ether(2 mL) was added and then hydrochloric acid was added until the pH of the mixture became ca. 4. After separation of the organic layer and subsequent concentration, the residual oil was diluted with methanol (1 mL) at 0°C. Suspension of sodium borohydride (20 mg) in methanol (0.5 mL) was added. The mixture was stirred at 0°C for 1h. After an extraction, the residual oil was obtained. The oil was treated with acetic anhydride (0.04 mL) and pyridine (0.06 mL) in $CH_2Cl_2$ (1.0 mL) at 0°C for 2 h. After usual work-up and silica gel column chromatography, the desired acetate **46** (36 mg, 0.18 mmol) was obtained. **46**: a colorless oil; $^1$H NMR ($CDCl_3$, 90 MHz) 0.89 (t, 3 H), 2.04 (s, 3 H), 2.74 (s, 2 H), 4.06 (t, 2 H), 5.20-5.60 (m, 4 H); $^{13}$C NMR ($CDCl_3$, 22.5 MHz) 14.0, 20.9, 22.6, 27.1, 28.5, 28.9, 29.4, 30.4, 31.5, 64.0, 127.4, 129.1, 129.6, 130.7, 172.0; IR (film) 1740, 965 cm$^{-1}$; MS exact mass m/e 238.1926 (calcd for $C_{15}H_{26}O_2$, 238.1933); MS m/e 238 (8, M), 179 (21), 150 (29), 135 (70), 122 (51), 108 (58), 97 (35), 78 (42), 57 (48), 32 (100).

**Synthesis of the Ketones 47 and 48.**

The nitrile **32** (5.1 mg) was treated with n-decanyl magnesium chloride in ether at 0°C. After treatment with hydrochloric acid, the desired ketone **47** (6.7 mg, 0.022 mmol) was obtained. The nitrile **36** (9.3 mg) was also treated by the same manner to give the nitrile **48** (13.3 mg, 0.043 mmol); Rf, 0.72 for **47** and 0.62 for **48**, ether:hexane = 1.4. **47**: mp 34.0-35.0 °C; $^1$H NMR ($CDCl_3$, 90 MHz) 0.87 (t, 3 H) 1.0-1.8 (m, 28 H), 1.80-2.20 (m, 4 H), 2.37 (t, 4 H), 5.25-5.45 (m, 2 H); $^{13}$C NMR ($CDCl_3$, 22.5 MHz) 129.3 and 131.6 (olefinic); IR (film) 1700, 960 cm$^{-1}$; MS m/e 308 (33, M), 251 (13), 237 (16), 197 (23), 169 (66), 124 (100). **48**: a colorless oil; $^1$H NMR ($CDCl_3$, 90 MHz) 0.88 (t, 3 H), 1.0-1.4 (m, 24 H), 1.60 (m, 4 H), 1.95 (m, 4 H), 2.32 (t, 4 H), 5.10-5.60 (m, 2 H); $^{13}$C NMR ($CDCl_3$, 22.5 MHz) 128.8 and 131.3 (olefinic); IR (film) 1710 cm$^{-1}$; MS m/e 308 (21, M), 197 (22), 167 (22), 124 (90).

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(10) From **19**, 3-trimethylsilylpropionitrile was also obtained in ca. 20% yield by way of fragmentation of the t-butyl group.

(11) In the course of the reaction, the corresponding (E)-isomer could not be detected by careful TLC examination. The (E)-isomer generated by the isomerization should spontaneously cause the fragmentation under the reaction condition.

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