

Nitrosyl chloride addition to cycloalkenyltrimethylsilanes. An unexpected reversal of regiochemistry of addition, and synthesis of β -aminosilanes

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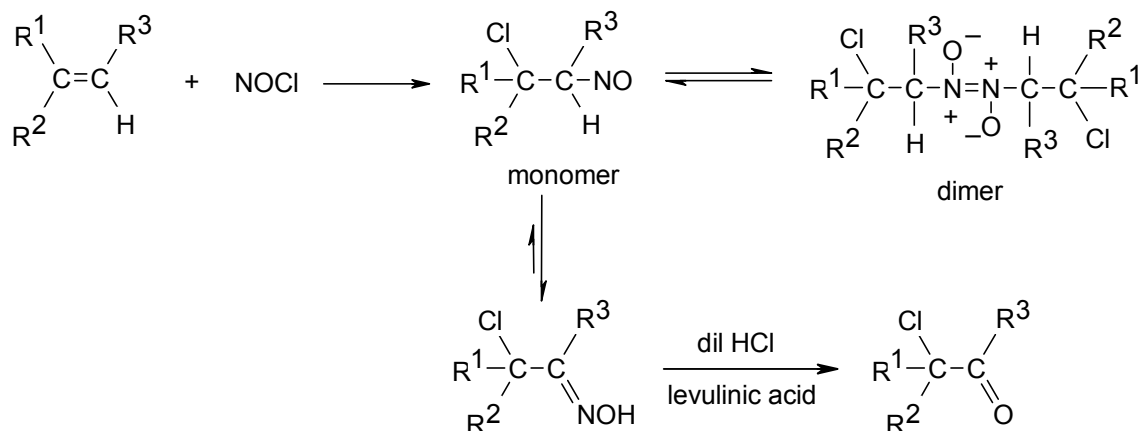
Abstract

Cycloalkenyltrimethylsilanes add nitrosyl chloride stereo- and regio- selectively. The addition is *syn*, with chlorine and nitrosyl group adding to C-1 and C-2 respectively. The products dimerize to diazene dioxides, whose stability depends on the conformational flexibility of the ring - the less flexible are more stable. The less stable adducts convert to oximes and further to 1,2-dichloro-1-nitrosocycloalkanes. The adducts can be hydrolysed to α -chloroketones and reduced to β -aminosilanes. Other interesting observations include transposition of keto group in α -chloroketones and X-ray crystal structure of the amide derivative **6f**, which reveals $-(CO)-HN\dots H-CH_2-(CO)-$ hydrogen contact.

Keywords: Cycloalkenyltrimethylsilanes, NOCl addition, α -chloro- β -nitrososilanes, 1,2-dichloro-1-nitrosocycloalkanes, α -chloroketones, conformational flexibility, β -aminosilanes, $N\dots H-C$ hydrogen contact

Introduction

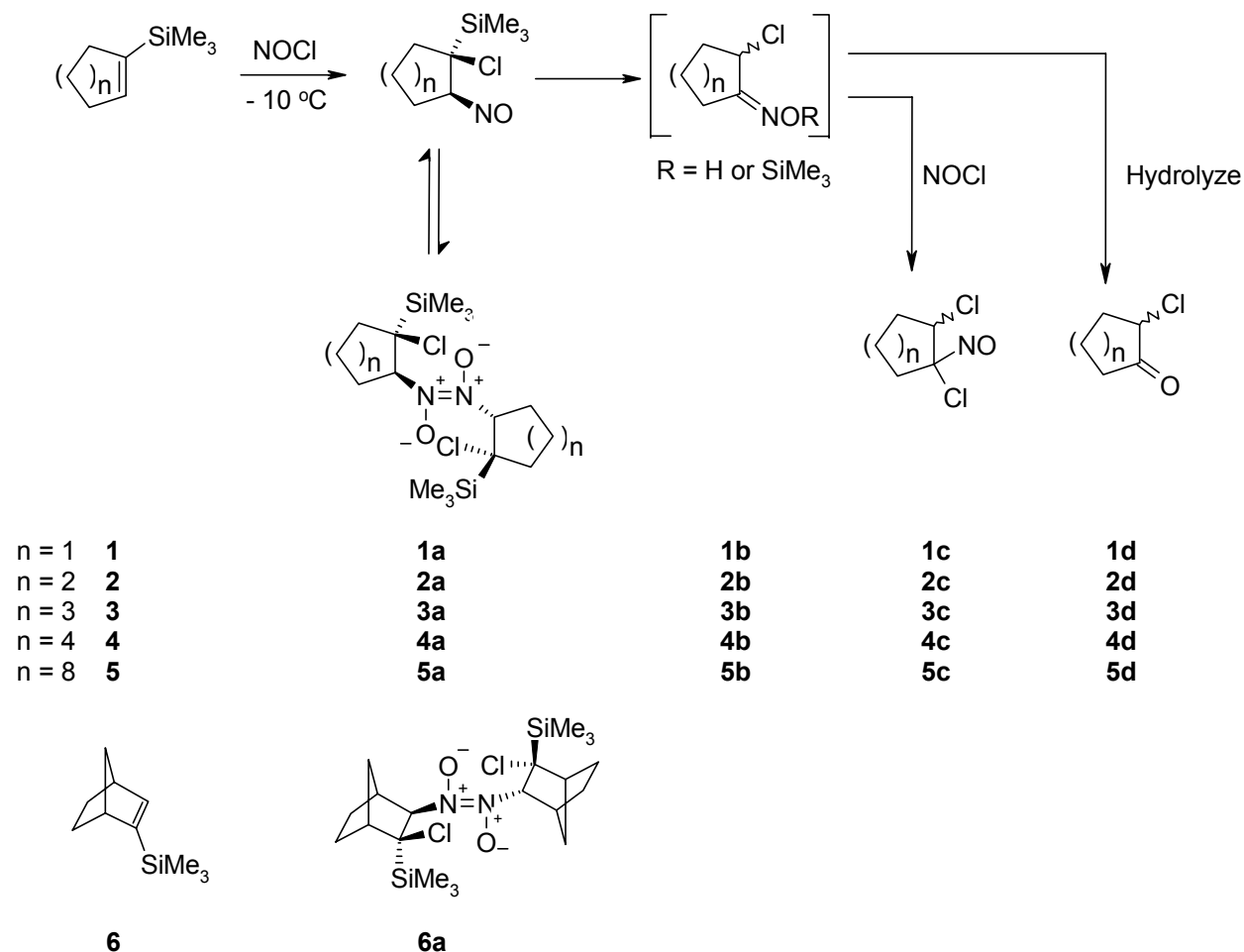
1-Chloro-2-nitroso compounds obtained by a simple addition reaction of nitrosyl chloride (NOCl) with olefins are versatile compounds and find many synthetic applications.¹⁻³ In pure state, the adducts exist usually in the form of dimers, called diazene dioxides, resulting from N-N connection and are stable substances (Scheme 1).



Scheme 1

The dimeric form is retained even in solution, though it may dissociate into monomer and equilibrium would be established between the two forms. The monomer in solution may undergo tautomerization (if α -hydrogen is present) to the corresponding oxime, which is however essentially irreversible.³ The oxime is generally much more stable than the nitroso compound. Nonetheless, the nitroso-to-oxime tautomerization is not a spontaneous process, and is catalyzed by acid or base. The ease of tautomerization also depends to some extent on the alkene structure. The α -chlorooxime can eventually be hydrolyzed to α -chloroketone⁴ or used in other ways.³ The NOCl addition to alkene is shown to be *trans*¹⁻³ as well as *cis*,^{5, 6} and usually follows Markovnikov regiochemistry^{2,7} as a result of which the α -chloroketone would have regio-defined structure.

In an earlier report we showed that NOCl addition to cycloalkenyltrimethylsilanes is both stereoselective and regioselective, in that, the reagent adds in a *cis* manner with NO attaching to the β -carbon and Cl to the α -carbon,⁸ (Scheme 2). Both these selectivity outcomes are contrary to expectation in view of the β -silicon effect,⁹ with electrophile adding to α -carbon in favour of β -cation formation.



Scheme 2

During this study we noted that the α -chloro- β -nitrososilanes **1a-5a** were far less stable than their unsilylated analogues, and underwent further reaction very rapidly to give finally 1,2-dichloro-1-nitrosocycloalkanes **1c-5c** and, under aqueous condition, α -chloroketones **1d-5d** presumably through the intermediacy of the oxime **1b-5b**. The directive influence of silicon in this transformation is easily recognizable. Our further study has revealed that the relatively close location of the silyl moiety and NO group, which is determined by the conformation of the ring, is crucial for this to be successful. We have also observed that through this sequence of reaction, a 1,2-migration of keto group can be achieved.¹⁰

In addition, the α -chloro- β -nitrososilanes are potential precursors for both α - as well as β -functionalized silanes. Among the β -functionalized silanes, β -aminosilanes have not been studied much. Very few reports are found in the literature on synthesis of β -aminosilanes.¹¹ The reduction of β -nitroso group to amino function in α -chloro- β -nitrososilanes **1a-6a** adducts provides a convenient method for making β -aminosilanes. The spectral investigations of the well-characterized solid derivatives of the β -aminosilanes were used to further confirm and

establish the regiochemistry and stereochemistry of NOCl addition to cycloalkenyltrimethylsilanes **1-6**.

Results and Discussion

The effective influence of silyl substituent in a ring system on a functional group or at a reaction site in cyclic systems has been shown to depend on the ring size in a crucial way, because the orientation of the silyl group relative to the functional group or its reactivity is determined by the conformational characteristics of the ring.^{12, 13} Our earlier study on the kinetics of a host of cyclic 1,2-dihydroxysilanes demonstrates the dependence of the rates on the conformational flexibility of the rings, which determines the correct orientation for the silanol elimination.¹⁴ Thus a series of cycloalkenyltrimethylsilanes such as **1-6** or monomers of **1a-6a** would yield much information on the conformational requirement for the silyl group to influence the reaction dealt in this paper.

To study the effect of silicon on nitroso-oxime tautomerism, we have chosen six cyclic systems **1a-6a** comprising very rigid system (**6a**) to highly flexible ring structures. α -Chloro- β -nitrosotrimethylsilylcycloalkanes **1a-6a** were prepared by adding NOCl to cycloalkenyltrimethylsilanes **1-6** (Scheme 2).

The source of NOCl was the well-known *in situ* reaction of *iso*-amyl nitrite with acetic acid-conc HCl mixture in one procedure. NOCl was also generated under anhydrous condition by treating *iso*-amyl nitrite with chlorotrimethylsilane¹⁵ either in dichloromethane or neat. The reactions were carried out between -20 °C and -10 °C. Though the formation of monomeric nitroso compounds could be easily recognized initially by their characteristic blue colour,¹⁶ only white dimeric diazene dioxides **1a-6a** and /or their secondary products, the 1,2-dichloro-1-nitroso derivatives **1c-5c** and α -chloroketones **1d-5d**, could be isolated. The yields and proportions of the products varied according to the method of generation of NOCl, and the ring size of adduct. The results are summarized in Table 1.

The NOCl addition to 1-trimethylsilylcycloalkenes **1-5** under aqueous acidic condition (Method A) produces secondary products **1c-5c** and **1d-5d** in high proportion, while under the anhydrous condition of Method C in CH₂Cl₂ solvent, the 1,2-dichloro-1-nitroso derivatives **1c-5c** are the only products. It is obvious that the presence of water in Method A is responsible for the formation of α -chloroketones **1d-5d**, whereas under anhydrous condition employed in the other two procedures, no α -chloroketones are formed.

It should be noted at this stage that the results of six membered ring (**2**) and norbornane ring (**6**) systems stand out, in that the former gives no trace of primary adduct **2a** but only products **2c** and **2d** of further reactions of **2a**, while the latter (**6**) gives only the stable dimeric primary adduct **6a**.

Table 1. NOCl addition to cycloalkenyltrimethylsilanes **1-6**

Vinylsilane	Method ^a	Time (h)	Product(s) (Yield, %)		
1			1a	1c	1d
	A	2.0	35	20	35
	B	1.5	52	40	-
	C	2.5	-	89	-
2			2a	2c	2d
	A	2.0	-	60	35
	B	1.5	-	85	-
	C	2.0	-	90	-
3			3a	3c	3d
	A	1.5	30	25	35
	B	1.5	65	30	-
	C	2.5	-	76	-
4			4a	4c	4d
	A	2.0	65	25	10
	B	1.5	75	25	-
	C	2.5	-	55	-
5^b			5a	5c	5d
	A	5.0	6	25	35
	B	4.0	8	75	-
	C	6.0	-	78	-
6			6a	-	6d
	A	0.25	92	-	-
	B	0.25	96	-	-
	C	0.50	94	-	-

^a Method A: (vinylsilane + *i*-AmONO + glacial HOAc) + (glacial HOAc + conc HCl).

Method B: (vinylsilane + *i*-AmONO) + (Me₃SiCl).

Method C: (vinylsilane + *i*-AmONO) in CH₂Cl₂ + (Me₃SiCl in CH₂Cl₂).

^b The conversion was about 40%. The yields of the products are based on recovered **5**.

The 2-trimethylsilylnorbornane adduct (**6a**) is the most stable adduct and the only product formed under all the three reaction conditions employed to generate NOCl. In the case of 1-trimethylsilylcyclohexene-NOCl addition, the primary adduct **2a** is so unstable that, instead of forming the isolable dimer, it undergoes further reaction rapidly to give 1,2-dichloro-1-nitrosocyclohexane (**2c**), and α -chlorocyclohexanone (**2d**) if NOCl is generated under aqueous acidic condition. The other four adducts **1a**, **3a-5a** could be isolated in the form of solid dimeric

diazene dioxides, provided they were isolated quickly enough from the reaction mixture at about $-10\text{ }^{\circ}\text{C}$, after allowing reasonable time required for adding the reagents (*i*-AmONO + HOAc + HCl or *i*-AmONO + Me₃SiCl) to generate NOCl. Though the reaction between NOCl and vinylsilane is instantaneous depending on the rate of NOCl generation the primary adducts undergo further reaction to give the secondary products. The time recorded for each reaction in Table 1 was the optimum that gave the best yield of the chloronitroso dimer. In the case of 2-trimethylsilylnorbornane adduct **6a**, because of its relatively high stability the time allowed for the reaction was not much of a deciding factor.

The isolated α -chloro- β -nitrososilane dimers **1a**, **3a-5a** on further treatment with NOCl at $-20\text{ }^{\circ}\text{C}$, instantaneously produced the corresponding 1,2-dichloro-1-nitroso compounds **1c-5c** in quantitative yield, while **6a** remained unchanged (Table 2).

Table 2. NOCl addition to **1a**, **3a-6a** by Method C

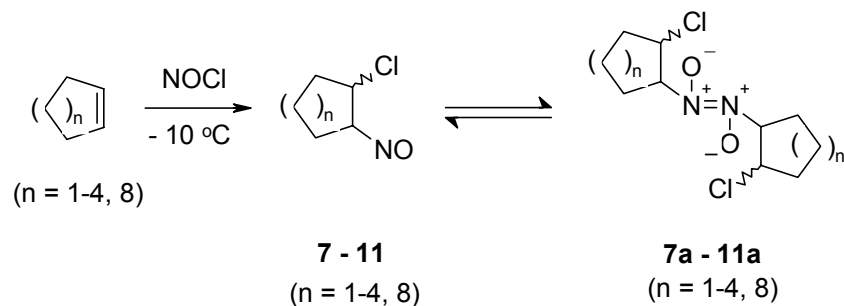
Compound	Time (min)	Product	Yield (%)
1a	30	1c	93
3a	15	3c	95
4a	15	4c	91
5a	20	5c	85
6a	No reaction		

The dimers **1a**, **3a-6a** produced the corresponding α -chloroketones **1d**, **3d-6d** in high yield when hydrolyzed with dilute HCl in dioxane at room temperature (Table 3). The presence of levulinic acid enhanced the rate of hydrolysis considerably.¹⁷

Table 3. Levulinic acid hydrolysis of **1a**, **3a-6a**

Compound	Temperature ($^{\circ}\text{C}$)	Time (h)	Product	Yield (%)
1a	r.t	2	1d	91
3a	r.t	0.5	3d	81
4a	r.t	0.5	4d	88
5a	r.t	0.5	5d	84
6a	50	3	6b	88
	75	5	6d	92

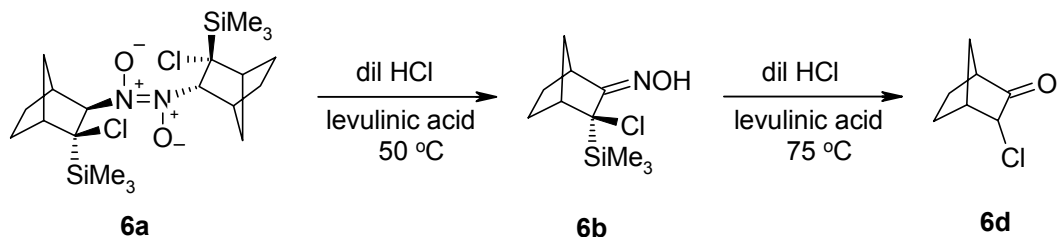
To compare the effect of Me₃Si group on tautomerization of **1a-5a**, we prepared the unsilylated NOCl adducts **7-11** from cyclopentene, cyclohexene, cycloheptene, cyclooctene and cyclododecene, under identical condition (Scheme 3).



Scheme 3

The adducts **7-11**, which were isolated only as dimers **7a-11a** were found to be far more stable both in solid state and in solution, from which they could be recovered unchanged even after several days at room temperature. In contrast, the Me_3Si containing adducts **1a**, **3a-5a** had to be recrystallized extremely cautiously from their saturated solutions in dichloromethane-petroleum ether (4:1 v/v) at lower than $-5\text{ }^\circ\text{C}$. Otherwise, they would tautomerize to α -chlorooximes (**1b**, **3b-5b**), or would undergo further hydrolysis to α -chloroketones (**1d**, **3d-5d**). Rapid tautomerization of **1a**, **3a**, and **4a** was noted during the recording of their NMR spectra in CDCl_3 when a ^{13}C signal due to oxime carbon appeared within 30 min after dissolving each adduct in CDCl_3 .

The conspicuous propensity of α -chloro- β -nitrososilanes **1a-5a** to tautomerize as compared to much higher stability of their unsilylated analogues **7a-11a**, which need more vigorous condition for tautomerization, is undoubtedly attributable to the involvement of silicon in the tautomerization process of the former compounds. However, one can also notice a remarkable variation along **1a-6a** in their tendency to tautomerize. The adduct 2-trimethylsilyl-2-chloro-3-nitrosobicyclo[2.2.1]heptane (**6a**) requires heating for 3 h at $50\text{ }^\circ\text{C}$ in dioxane in the presence of levulinic acid and dilute HCl to form its oxime **6b** with silicon intact. Further hydrolysis to α -chloroketone **6d** occurs only on heating for a longer time at higher temperature (5 h at $75\text{ }^\circ\text{C}$) (Scheme 4).

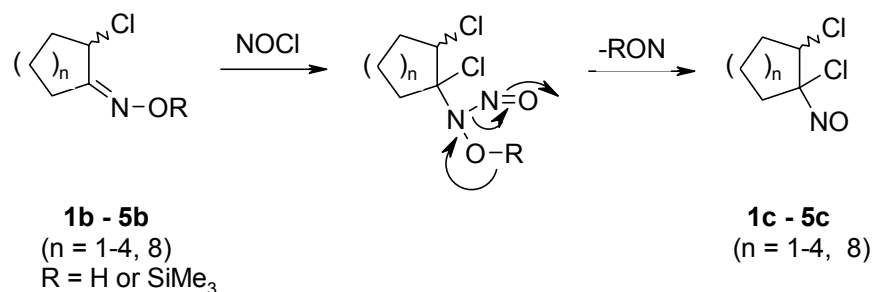


Scheme 4

On the contrary, the cyclohexane derivative **2a** is so unstable that it could not even be detected, but only its secondary product **2c** could be isolated, which would be accompanied by

α -chloroketone **2d**, when the reaction is run under aqueous condition. Among others the cyclopentane derivative **1a** is considerably more stable than **2a**, while the cycloheptane and cyclooctane derivatives **3a** and **4a** are moderately stable. The cyclododecane derivative **5a** is much more unstable than **1a**, **3a**, and **4a**, and it could be isolated only in very small amounts.

It is known that oximes react readily with NOCl to form *gem*-chloronitroso compounds and the mechanism has been worked out by Kyung and Clapp.¹⁸ The extraordinary ease with which the 1,2-dichloro-1-nitroso compounds **1c-5c** are produced clearly indicates that the oximes **1b-5b** are forming as intermediates, which react with NOCl to produce **1c-5c** (Scheme 5).

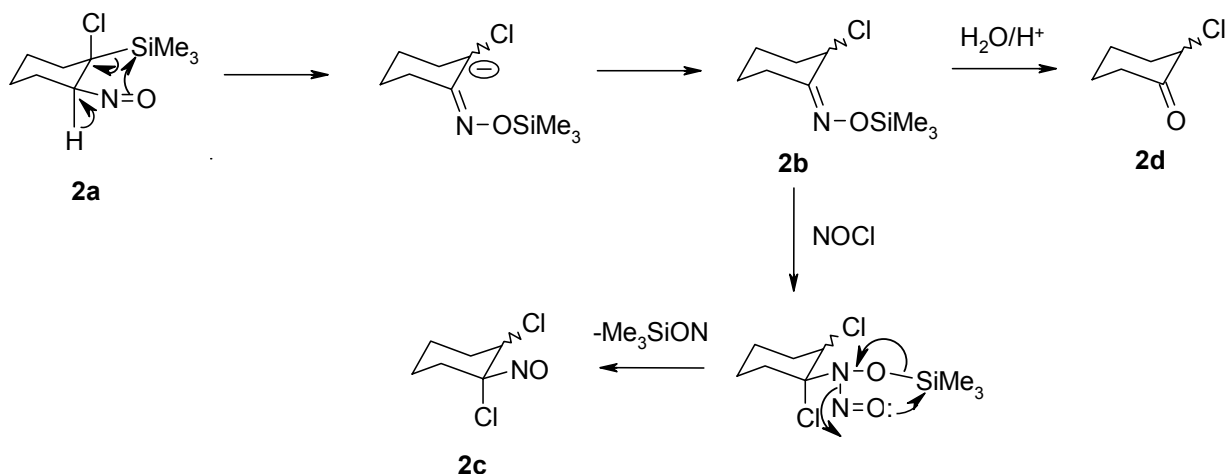


Scheme 5

We have isolated the oxime **4b** (R = H) in the reaction of NOCl with **4**. However, oximes **1b-3b** and **5b** were not detected. It should be noted that while the oxime **4b** has lost silicon at -10 °C, the oxime **6b** retained silicon even after acid catalyzed hydrolysis of **6a** at 50 °C. Since **6a** does not tautomerize during NOCl addition, it is clear that it does not give 2,3-dichloro-2-nitroso norbornane. The driving force for this effortless process of tautomerization of α -chloro- β -nitrososilanes **1a-5a**, we presume, is due to interaction of oxygen of nitroso group with silicon as shown for **2a**, in Scheme 6, when they are close enough for overlap of non-bonding electrons of oxygen with silicon *d* orbitals and are in contact for sufficient time to establish the O-Si bond. These factors are dependent upon the conformational characteristics of adducts **1a-6a**. Based on this concept, it is easy to understand why the norbornane derivative **6a** where NO and Me₃Si cannot come close enough is so remarkably stable as compared to other adducts **1a-5a**, especially **2a**, which could not even be detected. It is also easily understandable how the other α -chloro- β -nitrososilanes **1a**, and **3a-5a** show varying degrees of stability, which is ascribable to the considerable range of conformational flexibility of these ring systems.¹⁹

As has already been reported,⁸ the NOCl addition to cycloalkenyltrimethylsilanes leads to *cis* stereochemistry with Cl bonding to the α -carbon and NO to the β -carbon, which results in the Me₃Si and the NO groups adopting *trans* geometry. The most stable conformation of 1-trimethylsilyl-1-chloro-2-nitrosocyclohexane **2a** is very likely to be as shown in Scheme 6, with the Me₃Si and NO groups occupying *e,e-trans* position. This is a highly favourable geometrical setting for oxygen of NO to establish bond with silicon through the interaction of non-bonding

electrons with the empty *d* orbitals of silicon or C-Si σ^* orbital. This would lead to reorganization of various bonds to give eventually the oxime **2b**.

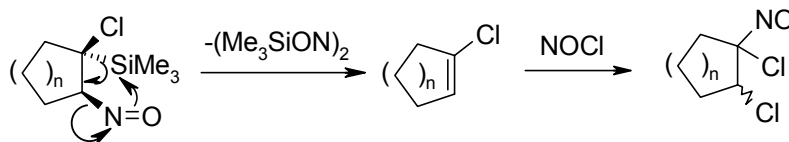


Scheme 6

Under aqueous acidic condition the oxime **2b** hydrolyzes to α -chloroketone **2d**. Thus the ease of formation of oxime from the monomeric adduct is directly related to the conformational diversity of the ring which would allow the two groups, NO and Me₃Si, to come together within an effective interacting distance. This argument explains why the norbornane derivative **6a** exhibits high stability, which is attributable to its rigidity that does not permit NO and Me₃Si to come close enough. It should also be noted that **6a** hydrolyzes to its oxime **6b** only under forced condition and that too without the loss of silicon (Scheme 4), indicating that silicon does not play any role in tautomerization of monomeric **6a**, which is similar to tautomerization of the unsilylated chloronitrosocycloalkanes **7-11**.

Because the five membered ring adduct **1a** has presumably half-chair conformation,²⁰ the separation between NO and Me₃Si here is probably midway between that in **2a** and **6a**. Hence it is far more stable than **2a**. Nevertheless, it tautomerizes smoothly as it can undergo some conformational changes. Since the other three α -chloro- β -nitrososilanes **3a-5a** have many more conformational possibilities,²⁰ the ease of interaction of NO and Me₃Si groups in these molecules is somewhere between **1a** and **2a**, and it is reflected in their reactivity relative to the other adducts, being that between **1a** and **2a**.

Mechanistically, the formation of the 1,2-dichloro-1-nitroso compounds **1c-5c** is also possible by the reaction of NOCl with 1-chlorocycloalkenes,⁷ which can in principle be formed as intermediates from the primary adducts of reaction as depicted in Scheme 7.



Scheme 7

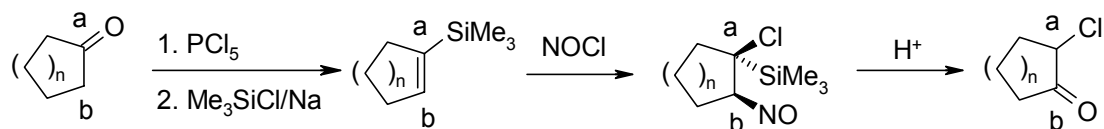
However, we have noted in separate control experiments that the addition of NOCl to 1-chlorocycloalkenes is very slow and usually incomplete even after 10 h, while 1-trimethylsilylcycloalkenes **1-5** react almost instantaneously to yield the 1,2-dichloro-1-nitroso compounds. Similar results have been observed by others in the addition of NOCl to 1-chloroolefins.²¹ Secondly, 1-chlorocycloalkenes have not been detected in our present work, which should have been possible in view of the fact that they add NOCl slowly. Thirdly, the oximes seem to react faster with NOCl than the starting 1-trimethylsilylcycloalkenes, as a result of which the former are difficult to be isolated or detected in the reaction. We succeeded in isolating the α -chlorocyclooctanone oxime (**4b**), but not its silylated analogue, from 1-trimethylsilylcyclooctene-NOCl reaction. It is worth mentioning here that twelve membered 1-trimethylsilylcyclododecene (**5**) is a mixture of *cis:trans* isomers in a ratio 48:52, and that *trans* isomer reacts relatively faster with NOCl than the *cis* isomer, as observed by the enrichment of *cis* vinylsilane in the un-reacted **5** when the molar ratio of NOCl is insufficient to consume **5** completely.

From these considerations it is clear that the preparation of 1,2-dichloro-1-nitroso compounds is best achieved by the reaction of vinylsilanes (and not vinylchlorides) with excess NOCl as it occurs under very mild conditions and gives excellent yields. 1,2-Dichloro-1-nitroso compounds are dark blue liquids that are sensitive to heat and light. Some of them dimerize below 0 °C to white crystalline solids. They are characterized with complete spectral data for the first time in the present work.

Regioselective 1,2-carbonyl migration

1,2-Carbonyl shift is a useful transformation in organic synthesis. Paquette and coworkers¹⁰ have achieved this by LAH reduction of α -silyl epoxides followed by oxidation-desilylation of the resulting β -silanols.

The reaction of NOCl with vinylsilanes described here provides a better alternative to achieve the same end with an additional chloro functional group in the α -position. Ketones can be converted by different methods to vinylsilanes, in which silicon would be bound to the carbonyl carbon of the ketone.²² Since the addition of NOCl is regioselective to form α -chloro- β -nitrososilane (as dimer) in high yield under solvent-free condition, the hydrolysis of the adduct leads to chloroketone product in which the new carbonyl function is placed on the carbon adjacent to the original keto carbon of the starting ketone (Scheme 8).



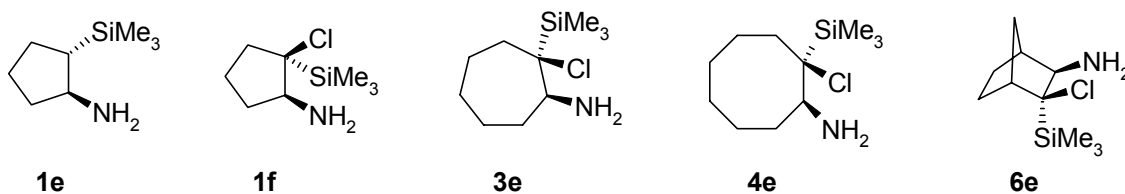
Scheme 8

This sequence offers a simple procedure for 1,2-transposition of a carbonyl group *via* vinylsilanes. Moreover, chlorine being introduced in the α -position, this provides an additional advantage of regioselectivity as α -chloroketones find many synthetic applications.⁴

β -Aminosilanes

The reduction of nitroso group in α -chloro- β -nitrososilanes **1a**, **3a**, **4a**, and **6a** can be easily accomplished with $\text{SnCl}_2\text{-HCl}$, but for the competing protodesilylation in the strong acid medium. Lithium aluminium hydride (LAH) was found to be the most suitable for reducing α -chloro- β -nitrososilanes **1a**, **3a**, **4a**, and **6a**. The LAH reduction when carried out at room temperature provided exclusively dechlorinated product **1e** in case of 2-chloro-1-nitroso-1-trimethylsilylcyclopentane (**1a**), while the other adducts **3a**, **4a**, and **6a** provided the β -aminosilanes **3e**, **4e** and **6e** respectively without chlorine being lost. However, the adduct **1a** when reduced at $-5\text{ }^\circ\text{C}$, provided a mixture of amines **1e** and **1f**. Surprisingly, reductive dechlorination, which usually occurs at reflux conditions was not observed for the adduct **6a** even when refluxed with excess LAH.

The amines **1e**, **1f**, **3e**, **4e** and **6e** obtained as viscous residues were characterized by converting them to suitable derivatives.



The amines **1e**, **1f**, and **6e** were converted to crystalline acetyl derivatives **1g**, **1h** and **6f** respectively.

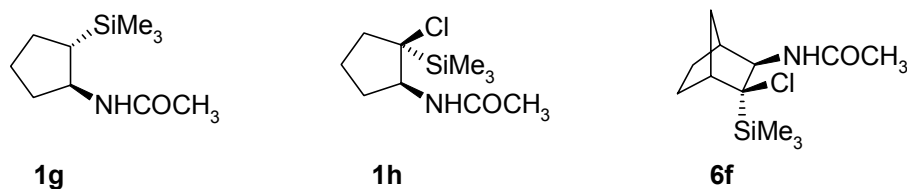


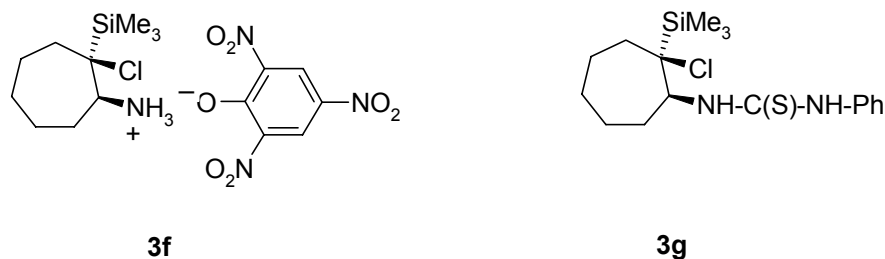
Table 4. LAH reduction of α -chloro- β -nitrososilanes **1a**, **3a**, **4a** and **6a**

α -chloro- β -nitrososilane	β -aminosilane	Temperature	Time ^a	Yield (%)
1a	1e	r.t	8 h	74
1a	1e + 1f	-5 °C	10 h	80
3a	3e	r.t	45 min	68
4a	4e	r.t	30 min	61
6a	6e	r.t	18 h	78

^a Time recorded for reduction of 10 mmol of α -chloro- β -nitrososilane

The investigation of IR spectrum of **1g**, **1h**, and **6f** reveal some interesting facts. While the NH stretching and bending vibrations in **1g** appear at 3297 and 1559 cm^{-1} , in both **1h** and **6f** they appear at 3266 and 1569 cm^{-1} . It is very much apparent that the absence of chlorine in **1g** makes the N-H bond different from what it is in **1h** and **6f**, which show the same values for the NH stretching and bending frequencies. Therefore, it would be difficult not to infer that the influence of chlorine on NH bond in **1h** and **6f** is the same in both. It is also noteworthy that carbonyl stretching in both **1h** and **6f** is at 1647 cm^{-1} , while it is at 1652 cm^{-1} in **1g**. Even NMR signals for NH proton in **1h** and **6f** are similar, with δ 5.27 and δ 5.38 respectively, while the NH proton signal for **1g** is at δ 6.05. With these data we presume that whatever geometrical correlation exists between NH and Cl in **6f** also exists in **1h**, which is obviously absent in **1g**.

The amine **3e** was converted to corresponding picrate **3f** and phenyl thiourea derivative **3g** as it did not form good acetyl derivative.



No suitable derivative of the amine **4e** could be made. However, **4e** was purified to about 99% by bulb-to-bulb distillation and characterized by its NMR and IR spectra.

As reported previously,⁸ the regio- and stereochemistry of addition in case of adducts **1a** and **6a** was established by single crystal X-ray diffraction studies. During this study, the reduction of α -chloro- β -nitrososilanes to corresponding amino derivatives, and characterization of their derivatives further established the reversal of regiochemistry. The appearance of the peak at 67.98 ppm as a signal from tertiary carbon atom in the ¹³C NMR DEPT spectrum of picrate **3f** is a clear indication of the fact that the chlorine atom and the Me₃Si group are on the same carbon in the precursor **3a**.

Crystal structure of the amide 6f

In our investigation of the single crystal X-ray structure²³ of the amide derivative **6f**, surprisingly we have not observed the $-C=O\dots H-N-$ interaction commonly found in amides.²⁴ Instead, a less common, $C-H\dots N$ intermolecular interaction²⁵ between the amide nitrogen and the methyl hydrogen was observed as depicted in Figure 1.

The donor-acceptor separation $C\dots N$ is 2.836 Å, and the $C-H\dots N$ angle is found to be 111.05°. Interestingly, the two molecules involved in the $C-H\dots N$ interaction are enantiomeric pairs, which is preserved throughout the crystal motif. In a bonding contact, the donor-proton-acceptor angle should be more than 90°, and when the angle is near or equal to 180°, it is called a linear contact. In the crystal structure of **6f**, the angle is well above the lower limit of 90°, but the contact is not quite linear.

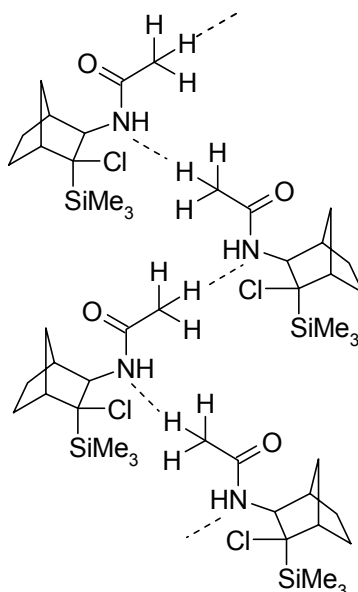


Figure 1

To our knowledge, this is the first observation of an amide having $C-H\dots N$ interaction in preference to the usual $N-H\dots O$ interactions, which is surprisingly absent in this structure. The participation of the hydrogen atoms attached to a methyl group in $C-H\dots O$ interaction is well documented in the literature.²⁶ However, the preferential bonding with nitrogen as an acceptor observed in this study is novel. The X-ray structure analysis also indicates intramolecular $C-H\dots Cl$ interaction between the *syn* hydrogen atom at the bridge methylene and the chlorine atom.

Conclusions

Not only the regioselectivity of NOCl addition to cycloalkenyltrimethylsilane, but also the further transformation of the resulting chloronitroso adduct to its tautomeric oxime is controlled by silicon through its interaction with β -nitroso group, which is dictated by the conformational mobility of the ring that allows the two interacting groups to approach within a favourable distance. The primary adducts can be further converted smoothly to 1,2-dichloro-1-nitroso derivatives in high yield, and this seems to be the best method for the preparation of these compounds. The dimeric adducts can be isolated under controlled and solvent free conditions, (the fact that the solvent is not needed indicates that this method is environmentally desirable,²⁷) and are easily hydrolysable to α -chloroketones, in which the keto function is shifted to the adjacent carbon and the chlorine is attached to the carbon of the original carbonyl carbon. This is a simple yet efficient method for regio controlled α -chloroketones from vinylsilanes. Further, the α -chloro- β -nitrososilanes serve as useful precursors to β -aminosilanes, which are novel class of compounds with potential synthetic utility.

Experimental Section

General Procedures. Melting points were determined by capillary method and are uncorrected. IR spectra ($400\text{-}4000\text{ cm}^{-1}$) were recorded in KBr pellets for solids and as thin film between NaCl plates for liquids on a Nicolet impact 400D single beam instrument. ^1H and ^{13}C NMR spectra were recorded at room temperature in $\text{CDCl}_3/\text{DMSO-d}_6$ solution and referenced to TMS (0 ppm) using a JEOL 300 MHz or Bruker AC-250 spectrometers. GC analysis was done on a Varian Vista 6000 instrument using 15% FFAP on chromosorb W column (2 m X 2 mm i.d). Elemental analyses were performed with a Carlo Erba 1160 instrument.

The starting cycloalkenyltrimethylsilanes **1-6** were synthesized according to known procedure.²⁸

General procedure for NOCl addition to cycloalkenyltrimethylsilanes 1-6

Method A. In a 50 mL two-necked flask, cycloalkenyltrimethylsilane (10 mmol) was cooled to $-10\text{ }^\circ\text{C}$ in an ice-salt bath. *iso*-Amylnitrite (12 mmol) and glacial acetic acid (1 mL) were introduced into the flask. The mixture was kept stirred magnetically at $-10\text{ }^\circ\text{C}$. A mixture of glacial acetic acid and conc HCl (3:1 v/v) was added slowly till the reaction was complete (as indicated by GC). Initially a greenish solution was formed which turned blue on further addition of NOCl. A white solid separated out from the blue solution was rapidly filtered, washed with cold ethanol (5 mL) and dried. The formation of white solid dimeric adduct was instantaneous for the vinylsilane **6**. For other vinylsilanes the formation of white solid took different lengths of time depending on factors like rate of addition of NOCl, and the rate of stirring. The best possible dimeric adduct yields and the reaction time are reported in Table 1. After filtering off the dimeric adduct, the blue coloured filtrate was diluted with water (10 mL), and extracted with

CH₂Cl₂. The extracts were washed with water, saturated NaHCO₃, and brine, dried over Na₂SO₄, filtered and concentrated. The residue was chromatographed on silica gel (60-120 mesh), first eluted with petroleum ether (40-60 °C) to give the 1,2-dichloro-1-nitrosocycloalkane as a blue liquid, followed by elution with 1% ethyl acetate in petroleum ether (40-60 °C) to give α -chloroketone as a colourless to pale yellow liquid. After chromatographing once more the 1,2-dichloro-1-nitrosocycloalkane was obtained in >99% purity.

Method B. In a 50 mL two-necked flask, a mixture of cycloalkenyltrimethylsilane (10 mmol) and *iso*-amyl nitrite (15 mmol) was cooled to -10 °C in an ice-salt bath. A freshly distilled sample of Me₃SiCl (15 mmol) was added slowly at a rate of 1 drop per 10 min with efficient stirring. After the reaction is complete (as indicated by GC), it was worked up as mentioned in method A above.

Method C. To a stirred solution of cycloalkenyltrimethylsilane (10 mmol) and *iso*-amyl nitrite (12 mmol) in 10 mL of dry CH₂Cl₂ was added Me₃SiCl (12 mmol) in dry CH₂Cl₂ (5 mL) at -10 °C. At the end of the reaction (as indicated by GC), the bluish-green solution was diluted with CH₂Cl₂ (15 mL) and transferred to a separatory funnel, washed with water, saturated NaHCO₃, water, brine, dried over Na₂SO₄, filtered and concentrated. The removal of solvent resulted in a white solid in the case of vinylsilane **6**. In other cases a greenish residue was obtained which was chromatographed on silica gel to isolate the blue coloured 1,2-dichloro-1-nitrosocycloalkane compound as described in method A above.

1a. mp 110-112 °C; ¹H NMR (CDCl₃) (dimer) δ : 0.1 (9H, s), 1.6-1.9 (3H, m), 2.18 (2H, m), 2.7 (1H, m), 5.81 (1H, t, $J=8.0$ Hz); ¹³C NMR (CDCl₃) (dimer) δ : -3.17, 21.17, 27.73, 38.76, 66.94, 69.68; IR (KBr, cm⁻¹) 2960, 2919, 1455, 1388, 1228, 1253, 1171, 845, 757; Anal. Calcd. for C₈H₁₆Cl₂NO: C, 46.70; H, 7.84; N, 6.81. Found: C, 46.71; H, 8.02; N, 6.83.

3a. mp 90-92 °C; ¹H NMR (CDCl₃), (monomer-dimer mixture in solution) δ : 0.16 (s), 0.19 (s) (together 9H), 1.57-1.96 (7H, m), 2.13-2.64 (3H, m), 4.33 (dd, $J=2.4, 1.8$ Hz, monomer), and 5.87 (dd, $J=2.1, 1.8$ Hz, dimer) (together 1H); IR (KBr, cm⁻¹) 2934, 2872, 1460, 1212, 1253, 1186, 850, 762; Anal. Calcd. for C₁₀H₂₀Cl₂NO: C, 51.37; H, 8.62; N, 5.99. Found: C, 51.43; H, 8.77; N, 6.17.

4a. mp 85-87 °C; ¹H NMR (CDCl₃), (monomer-dimer mixture in solution) δ : 0.15 (s), 0.25 (s) (together 9H), 1.5-1.9 (8H, m), 2.1-2.7 (4H, m), 4.6 (m, monomer) and 6.01 (m, dimer) (together 1H); IR (KBr, cm⁻¹) 2945, 2867, 1476, 1450, 1228, 1248, 1191, 845, 762; Anal. Calcd. for C₁₁H₂₂Cl₂NO: C, 53.31; H, 8.95; N, 5.65. Found: C, 53.32; H, 9.23; N, 5.92.

6a. mp 150-152 °C; ¹H NMR (CDCl₃) (dimer) δ : 0.3 (9H, s), 1.2-1.7 (5H, m), 2.5 (2H, m), 2.73 (1H, br. s), 4.93 (1H, s); ¹³C NMR (CDCl₃) (dimer) δ : -0.67, 25.59, 26.37, 38.08, 41.33, 50.43, 68.12, 74.88; IR (KBr, cm⁻¹) 2991, 2960, 2882, 1248, 1232, 839, 756; Anal. Calcd. for C₁₀H₁₈Cl₂NO: C, 51.82; H, 7.83; N, 6.04. Found: C, 51.97; H, 7.90; N, 6.16.

1c. mp 71-72 °C {lit.²¹ mp 69-70 °C}; ¹H NMR (CDCl₃) δ : 2.0-2.3 (2H, m), 2.48 (1H, m), 2.63 (1H, m), 2.85 (2H, m), 4.72 (1H, t, $J=6.6$ Hz); ¹³C NMR (CDCl₃) δ : 21.44, 34.67, 35.21, 66.08, 118.43; IR (KBr, cm⁻¹) 3069, 2986, 2960, 2898, 1434, 1316, 1279, 1233, 1078, 964, 897, 788, 674; Anal. Calcd. for C₅H₇Cl₂NO: C, 35.74; H, 4.20; N, 8.34. Found: C, 35.48; H, 3.97; N, 8.08.

2c. Blue liquid; ^1H NMR (CDCl_3) δ : 1.63-2.10 (6H, m), 2.48-2.72 (2H, m), 5.1 (1H, $J=1.8, 3.3$ Hz); ^{13}C NMR (CDCl_3) δ : 21.08, 21.84, 31.01, 31.91, 61.10, 109.18; IR (neat, cm^{-1}) 2950, 2867, 1590, 1574, 1455, 855, 710, 643; Anal. Calcd. for $\text{C}_6\text{H}_9\text{Cl}_2\text{NO}$: C, 39.59; H, 4.98; N, 7.69. Found: C, 39.79; H, 4.77; N, 7.75.

3c. Blue liquid; ^1H NMR (CDCl_3) δ : 1.55-2.10 (6H, m), 2.31-2.82 (4H, m), 5.08 (1H, m); ^{13}C NMR (CDCl_3) δ : 21.49, 24.36, 26.99, 31.18, 33.47, 64.82, 113.58; IR (neat, cm^{-1}) 2940, 2867, 1574, 1460, 1352, 1279, 876, 855, 622; Anal. Calcd. for $\text{C}_7\text{H}_{11}\text{Cl}_2\text{NO}$: C, 42.88; H, 5.65; N, 7.14. Found: C, 42.67; H, 5.56; N, 7.01.

4c. Blue liquid; ^1H NMR (CDCl_3) δ : 1.56-2.10 (8H, m), 2.19-2.82 (4H, m), 5.09 (1H, m); IR (neat, cm^{-1}) 2929, 2857, 1574, 1455, 1336, 757; Anal. Calcd. for $\text{C}_8\text{H}_{13}\text{Cl}_2\text{NO}$: C, 45.73; H, 6.24; N, 6.67. Found: C, 46.03; H, 6.20; N, 6.81.

5c. mp 58-60 $^\circ\text{C}$; ^1H NMR (CDCl_3) δ : 1.4-1.6 (12H, m), 2.2-2.6 (6H, m), 3.25 (2H, m), 4.68 (1H, d, $J=10.8$ Hz); ^{13}C NMR (CDCl_3) δ : 19.96, 21.35, 22.58, 22.64, 22.77, 24.77, 25.47, 25.84, 30.51, 32.27, 66.32, 112.12; IR (neat, cm^{-1}) 2940, 2867, 1584, 1564, 1471, 1445, 1352, 731, 540; Anal. Calcd. for $\text{C}_{12}\text{H}_{21}\text{Cl}_2\text{NO}$: C, 54.14; H, 7.95; N, 5.26. Found: C, 53.98; H, 8.02; N, 5.02.

1d. bp 55-56 $^\circ\text{C}$ /3 Torr {lit.^{4, 17, 29} 87-90 $^\circ\text{C}$ /23 Torr}; ^1H NMR (CDCl_3) δ : 1.9-2.4 (6H, m); 4.15 (1H, t, $J=7.2$ Hz); IR (neat, cm^{-1}) 2966, 2924, 1755, 1155, 959, 684.

2d. bp 79-81 $^\circ\text{C}$ /10 Torr {lit.^{4, 17, 29} 77-80 $^\circ\text{C}$ /10 Torr}; ^1H NMR (CDCl_3) δ : 1.7-2.5 (8H, m), 4.4 (1H, m); IR (neat, cm^{-1}) 2950, 2867, 1729, 1450, 1264, 1067, 721.

3d. bp 85-87 $^\circ\text{C}$ /6 Torr {lit.^{4, 17, 29} 109-111 $^\circ\text{C}$ /27 Torr}; ^1H NMR (CDCl_3) δ : 1.5-2.1 (8H, m), 2.4-2.6 (2H, m), 5.0 (1H, t, $J=5.1$ Hz); IR (neat, cm^{-1}) 2945, 2867, 1714, 1455, 767, 659.

4d. bp 65-67 $^\circ\text{C}$ /1 Torr {lit.^{4, 29} 72-74 $^\circ\text{C}$ /3 Torr}; ^1H NMR (CDCl_3) δ : 1.6-2.2 (10H, m), 2.5-2.8 (2H, m), 4.7 (1H, t, $J=7.7$ Hz); IR (neat, cm^{-1}) 2940, 2862, 1710, 1455, 1264, 762.

5d. mp 41-42 $^\circ\text{C}$ {lit.^{4, 29} bp 114-117 $^\circ\text{C}$ /2 Torr}; ^1H NMR (CDCl_3) δ : 1.25 (18H, m), 2.0 (2H, m), 2.7 (2H, m), 4.25 (1H, dd); ^{13}C NMR (CDCl_3) δ : 21.51, 21.71, 22.03, 22.68, 23.11, 23.62, 25.52, 25.57, 32.94, 34.01, 62.64, 205.53; IR (KBr, cm^{-1}) 2934, 2867, 1719, 1476, 1450, 747.

Levulinic acid hydrolysis

A mixture of 5 mmol of the dimer **6a** and 20 mmol of levulinic acid in 5 mL of 2N HCl and 20 mL of dioxane was stirred at 50 $^\circ\text{C}$ for 3 h till a clear solution was formed. After the hydrolysis was complete, the mixture was diluted with water (50 mL), and extracted into ether (4 x 25 mL). The combined ether layers were washed with water, saturated NaHCO_3 , water, and brine, dried over Na_2SO_4 . After removing the solvent, the residue obtained was a mixture of white solid and traces of pale yellow liquid. Petroleum ether 40-60 $^\circ\text{C}$ (10 mL) was added to the residue, the white solid was filtered off, washed with petroleum ether (3 x 10 mL) to give crude oxime **6b** (88%), which was further purified by recrystallization from ethanol-water (3:1) mixture. The combined filtrate was evaporated to give *exo*-chloronorcamphor **6d** (10%).

By heating to 75 $^\circ\text{C}$ for 5 h the dimer **6a** was completely converted to *exo*-chloronorcamphor (**6d**).

Similarly, by following the above procedure, the hydrolysis of other dimers **1a**, **3a**, and **4a** was carried out at room temperature to give the α -chloroketones **1d**, **3d**, and **4d** respectively.

6b: mp 132-134 °C; ^1H NMR (CDCl_3) δ : 0.15 (9H, s), 1.23-1.80 (5H, m), 2.13 (1H, m), 2.4 (1H, d, $J=3.0$ Hz), 3.5 (1H, d, $J=2.4$ Hz), 7.1 (1H, s); ^{13}C NMR (CDCl_3) δ : -2.41, 23.01, 24.65, 36.06, 37.49, 46.01, 74.06, 171.71; IR (neat, cm^{-1}) 3380, 3240, 2960, 2882, 1672, 1440, 1253, 840, 757.

6d: bp 100 °C /10 Torr {lit.³⁰ 87-89 °C /4.5 Torr}; ^1H NMR (CDCl_3) δ : 1.3-2.4 (6H, m); 2.7 (2H, m), 3.6 (1H, s); IR (KBr, cm^{-1}) 2980, 2880, 1760, 1450, 1300, 940, 750, 690, 650.

General procedure for LAH reduction

To a stirred solution of LAH (12.5 mmol) in 50 mL dry ether was added a solution of the α -chloro- β -nitrososilane (10 mmol) in 25 mL dry ether over a period of 30 min. The stirring was continued for different lengths of time (Table 4) till the completion of the reduction. The supernatant liquid was transferred to a conical flask, and the residue was washed with dry ether. The combined ether layers were washed with water and the β -aminosilane was extracted into 10% HCl. The HCl extract was neutralized with 20% NaHCO_3 and the free amine was extracted back into ether. The ether layer was washed with water, brine, dried over Na_2SO_4 , and distilled out to obtain the β -aminosilane as a thick viscous liquid, which was converted to suitable derivative as described below.

Acetyl derivative 1g. The β -aminosilane **1e** (5 mmol) was treated with 1 mL of freshly distilled acetic anhydride at 10 °C. After shaking the mixture for 15 min, the excess acetic anhydride was destroyed by adding hot water and heating to 50 °C for 15 min. The acetyl derivative **1g**, which crystallized out upon cooling to room temperature, was purified by recrystallization from ethanol-water (60: 40) mixture.

1g: mp 124-126 °C; ^1H NMR (CDCl_3) δ : 0.02 (9H, s), 1.3-1.8 (7H, m), 1.96 (3H, s), 4.55 (1H, m), 5.27 (NH, br. s); ^{13}C NMR (CDCl_3) δ : -1.66, 23.69, 23.95, 26.15, 32.45, 35.59, 53.26, 168.65; IR (KBr, cm^{-1}) 3297, 3090, 2966, 2878, 1652, 1559, 1372, 1295, 1259, 1145, 845, 762; Anal. Calcd. for $\text{C}_{10}\text{H}_{21}\text{NOSi}$: C, 60.25; H, 10.62; N, 7.03. Found: C, 60.06; H, 10.82; N, 6.74.

Acetyl derivative 1h. The mixture of β -aminosilanes **1e** and **1f** (5 mmol) obtained from the LAH reduction of **1a** at -5 °C was treated with 1 mL of freshly distilled acetic anhydride at 10 °C. After shaking the mixture for 15 min, the excess acetic anhydride was destroyed by adding hot water and heating to 50 °C for 15 min. The acetyl derivatives **1g** and **1h**, which crystallized out upon cooling to room temperature, were separated by fractional crystallization from ethanol-water (60: 40) mixture. The acetyl derivative **1g** crystallized out first.

1h: mp 104-106 °C; ^1H NMR (CDCl_3) δ : 0.17 (9H, s), 1.23-1.61 (5H, m), 1.97 (3H, s), 4.05 (1H, m), 6.05 (NH, br.s); ^{13}C NMR (CDCl_3) δ : -1.78, 23.30, 24.86, 26.85, 36.41, 56.56, 74.69, 168.61; IR (KBr, cm^{-1}) 3266, 3084, 2971, 2971, 1893, 1636, 1564, 1383, 1248, 1171, 902, 860, 752, 622; Anal. Calcd. for $\text{C}_{10}\text{H}_{20}\text{ClNOSi}$: C, 51.37; H, 8.62; N, 5.99. Found: C, 51.49; H, 8.54; N, 5.70.

Acetyl derivative 6f. The β -aminosilane **6e** (5 mmol) was treated with 1 mL of freshly distilled acetic anhydride at 10 °C. After shaking the mixture for 15 min, the excess acetic anhydride was

destroyed by adding hot water and heating to 50 °C for 15 min. The acetic acid formed was neutralized with 20% NaHCO₃, and the acetyl derivative was extracted into ether. The ether layer was washed with water and dried over Na₂SO₄ and concentrated to obtain the crude acetyl derivative **6f**, which was purified by crystallization from ethanol-water (60: 40) mixture.

6f. mp 77-79 °C; ¹H NMR (CDCl₃) δ: 0.018 (9H, s), 1.2-1.7 (4H, m), 1.91 (3H, s), 2.14 (1H, m), 2.45 (1H, m), 4.06 (1H, m), 5.38 (NH, br. s); ¹³C NMR (CDCl₃) δ: -1.79, 23.38, 24.85, 26.84, 36.41, 44.39, 50.33, 56.59, 74.68, 168.73; IR (KBr, cm⁻¹) 3266, 3079, 2971, 2883, 1647, 1569, 1378, 1253, 1171, 850, 757; Anal. Calcd. for C₁₂H₂₂CINOSi: C, 55.47; H, 8.53; N, 5.39. Found: C, 55.50; H, 8.72; N, 5.10.

Crystal data for **6f**: C₁₂H₂₂CINOSi, *M* = 259.85, orthorhombic, *a* = 9.480(3) Å, *b* = 20.931(2) Å, *c* = 7.699(3) Å, α = 90°, β = 90°, γ = 90°, *U* = 1527.7(7) Å³, *T* = 293 K, space group *Pna*2₁, *Z* = 4, μ = 0.312 mm⁻¹, 2157 reflections measured, 2157 independent reflections (*R*_{int} = 0.0000), final *R* value [*I* > 2σ(*I*)] = 0.0735, *wR*(*F*²) = 0.2180, *R* (all data) = 0.1557, *wR*(*F*²) = 0.2956.

Picrate 3f. 5 mmol crude β-aminosilane **3e** was dissolved in 2 mL of 10% HCl. A saturated solution of picric acid (2 mL) was added slowly to obtain a yellow precipitate, which was filtered, and purified by crystallization from toluene.

3f. mp 192-196 °C; ¹H NMR (DMSO-*d*₆) δ: 0.19 (9H, s), 1.31-1.53 (11H, m), 3.17 (1H, br.s), 3.46 (1H, br. s), 7.62 (1H, br. s), 8.38 (2H, s); ¹³C NMR (DMSO-*d*₆) δ: -2.722, 21.78, 21.88, 26.40, 28.81, 35.86, 55.58, 67.98, 124.04, 125.10, 141.75, 160.69; IR (KBr, cm⁻¹) 3306, 2955, 2873, 1608, 1588, 1572, 1548, 1368, 1328, 1284, 1268, 1172, 1080, 848, 799, 755, 715; Anal. Calcd. for C₁₀H₂₂CINSi.C₆H₃N₃O₇: C, 42.81; H, 5.61; N, 12.48. Found: C, 42.74; H, 5.51; N, 12.74.

Phenylthiourea derivative 3g. 5 mmol of crude β-aminosilane **3e** dissolved in ethanol (1 mL) was treated with phenylisothiocyanate (1 mL) at 60 °C. The reaction mixture was cooled to 0 °C to crystallize out the phenylthiourea derivative **3g**, which was purified by recrystallization from ethanol.

3g. mp 108-110 °C; ¹H NMR (CDCl₃) δ: 0.19 (9H, s), 1.19-2.14 (11H, m), 2.77 (NH, s), 7.1-7.4 (5H, m), 7.90 (NH, s); IR (KBr, cm⁻¹) 3147, 3038, 2955, 2924, 2857, 1600, 1522, 1450, 1253, 1181, 1103, 850, 757, 700; Anal. Calcd. for C₁₇H₂₇CIN₂SSi: C, 57.51; H, 7.67; N, 7.89. Found: C, 57.81; H, 7.72; N, 8.11.

4e. Pale yellow viscous oil; ¹H NMR (CDCl₃) δ: 0.07 (9H, s), 1.48-1.80 (10H, m), 2.28 (2H, m), 2.42 (1H, m); ¹³C NMR (CDCl₃) δ: 0.72, 24.08, 24.31, 27.31, 29.26, 30.09, 33.51, 43.59, 66.63; IR (neat, cm⁻¹) 3421, 2934, 2857, 1626, 1476, 1450, 1259, 850, 757.

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