Addition of NOCl to cyclic vinylsilanes: an unexpected reversal of regiochemistry

M. Narendra Mallya,[a] Gopalpur Nagendrappa,[a,*] J. Shashidhara Prasad,[b] M. A. Sridhar,[b] N. K. Lokanath[b] and N. S. Begum[a]

[a]*Department of Chemistry, Bangalore University (Central College Campus), 560 001 Bangalore, India*
[b]*Department of Physics, University of Mysore, Manasagangotri, 570 006 Mysore, India*

Abstract—NOCl adds to cyclic vinylsilanes in a *syn* manner with NO^+ bonding to the β-carbon and Cl^- to the α-carbon, which is a reversal of the regiochemistry expected from the β-silicon effect. The adducts dimerize to a single diastereomer containing enantiomeric pairs and/or give secondary products on further reaction. © 2001 Elsevier Science Ltd. All rights reserved.
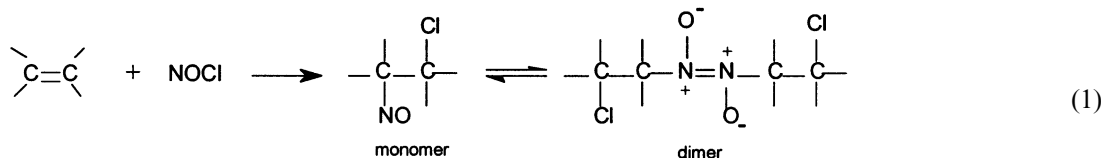
Electrophilic addition and substitution reactions of vinylsilanes are valuable in organic synthesis. An important aspect of the chemistry involved in these reactions is the high degree of predictability of their stereo- and regiochemical outcome arising from the β-silicon effect.[1]

Electrophilic addition of NOCl to an olefin (Eq. (1)) is a well studied reaction and is known to follow Markovnikov's mode of regiochemistry.[2,3] Considerable theoretical and experimental work has been recently directed to the study of the structure of NOCl and related molecules.[4] Our work on NOCl addition to cyclic vinylsilanes has yielded interesting results in the context of the directing influence of silicon on stereo- and regiochemistry, which are reported here.

The cyclic vinylsilanes **1**–**6** were employed for the present study. Different reaction conditions and various sources of NOCl were tried. The best yields of the chloronitroso adducts, **7** and **9**–**12** isolated as dimers, were obtained when NOCl was generated in situ by the reaction of isoamylnitrite (AmONO) with chloro-trimethylsilane (TMSCl) without solvent.[5,6] In addition,
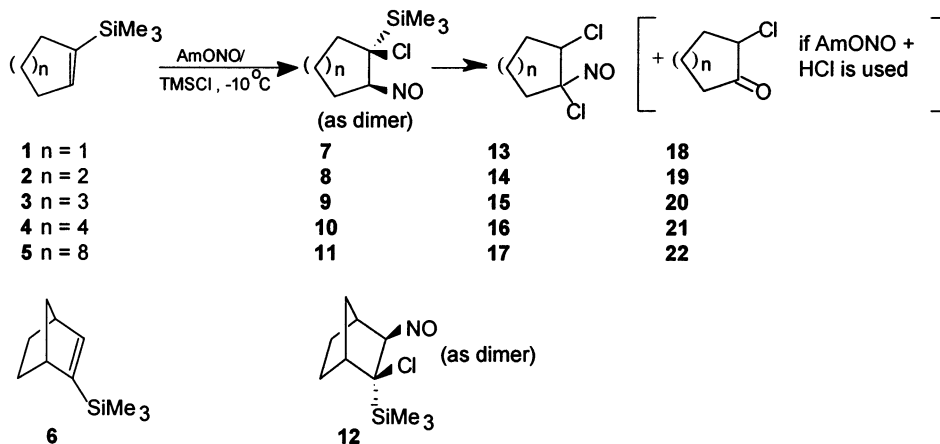
secondary products **13**–**17** were formed in some measure (Scheme 1). The results are summarized in Table 1. A higher proportion of the secondary products were isolated when solvents were used. Chloroketones **18**–**22** were also observed if NOCl was generated under aqueous conditions, e.g. AmONO+conc. HCl+AcOH. Vinylsilane **6** gave compound **12** alone while **2** gave only secondary products under all conditions.

The structures of **7** and **12** were established by single crystal X-ray analysis (Figs. 1 and 2). The NO and Cl groups are *cis* in both **7** and **12** with Cl on the α-carbon and NO on the β-carbon, and in **12** they are in the *exo* position (see ORTEP diagrams). It is interesting to note that both **7** and **12** crystallized out as a single diastereomeric dimer consisting of a pair of enantiomers (1*R*,2*S*-2*R*,1*S* pair in the case of **7** and 2*R*,3*S*-3*R*,2*S* pair in the case of **12**) with a center of symmetry passing through the N=N bond. The other two possible diastereomers (1*R*,2*S*-2*S*,1*R* and 1*S*,2*R*-2*R*,1*S* in the case of **7**, and 2*S*,3*R*-3*R*,2*S* and 2*R*,3*S*-3*S*,2*R* in the case of **12**) are not formed in either case. Thus, there is a type of molecular recognition in this dimer formation. The other adducts, **9**–**11**, did not give crystals suitable

$$\text{C=C} + NOCl \longrightarrow -\overset{|}{\underset{NO}{C}}-\overset{Cl}{\underset{|}{C}}- \rightleftharpoons -\overset{|}{\underset{Cl}{C}}-\overset{|}{C}-\overset{O^-}{\underset{+}{N}}=\overset{+}{\underset{O^-}{N}}-\overset{|}{C}-\overset{Cl}{\underset{|}{C}}-$$

monomer   dimer

(1)

Scheme 1.

Table 1. NOCl addition to cyclic vinylsilanes **1–6**

Vinylsilane	Products[a] (% yield)	
1	**7** (52)	**13** (40)
2	**8** (–)	**14** (85)
3	**9** (65)	**15** (30)
4	**10** (75)	**16** (25)
5[b]	**11** (8)	**17** (75)
6	**12** (96)	–

[a] The product distribution given here is only for the procedure reported in Ref. 6.

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

for X-ray analysis and the stereochemistry could not be proven in these cases. However, similarities in their NMR spectra[7] indicated that the regiochemistry is likely to be the same with Cl and NO groups in α- and β-positions, respectively.

A striking feature of the addition is the regioselectivity, which is the reverse of that expected from the polarity of NOCl and the β-silicon effect. NOCl has been shown by extensive theoretical and experimental work to be reasonably ionic with NO bearing the positive charge and chlorine the negative charge.[4] Electrophilic addition and substitution reactions of vinylsilanes have been found to be such that the electrophile mostly attacks the α-carbon, due to β-cation stabilization by silicon, provided the geometric requirement is fulfilled. However, electronic effects caused by other substituents or steric factors can reverse this trend.[1] Addition of ICl, IOMe, IN$_3$ and other reagents[8–10] are found to conform to this regioselectivity model in which positive and negative segments of the reagents add to α- and β-carbons, respectively. We have observed the same pattern in the nitration of **1–6** where NO$_2^+$ attacks the α-carbon.[11] Therefore, the NO$^+$ group adding to the β-carbon and Cl$^-$ to the α-carbon in the present study is rather unusual.
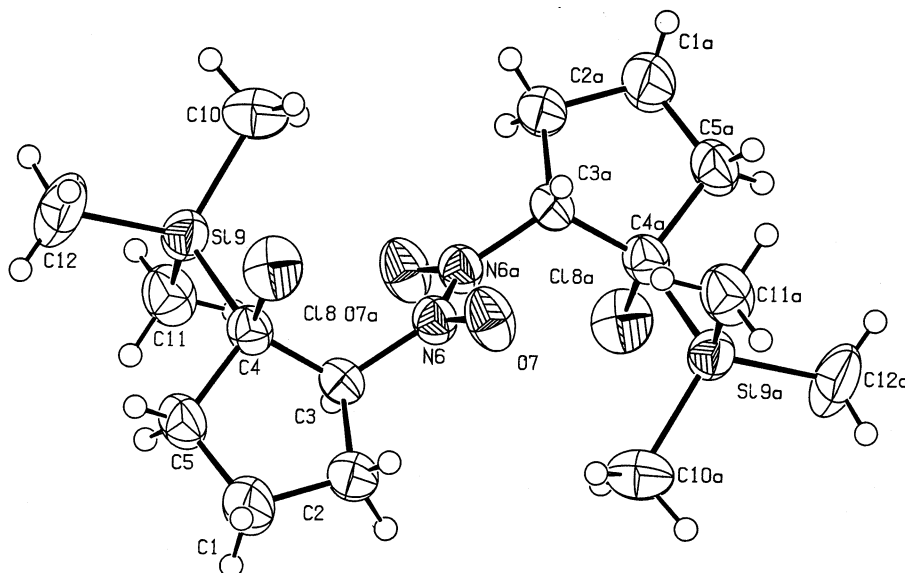

Figure 1. Crystal data for **7**: C$_8$H$_{16}$ClNOSi, $M = 205.78$, monoclinic, $a = 9.0610(8)$, $b = 11.2500(12)$, $c = 10.826(3)$ Å, $\alpha = 90$, $\beta = 95.344(13)$, $\gamma = 90°$, $U = 1098.8(3)$ Å^3, $T = 293$ K, space group $P2_1/n$, $Z = 4$, $\mu = 0.416$ mm^{-1}, 1353 reflections measured, 1343 independent reflections ($R_{int} = 2.7001$), final R value [$I > 2\sigma(I)$] = 0.0388, R (all data) = 0.0546, $wR(F^2) = 0.1321$; selected bond lengths: C–N = 1.490(3) Å, N–N = 1.326(4) Å, N–O = 1.259(3) Å.
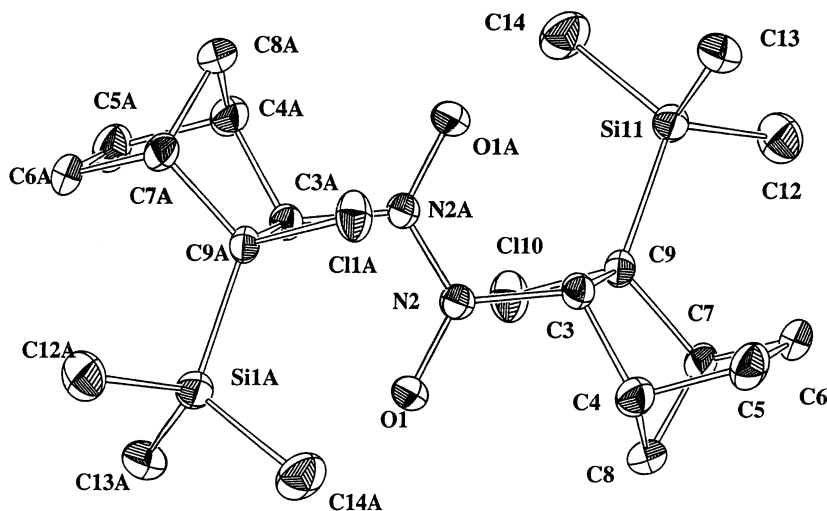
Figure 2. Crystal data for **12**: $C_{10}H_{18}ClNOSi$, $M = 231.79$, monoclinic, $a = 6.681(8)$, $b = 14.689(2)$, $c = 12.596(2)$ Å, $\alpha = 90$, $\beta = 104.09$, $\gamma = 90$, $U = 1199.0(3)$ Å^3, $T = 293$ K, space group $P2_1/c$, $Z = 4$, $\mu = 0.389$ mm^{-1}, 2289 reflections measured, 2097 independent reflections ($R_{int} = 0.0459$), final R value $[I > 2\sigma(I)] = 0.0304$, R (all data) $= 0.0339$, $wR(F^2) = 0.0736$; selected bond lengths: C–N $= 1.478(2)$ Å, N–N $= 1.312(3)$ Å, N–O $= 1.267(2)$ Å.

It has not been easy to rationalize the regiochemical outcome. One explanation that we consider to have some merit is the following. If NOCl approaches the double bond with NO approaching the α-carbon, the positively charged oxygen would be spatially close to the electropositive silicon **24**, which possibly causes a repulsive effect between the two atoms, either because of orbital interactions or of electronegativity effects or both. This can offset the delicately balanced stabilizing effect of silicon on the incipient β-cation. However, in **23** in which NO is turned away from Si, this repulsion is absent or diminished. Another plausible explanation[12] could be a weak Lewis acid effect of silicon, i.e. formation of an ON···Cl···Si complex, in which 'ion-pairing' of the SiCl complex and the cyclic

9–11 give the secondary products when treated with NOCl. We have been able to isolate chlorooxime **26** from **10** under aqueous conditions. The adduct **12** also produced the oxime **27** but only when heated to 50°C in dioxane containing levulinic acid and HCl.
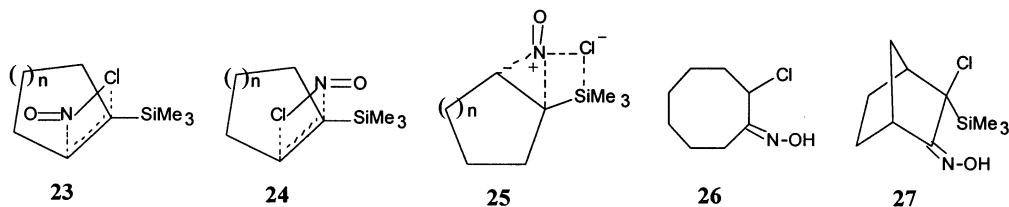
nitrosonium ion **25** may: (a) stabilize the intermediate; (b) direct the chloride ion from the same side as the NO, as well as to the α-position. Although NOCl addition to olefins is found to be *trans* in most cases, *cis* addition is not unknown. It is reported that norbornene and some of its derivatives give only *exo,cis* adducts.[13] In these cases the authors have proposed a four-centered cyclic transition state and the same mechanism may be involved in our case.

The formation of dichloronitroso compounds **13–17** is a consequence of isomerization of the primary adducts to the respective α-chlorooximes which are known to produce dichloronitroso compounds when treated with NOCl or hydrolyze to chloroketones if water is present.[14,15] We have confirmed that the dimers **7** and

References

1. (a) Chiavarino, B.; Crestoni, M. E.; Fornarini, S. *J. Am. Chem. Soc.* **1998**, *120*, 1523; (b) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677; (c) Fleming, I.; Barbero, A.; Walter, D. *Chem. Rev.* **1997**, *97*, 2063; (d) Nagendrappa, G.; Begum, N. S. *Tetrahedron* **1999**, *55*, 7923 and references cited therein.
2. (a) Freeman, F. *Chem. Rev.* **1975**, *75*, 471; (b) Kadzyauskas, P. P.; Zefirov, N. S. *Russian Chem. Rev.* **1968**, 543.
3. Glasser, R.; Murmann, R. K.; Barnes, C. L. *J. Org. Chem.* **1996**, *61*, 1047.
4. (a) Gatehouse, B.; Muller, H. S. P.; Heineking, N.; Gerry, M. C. L. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 347; (b) Meredith, C.; Quelch, G. E.; Schaefer, III, S. F. *J. Chem. Phys.* **1992**, *96*, 480.

5. For the generation of NOCl using TMSCl and organic or inorganic nitrites, see: (a) Weiß, R.; Wagner, K. G.; Hertel, M. *Chem. Ber.* **1984**, *117*, 1965; (b) Haub, K. E.; Lizano, A. C.; Noble, M. E. *Inorg. Chem.* **1995**, *34*, 1440.

6. Brief experimental procedure: A well-stirred mixture of cyclic vinylsilane (10 mmol) and *iso*-amylnitrite (12.5 mmol) at −15°C was treated dropwise with TMSCl (12.5 mmol). After the disappearance of the vinylsilane (monitored by GC), the solid dimeric primary adduct formed was filtered rapidly, washed with cold ethanol (5 mL) and dried. The filtrate was worked up in the usual manner and the secondary products were separated by silica gel chromatography (dichloronitroso compounds were eluted with pure petroleum ether, bp 40–60°C and α-chloroketones formed in aqueous conditions were eluted with 1% ethyl acetate in petroleum ether). All new compounds were characterized by satisfactory elemental analysis and spectral data. The known products were identified by comparing their properties with those reported in the literature and in many cases with authentic compounds prepared from known procedures.

7. Selected characterization data (NMR spectra were taken in $CDCl_3$). Compound **7**: mp 110–112°C. ^{1}H NMR (dimer): δ 5.81 (t, $J = 8.0$ Hz, 1H), 2.7 (m, 1H), 2.18 (m, 2H), 1.6–1.9 (m, 3H), 0.1 (s, 9H). ^{13}C NMR: δ 69.68, 66.94, 38.76, 27.73, 21.17, −3.17. Anal. calcd for $C_8H_{16}ClNOSi$: C, 46.70; H, 7.84; N, 6.81. Found: C, 46.71; H, 8.12; N, 6.83. Compound **9**: mp 90–92°C. ^{1}H NMR (monomer–dimer mixture in solution): δ 5.87 (dd, $J = 1.8$ Hz, 2.1 Hz, dimer), 4.33 (dd, $J = 2.4$ Hz, 1.8 Hz, monomer) (together 1H), 2.13–2.64 (m, 3H), 1.57–1.96 (m, 7H), 0.19 (s), 0.16 (s) (together 9H). Anal. calcd for $C_{10}H_{20}ClNOSi$: C, 51.48; H, 8.65; N, 6.01. Found: C, 51.43; H, 8.77; N, 6.17. Compound **10**: mp 85–87°C. ^{1}H NMR (monomer–dimer mixture in solution): δ 6.01 (m, dimer), 4.6 (m, monomer) (together 1H), 2.1–2.7 (m, 4H), 1.5–1.9 (m, 8H), 0.25 (s), 0.15 (s) (together 9H). Anal. calcd for $C_{11}H_{22}ClNOSi$: C, 53.31; H, 8.95; N, 5.65. Found: C, 53.32; H, 9.23; N, 5.92. Compound **11** could not be fully characterized because of its poor yield and difficulty in its purification. Compound **12**: mp 150–152°C. ^{1}H NMR (dimer): δ 4.93 (s, 1H), 2.73 (broad s, 1H), 2.5 (m, 2H), 1.2–1.7 (m, 5H), 0.3 (s, 9H). ^{13}C NMR: δ 74.88, 68.12, 50.43, 41.33, 38.08, 26.37, 25.59, −0.67. Anal. calcd for $C_{10}H_{18}ClNOSi$: C, 51.95; H, 7.79; N, 6.06. Found: C, 51.97; H, 7.90; N, 6.16.

8. (a) Duboudin, F. *J. Organomet. Chem.* **1979**, *174*, C18–C20; (b) Grayson, E. J.; Whitham, G. H. *Tetrahedron* **1988**, *44*, 4087.

9. Seyferth, D.; Kahlen, N. *Z. Naturforsch.* **1959**, *14b*, 137.

10. Cook, E.; Moerck, R.; Schwindeman, J.; Magnus, P. *J. Org. Chem.* **1980**, *45*, 1046.

11. Patil, G. S.; Nagendrappa, G. *Chem. Commun.* **1999**, 1079.

12. The authors thank the referee for this suggestion.

13. (a) Meinwald, J.; Meinwald, Y. C.; Baker, T. N. *J. Am. Chem. Soc.* **1964**, *86*, 4074; (b) Brown, H. C.; Kawakami, J. H.; Liu, K. T. *J. Am. Chem. Soc.* **1973**, *95*, 2209; (c) Nelson, D. J. *Tetrahedron Lett.* **1999**, *40*, 5823.

14. Kyung, J. H.; Clappa, L. B. *J. Org. Chem.* **1976**, *41*, 2024.

15. Ponder, B. W.; Walker, D. R. *J. Org. Chem.* **1967**, *32*, 4136.