Reaction of a Stable Silylene–Isocyanide Complex with Nitrile Oxides: A New Approach to the Generation of a Silanone

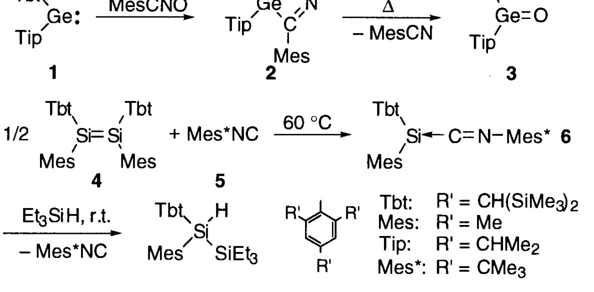
Nobuhiro Takeda, Norihiro Tokitoh,* and Renji Okazaki*†#
Institute for Fundamental Research of Organic Chemistry, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581
†Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033

(Received November 29, 1999; CL-991010)

An overcrowded silanone [Tbt(Mes)Si=O; Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Mes = mesityl] (**8**) was generated via intermediary 1,2,4-oxazasiletes by the reaction of a stable silylene–isocyanide complex with nitrile oxides. In a THF solution, silanone **8** underwent intramolecular cyclization with migration of a trimethylsilyl group in Tbt group to the oxygen atom of the Si=O double bond.

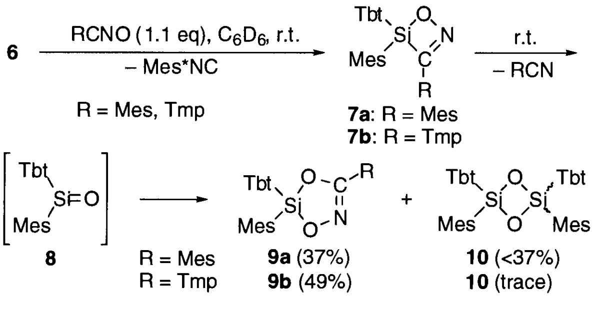
Silanones, silicon–oxygen double-bond compounds, have been postulated as intermediates in a variety of reactions of organosilicon compounds, and its chemistry has been extensively studied in recent decades.[1] Although observation of a few transient silanones in low temperature matrices by IR spectroscopy and several chemical trapping experiments of intermediary silanones have already been reported,[1] no stable silanones have been isolated so far. The absence of stable silanones is probably due to the lack of a suitable synthetic method for the isolation of stable silanones as well as to the difficulty in stabilizing the highly reactive silicon–oxygen double bond. Since transient silanones are usually generated under severe conditions such as thermolysis at high temperature or photolysis, it is desirable to develop a new method for the isolation of stable silanones under much milder reaction conditions.

We have already succeeded in the synthesis of novel double-bond compounds between group 14 metals and group 16 elements, Tbt(Ar)M=X (M = Si, Ge, Sn; X = S, Se, Te),[2-4] by taking advantage of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl[5] (denoted as Tbt in this paper). We have also reported the generation of germanone **3** bearing a Tbt group, which is stable in solution at room temperature for several hours, by two methods , *i. e.*, the reaction of germylene **1** with amine *N*-oxide[6] and the thermolysis of the corresponding 1,2,4-oxazagermete **2** prepared by [1+3] cycloaddition reaction of germylene **1** with mesitonitrile oxide.[7] Moreover, we have reported the synthesis of the first stable silylene–Lewis base complex **6** by the thermal reaction of an extremely hindered disilene **4** with an overcrowded isocyanide **5**, and its unique reactivity as a silylene equivalent under very mild conditions.[8]



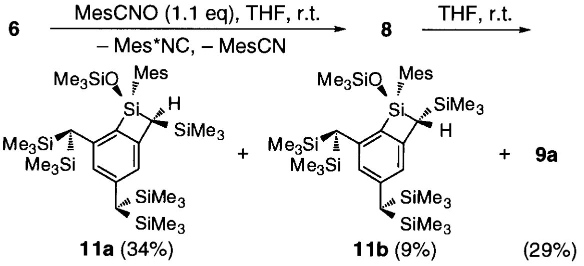
In this paper, we describe a new method for the generation of a silanone **8** by the reaction of silylene–isocyanide complex **6** with nitrile oxides.

When a C_6D_6 solution of the silylene–isocyanide complex **6** was added to 1.1 equivalent of mesitonitrile oxide at room temperature, the blue color of **6** immediately disappeared. The ^{29}Si and ^{13}C NMR spectra of the reaction mixture exhibited characteristic strong signals (δ_{Si} = 26.9, δ_C = 184.3) assignable to those of compound **7a** having a novel 1,2,4-oxazasilete ring system.[9,10] Standing the mixture at room temperature for 1 day resulted in the disappearance of these signals and the formation of 1,3,4,2-dioxazasilole **9a**[11] (37%) and (*E*)- and (*Z*)-1,3,2,4-dioxadisiletanes **10**[12] (<37%) along with the corresponding isocyanide **5** (82%) and mesitonitrile (67%).[14] This result can be reasonably explained as follows. Dissociation of oxazasilete **7a** gives silanone **8** and mesitonitrile at ambient temperature, and silanone **8** thus generated undergoes [2+3] cycloaddition with the nitrile oxide and head-to-tail dimerization reaction to give **9a** and **10**, respectively. Similarly, the reaction of **6** with TmpCNO (Tmp = 2,4,6-trimethoxyphenyl) in C_6D_6 resulted in the initial observation of the intermediary oxazasilete **7b** (δ_{Si} = 25.2) followed by the disappearance of the signal and the formation of [2+3] cycloadduct **9b**[11] (49%) and **10** (trace). The instability of **7a,b** at room temperature is in sharp contrast to the fact that the germanium analogue **2** is a crystalline compound stable at room temperature. This is most likely due to larger steric repulsion among the substituents in **7a,b** as compared to that in the germanium analogue, which is caused by the shorter Si–C bond of the oxazasilete ring than the Ge–C bond of the oxazagermete ring.



The reaction of complex **6** with mesitonitrile oxide in THF differed from that in C_6D_6. In contrast to the above-mentioned reaction in C_6D_6 giving dimerization products **10**, the reaction in THF gave diastereoisomers of benzosilacyclobutenes, **11a**[11] (34%) and **11b**[11] (9%), together with the [2+3] cycloadduct **9a** (29%), isocyanide **5** (98%), and mesitonitrile (52%). The relative configuration of **11a**,**b** was definitively determined by the

X-ray structural analysis of **11a**,**b**.[15] The molecular structure of **11a** is shown in Figure 1. The reaction mechanism for the formation of **11a**,**b** is considered to be similar to that for the analogous cyclization reaction of germanone **3**.[6,7] The nucleophilic attack of the oxygen atom in the Si=O double bond of **8** to the silicon atom of the *o*-bis(trimethylsilyl)methyl group, followed by intramolecular cyclization with the C–Si bond formation affords **11a** and **11b**. The difference in the products between the reactions in C_6D_6 and in THF is probably due to the larger polarization of the Si=O double bond of **8** in THF which is more polar and higher in coordination ability. The fact that the corresponding silanethione [Tbt(Mes)Si=S], the sulfur analogue of silanone **8**, does not give such an intramolecular cyclization product but the corresponding dimerization products[2] even in THF,[16] is in keeping with the higher polarization of the Si=O double bond than the Si=S double bond.[2,17]



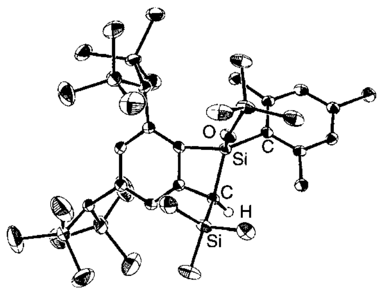
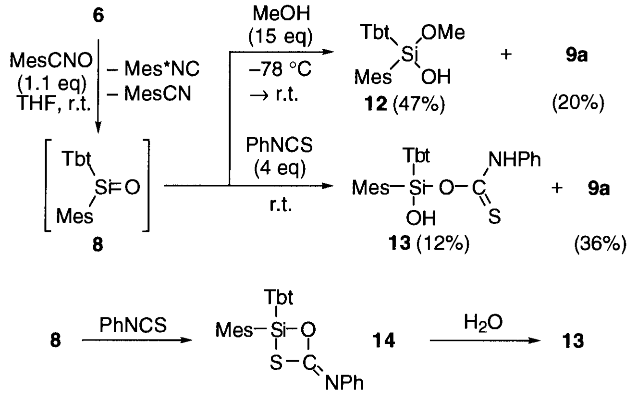


Figure 1. ORTEP drawing of benzosilacyclobutene **11a**

Although the isolation and spectroscopic observation of silanone **8** has been so far unsuccessful, **8** was trapped by methanol and phenyl isothiocyanate. Thus, treatment of silylene–isocyanide complex **6** with 1.1 equivalent of mesitonitrile oxide in THF at room temperature followed by the addition of an excess amount of methanol gave methoxysilanol **12**[11] (47%) and 1,3,4,2-dioxazasilole **9a** (20%) along with the corresponding isocyanide **5** (82%), isocyanate Mes*NCO[18] (14%), and mesitonitrile (76%). Compound **12** is considered to be formed by 1,2-addition of methanol to the Si=O double bond of **8**. In the trapping experiment with phenyl isothiocyanate, thiocarbamate **13**[11] (12%) and **9a** (36%) were obtained together with **5** (80%), Mes*NCO (8%), and mesitonitrile (65%). The formation of **13** can be rationalized by the initial cycloaddition of **8** with phenyl isothiocyanate giving the corresponding [2+2] cycloadduct, 1,3,2-oxathiasiletane **14**, and its subsequent hydrolysis during separation.



This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas (A) (No. 11133247) from the Ministry of Education, Science, Sports and Culture, Japan. We are grateful to Central Glass, Shinetsu Chemical, and Tosoh Akzo Co. Ltd., for the generous gifts of tetrafluorosilane, chlorosilanes, and alkyllithiums, respectively.

References and Notes

[#] Present address: Department of Chemical and Biological Sciences, Faculty of Science, Japan Women's University, 2-8-1 Mejirodai, Bunkyo-ku, Tokyo 112-8681, Japan.

1 Reviews on silanones, see: L. E. Gusel'nikov and N. S. Nametkin, *Chem. Rev.*, **79**, 529 (1979); G. Raabe and J. Michl, *Chem. Rev.*, **85**, 419 (1985); A. G. Brook and K. M. Bains, *Adv. Organomet. Chem.*, **25**, 1 (1986); N. Tokitoh and R. Okazaki, in "The Chemistry of Organic Silicon Compounds," ed by Z. Rappoport and Y. Apeloig, John Wiley & Sons Ltd., New York (1998), Vol. 2, Chap. 17, p. 1063.

2 H. Suzuki, N. Tokitoh, R. Okazaki, S. Nagase, and M. Goto, *J. Am. Chem. Soc.*, **120**, 11096 (1998).

3 N. Tokitoh, T. Matsumoto, and R. Okazaki, *Bull. Chem. Soc. Jpn.*, **72**, 1665 (1999).

4 M. Saito, N. Tokitoh, and R. Okazaki, *J. Am. Chem. Soc.*, **119**, 11124 (1997).

5 R. Okazaki, M. Unno, and N. Inamoto, *Chem. Lett.*, **1987**, 2293.

6 N. Tokitoh, T. Matsumoto, and R. Okazaki, *Chem. Lett.*, **1995**, 1087.

7 T. Matsumoto, N. Tokitoh, and R. Okazaki, *Chem. Commun.*, **1997**, 1553.

8 N. Takeda, H. Suzuki, N. Tokitoh, R. Okazaki, and S. Nagase, *J. Am. Chem. Soc.*, **119**, 1456 (1997).

9 The ^{13}C NMR spectrum of oxazagermete **2** showed a signal of the oxazagermete ring carbon at 174.8 ppm.[7]

10 The ^{1}H NMR of the reaction mixture at this stage showed signals of **7a** as a main product together with those of **9a**, mesitonitrile oxide, and mesitonitrile.

11 All the new products here obtained showed satisfactory spectral and analytical data.

12 Compounds **10** could not be isolated by gel permeation liquid chromatography and preparative TLC. The existence of the two isomers of **10** was confirmed by the ^{29}Si NMR spectrum [(*E*)-**10**: $\delta_{Si} = -4.39$, (*Z*)-**10**: $\delta_{Si} = -6.04, -5.90$].[13]

13 H. Suzuki, N. Tokitoh, R. Okazaki, J. Harada, K. Ogawa, S. Tomoda, and M. Goto, *Organometallics*, **14**, 1016 (1995).

14 The reaction of **6** with an excess amount of mesitonitrile oxide (8 eq.) gave **9a** in 58% yield.

15 Crystal data for **11a,b**. **11a:** $C_{36}H_{70}OSi_7$, FW = 715.55, triclinic, space group $P\bar{1}$, a= 20.1435(4) Å, b = 22.4146(4) Å, c = 11.5287(2) Å, α = 91.4523(8)°, β = 106.1859(5)°, γ = 68.8571(5)°, V = 4646.0(1) $Å^3$, Z = 4, d_{calc} = 1.023 g cm^{-3}, temperature 93 K, R1 = 0.048 for 16569 observed reflections [$I \geq 2\sigma(I)$] from 45039 unique data, wR2 = 0.144 for all data. **11b**: $C_{36}H_{70}OSi_7$, FW = 715.55, orthorhombic, space group *Pbcn*, a = 23.524(5) Å, b = 19.999(5) Å, c = 19.604(9) Å, V = 9222(8) ^{Å3}, Z = 8, d_{calc} = 1.031 g cm^{-3}, temperature 133 K, R = 0.075, R_w = 0.089 for 4925 observed [$I \geq 3\sigma(I)$] reflections from 8143 unique data.

16 H. Suzuki, N. Tokitoh, and R. Okazaki, unpublished results.

17 T. Kudo and S. Nagase, *Organometallics*, **5**, 1207 (1986).

18 The isocyanate (Mes*NCO) is most likely produced by the reaction of mesitonitrile oxide with isocyanide **5** generated from complex **6**.