

Synthesis and Fragmentation of 2,2-Diazido-1,3,2-dioxasila-5-cycloheptenes. The Chemical Vapor Deposition of SiO₂

Rainer Herges* and Felix Starck

Contribution from the Institut für Organische Chemie, Technische Universität Braunschweig, Hagenring 30, D-38106 Braunschweig, Germany

Received May 13, 1996. Revised Manuscript Received October 18, 1996[®]

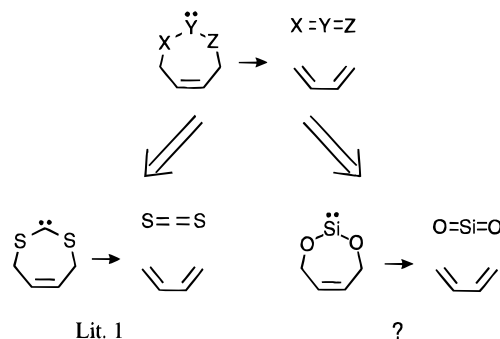
Abstract: *Ab initio* (MP2/6-31G*) and density functional theory (B3LYP/6-31G*) calculations were performed to check the feasibility for the fragmentation of 1,3,2-dioxasila-5-cycloheptene-2-diyl to form SiO₂. According to the theoretical results the reaction is not synchronous but concerted and endergonic and requires an energy of activation of about 50–60 kcal mol⁻¹. Semiempirical calculations (PM3) indicate that the process should be favored as a chemical vapor deposition process at the growing surface of quartz. For the experimental realization of the fragmentation reaction the corresponding diazido silanes were chosen as silylene precursors. Two different strategies for the synthesis of 4,4',7,7'-tetramethyl-2,2-diazido-1.3.2-dioxasila-5-cycloheptene are presented. Unlike the 4,7-dimethyl- and the unsubstituted system the tetramethyl derivative is stable toward polymerization. It decomposes under flash vacuum pyrolysis conditions at 650 °C and can be used for the chemical vapor deposition of amorphous quartz.

Using our methods for the computer-aided search and the rational design of reactions (reaction planning) we developed a novel elimination reaction, based on the fragmentation of 1,3-dithiepine-2-ylidenes which can be used for the synthesis of dienes.¹ We now are systematically investigating hetero-variations of the general reaction scheme (Scheme 1). Fragmentation of a 1,3,2-dioxasila-5-cycloheptene-2-diyl should give silicon dioxide and a diene. This should be interesting both for synthesizing dienes and (under suitable reaction conditions) for the generation of monomeric silicon dioxide.² The design of the dithiepine fragmentation¹ and the siloxepine reaction which is the topic of the paper presented here demonstrate how the information of preceding theoretical calculations can be successfully used to guide experiments.

Theoretical Calculations

Prior to the experiments we performed *ab initio* (MP2/6-31G*)³ and density functional theory (B3LYP/6-31G*)^{4,5} calculations⁶ to check the experimental feasibility of the fragmentation reaction by computation of the reaction parameters (heat of reaction and activation enthalpy) and to reveal details of the reaction mechanism. All stationary points were checked by inspection of the number of negative eigenvalues of the Hessian matrix and imaginary frequencies according to a normal coordinate analysis. All energies are given including zero point energy (ZPE) relative to the reactant(s).

Scheme 1



Accuracy and reliability of both the *ab initio* MP2 and the density functional theory (DFT) B3LYP method have been tested with a variety of pericyclic and other concerted reactions.^{7–10} In the parent Diels–Alder reaction, butadiene + ethylene → cyclohexene, the activation barrier is underestimated at the MP2/6-31G* level by 7.5 kcal mol⁻¹ and at the B3LYP/6-31G* level by 4.8 kcal mol⁻¹ compared to the experimental values. The heat of reaction is too exothermic by 7.5 kcal mol⁻¹ at the MP2 level and too endothermic by 1.8 kcal mol⁻¹ at the B3LYP level.⁷ Similar trends have been observed in assessment calculations with other pericyclic reactions.^{8,9} However, it should be noted that there is little experience with DFT methods applied on reactions involving silicon as reacting atoms in the transition state.¹¹ Nevertheless, we assume that the B3LYP energies are more reliable than those of the MP2 calculations and that they are correct within 5–8 kcal mol⁻¹.

* Corresponding author. E-mail: R.Herges@tu-bs.de.
[®] Abstract published in *Advance ACS Abstracts*, December 1, 1996.
 (1) Herges, R.; Hoock, C. *Science* **1992**, 255, 711–713.
 (2) Schnöckel, H. *Angew. Chem.* **1978**, 90, 638–639; *Angew. Chem., Int. Ed. Engl.* **1978**, 17, 616.
 (3) Möller, C.; Plesset, M. S. *Phys. Rev.* **1934**, 46, 618.
 (4) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648–5652.
 (5) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, 37, 785.
 (6) Gaussian 92, Revision B: M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1992.

(7) Goldstein, E.; Beno, B.; Houk, K. N. *J. Am. Chem. Soc.* **1996**, 118, 6036–6043.

(8) Torrent, M.; Duran, M.; Solá, M. *J. Mol. Struct. (THEOCHEM)* **1996**, 362, 163.

(9) Barone, V.; Arnaud, R. *Chem. Phys. Lett.* **1996**, 251, 393.

(10) Houk, K. N.; Li, Y.; Evanseck, J. D. *Angew. Chem.* **1992**, 104, 711; *Angew. Chem., Int. Ed. Engl.* **1992**, 31, 682–710.

(11) Nachtigall, P.; Jordan, K. D.; Smith, A.; Jonsson, H. *J. Chem. Phys.* **1996**, 104, 148.

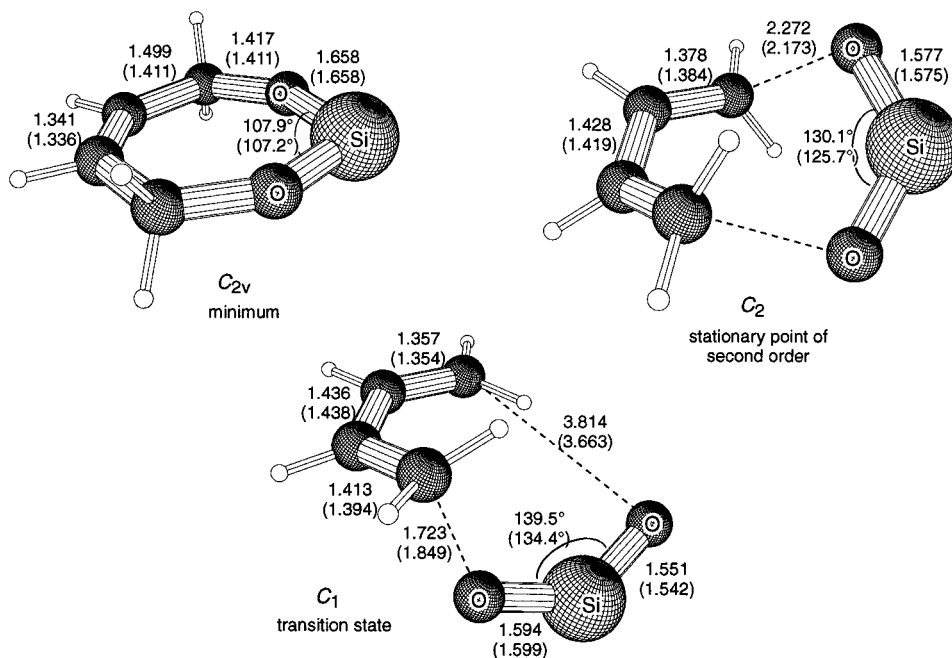






Figure 1. MP2/6-31G* and B3LYP/6-31G* (in parentheses) optimized structures of stationary points on the reaction hypersurface of the 1,3,2-dioxasilacyclohept-5-ene-2-diyl fragmentation. Bond lengths are given in Å and angles in deg.

Table 1. *Ab Initio* (MP2/6-31G*//MP2/6-31G*) and Density Functional Theory (B3LYP/6-31G*//B3LYP/6-31G*) Calculated Thermodynamic and Kinetic Parameters of the 1,3,2-Dioxasilacyclohept-5-ene-2-diyl Fragmentation^a

						<i>D_{00h}</i>
		<i>C_{2v}</i>	<i>C₂</i>	<i>C₁</i>	<i>C_{2v}</i>	<i>D_{00h}</i>
MP2/6-31G*	ΔH_{rel}	0.0	59.7	49.6		28.3
B3LYP/6-31G*	ΔH_{rel}	0.0	73.0	59.8		38.3
PM3	ΔH_{rel}	0.0	104.9	50.1		41.9
MP2/6-31G*	ΔS_{rel}	0.0	-1.2	3.3		37.0
B3LYP/6-31G*	ΔS_{rel}	0.0	0.2	7.6		39.1
Nimag		0	2	1		0

^a Enthalpy (ΔH_{rel} , kcal mol⁻¹) and entropy values (ΔS_{rel} , cal mol⁻¹ K⁻¹) are relative to the reactant and are given including zero point energy. ΔS_{rel} is calculated as the sum of translational, rotational, and vibrational contributions at 298 K. Nimag is the number of imaginary frequencies according to a normal coordinate analysis. Nimag for each structure is identical at all levels.

Table 1 and Figure 1 give the relative energies and the structures of the most important stationary points that were found on the energy hypersurface of the system. Both *ab initio* and density functional theory (DFT) methods predict the reactant silylene to have a flat *C_{2v}* ring structure (in contrast to the boat conformation of the dithiepine, see Scheme 1). According to the Woodward–Hoffmann rules¹² the fragmentation should proceed with conservation of *C₂* symmetry (supra, antara). A corresponding stationary point for this process was indeed found by transition state optimization.¹³ However, the relative energy (*ab initio*, 59.6; DFT, 73.0 kcal mol⁻¹) is probably much too high for a thermal activation under “laboratory conditions”. Moreover, according to a harmonic frequency analysis the stationary point turned out to be of second order and thus it is not a true transition state. The true transition state (one imaginary frequency) connecting¹⁴ the reactant dioxasilene and

(12) Woodward, R. B.; Hoffmann, R. *Angew. Chem.* **1969**, *81*, 797–869; *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781–853.

(13) Baker, J. J. *Comput. Chem.* **1986**, *7*, 385–95.

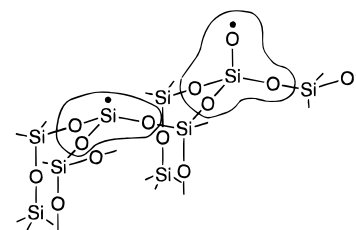


Figure 2. Simplified model of the growing surface of amorphous quartz.

the products butadiene and silicon dioxide is asymmetric. In the transition structure both C–O bonds that are broken during the reaction differ considerably in length (*ab initio*, 1.723 and 3.184 Å; DFT, 1.849 and 3.663 Å). A quite substantial diradical character is to be expected for such a species. Even though DFT methods should reasonably describe structures even with a large open shell character¹⁵ we checked the transition state energy and structure by performing unrestricted DFT calculations (UB3LYP/6-31G*) but reproduced the results of the closed shell calculations. With a barrier of activation of 49.6 kcal mol⁻¹ (*ab initio*) or 59.8 kcal mol⁻¹ (DFT level) the fragmentation still should be hard to perform by thermal activation in solution. Flash pyrolysis at high temperatures, however, should provide suitable conditions for our fragmentation reaction.¹⁶ At temperatures of 492 °C (*ab initio*) or 706 °C (DFT) the large reaction entropy (37 e.u., *ab initio*; 39.1 e.u., DFT) outweighs the endothermic reaction enthalpy and the reaction becomes exergonic. Moreover, because of the large energy of crystallization of SiO₂, the fragmentation should proceed smoothly

(14) The connectivity was checked by intrinsic reaction coordinate analysis see: (a) Truhlar, D. G.; Kuppermann, A. *J. Am. Chem. Soc.* **1971**, *93*, 1840–1851. (b) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363–368. (c) Fukui, K. *Pure Appl. Chem.* **1982**, *54*, 1825–1836.

(15) DFT methods intrinsically include correlation energy. This was first recognized by Slater: Slater, J. C. *Phys. Rev.* **1951**, *81*, 385. For a quantitative assessment we calculated the singlet potential energy surface for the homolytic dissociation of ethane in two methyl radicals at the B3LYP/6-31G* and the UB3LYP/6-31G* level. The energies are identical within the numerical error of the Gaussian94 program up to a C–C distance of 2.4 Å. At this point according to a CAS(10,8)/6-31G* calculation (10-electron 8-orbital complete active space) 20% of higher configurations contribute to the overall wavefunction: Herges, R. Unpublished results.

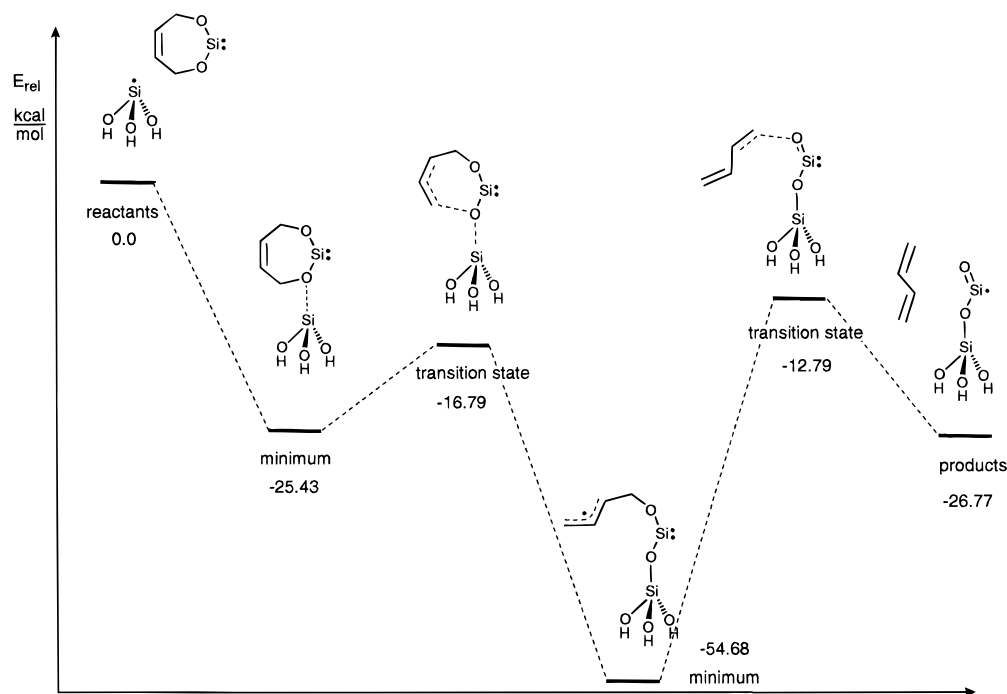


Figure 3. PM3-calculated relative energies of the stationary points of the siloxepine fragmentation catalyzed by trihydroxysilane radical used as a model of active silicon on a SiO₂ surface during vapor deposition.

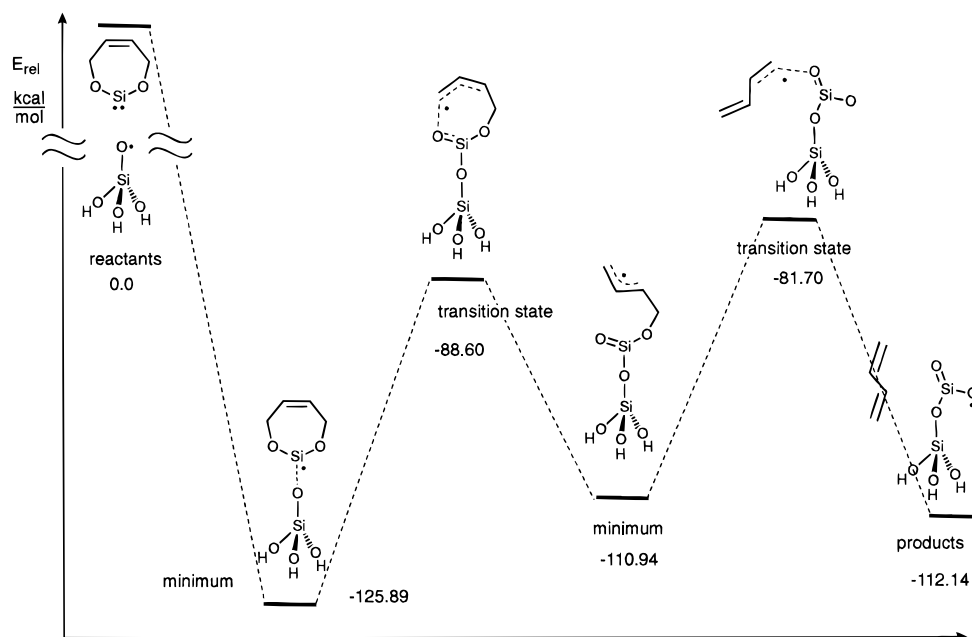


Figure 4. PM3-calculated relative energies of the stationary points of the siloxepine fragmentation catalyzed by trihydroxyoxysilane radical used as a model of active oxygen on a SiO₂ surface during vapor deposition.

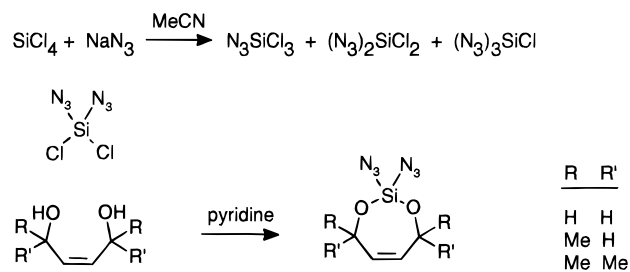
and irreversibly at these temperatures. Using the Eyring equation and the kinetic data of Table 1 a half-life of 1.2 s (at 492 °C, *ab initio*) and 0.016 s (at 706 °C, DFT) for the fragmentation of the siloxepine can be predicted. Temperatures of 700 °C and a time of contact of 0.01–0.1 s are in the range of a typical flash pyrolysis experiment and were considered to be the approximate conditions for an experimental realization

(16) Thermodynamic and kinetic data are similar to, for example, the Diels–Alder cycloreversion of cyclohexene to butadiene and ethylene with $\Delta H^\ddagger = 65.2 \text{ kcal mol}^{-1}$, $\Delta_R H_0 = 40.5 \text{ kcal mol}^{-1}$, and $\Delta_R S_0^{298} = 44.8 \text{ cal mol}^{-1} \text{ K}^{-1}$. (a) Tardy, D. C.; Ireton, R.; Gordon, A. S. *J. Am. Chem. Soc.* **1979**, *101*, 1508–1514. The fragmentation proceeds under flash pyrolysis conditions at 700–800 °C, ~10 Torr, time of contact 0.01–0.03 s with ~90% yield. (b) Rice, F. O.; Ruoff, P. M.; Rodowskas, E. L. *J. Am. Chem. Soc.* **1938**, *60*, 955–961.

of our fragmentation reaction (see the Experimental Section). *Ab initio* and DFT calculations, however, do not necessarily represent the conditions in a flash pyrolysis or chemical vapor deposition (CVD) experiment. The experimental results (see Experimental Realization) prompted us to investigate conceivable reactions that might occur at the growing surface of amorphous quartz which is the final product of the fragmentation. During crystallization of monomeric SiO₂ free valencies at silicon and oxygen atoms are formed which are highly reactive and at which the precursor siloxepin could coordinate and decompose. A simplified surface structure of amorphous SiO₂ is shown in Figure 2.

For a practical treatment within computational quantum chemistry the system has to be further simplified. We consid-

Scheme 2. Method A



ered the trihydroxysilane radical and the trihydroxysilane oxide radical as very approximate models of the genuine structural and electronic properties of the growing surface of amorphous SiO_2 . Since high-level *ab initio* and DFT calculations are too expensive for a thorough investigation of the reaction hyper-surface semiempirical methods were considered for a first approach. Assessment calculations of the stationary points of the fragmentation reaction proved that the PM3 method is in reasonable agreement with our correlated *ab initio* and DFT calculations (see Table 1). Thus, the results of the semiempirical treatment should at least be interpretable in a qualitative way and the trends in kinetic and thermodynamic parameters compared to the gas phase reaction should become apparent. Figure 3 gives the relative energies of the most important stationary points that were found for the fragmentation of the precursor coordinated at the oxygen with a silicon radical, and Figure 4, the corresponding energies of siloxepin coordinated at the silylene center with an oxygen radical of the model compound.

On our simplified model surface the reaction is stepwise in both cases. The activation barrier ΔH^\ddagger for the cleavage of the first C–O bond in siloxepine is predicted with $8.6 \text{ kcal mol}^{-1}$ by coordination at the siloxepin oxygen and $37.3 \text{ kcal mol}^{-1}$ by coordination to the silylene silicon atom. The first reaction is endothermic with $26.8 \text{ kcal mol}^{-1}$, and the second pathway now is exothermic with $-112.1 \text{ kcal mol}^{-1}$. Thus by coordination at the surface the fragmentation is strongly catalyzed and thermodynamically more favorable than the gas phase reaction. Breaking of the second C–O bond most probably again is catalyzed by coordination of an additional precursor molecule and the deposition of SiO_2 proceeds as a radical chain reaction. The radical intermediates by rearrangement at the elevated temperatures probably give rise to the variety of unsaturated products that were observed in the experiment (see Experimental Realization).

Experimental Realization

Synthesis of the Silylene Precursors. Carbon-substituted diazido silanes are known to form silylenes by thermo- and photochemical elimination of nitrogen and they are easily accessible.¹⁷ The reactions should also apply to alkoxy-substituted silanes. For the experimental verification of our anticipated reaction we therefore chose the corresponding geminal diazido compounds as silylene precursors. In principle there are two different ways to synthesize the diazido silylenes (methods A and B). For the first step of method A (Scheme 2)

(17) (a) Barash, L.; Wasserman, E.; Yager, W. A.; *J. Am. Chem. Soc.* **1967**, *89*, 3931–3932. (b) Moriarty, R. M.; Kliegman, J. M.; Shovlin, C. *J. Am. Chem. Soc.* **1967**, *89*, 5958–5959. (c) Moriarty, R. M.; Kliegman, J. M.; *J. Am. Chem. Soc.* **1967**, *89*, 5959–5960. (d) Welsh, K. M.; Michl, J.; West, R. *J. Am. Chem. Soc.* **1988**, *110*, 6689–6696. (e) Khabashesku, V. N.; Balaji, V.; Boganov, S. E.; Nefedov, O. M.; Michl, J. *J. Am. Chem. Soc.* **1994**, *116*, 320–329.

Table 2. Equilibrium Molar Ratios (%) of Chloroazidosilanes in the Reaction $\text{SiCl}_4 + x\text{NaN}_3 \rightarrow \text{SiCl}_4 + \text{Si}(\text{N}_3)\text{Cl}_3 + \text{Si}(\text{N}_3)_2\text{Cl}_2 + \text{Si}(\text{N}_3)_3\text{Cl} + \text{Si}(\text{N}_3)_4$ in Acetonitrile-*d*₃ Determined by ²⁹Si-NMR Spectroscopy (Pulse Delay of 15 s)

SiCl ₄ +	2NaN ₃	2.5NaN ₃	3NaN ₃
SiCl ₄	6		
Si(N ₃)Cl ₃	30	12	3
Si(N ₃) ₂ Cl ₂	46	44	30
Si(N ₃) ₃ Cl	18	44	49
Si(N ₃) ₄			18

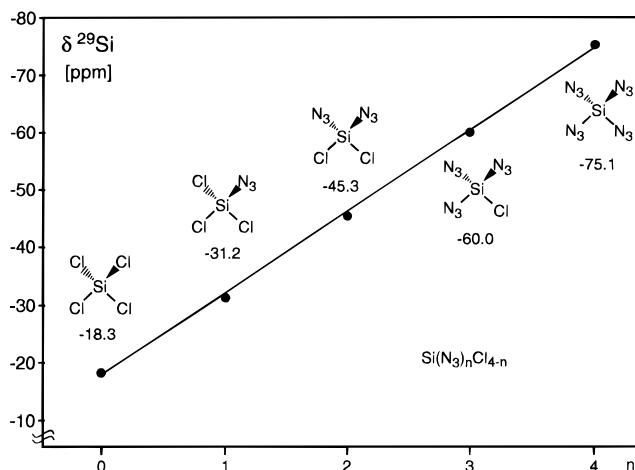


Figure 5. ²⁹Si-NMR chemical shifts of the silanes $\text{Si}(\text{N}_3)_n\text{Cl}_{4-n}$ ($n = 0-4$).

silicon tetrachloride was reacted with 2 equiv of sodium azide in acetonitrile to form $\text{SiCl}_2(\text{N}_3)_2$ by chloride–azide exchange.¹⁸

According to ²⁹Si-NMR spectroscopy in acetonitrile-*d*₃ at room temperature $\text{SiCl}_2(\text{N}_3)_2$ is not the only product but there is an equilibrium between SiCl_4 and mono-, di-, and triazide. Increasing proportions of sodium azide shift the equilibrium towards the higher azides (Table 2).

Care should be taken that not more than 2.5 equiv of sodium azide are used. Under these conditions $\text{Si}(\text{N}_3)_4$ is formed which is highly and violently explosive.¹⁹ Moisture also has to be excluded to prevent formation of HN_3 . The different silanes can be easily detected by ²⁹Si-NMR. The ²⁹Si-NMR shift is a linear function of the number of chloride replaced by azide ligands (Figure 5).

The line widths of the ²⁹Si-NMR signals increase with increasing number of azide ligands because of the decreasing spin–lattice relaxation times induced by ¹⁴N. For a quantitative analysis very long pulse delay times (15 s) had to be employed. A separation and further characterization of the silanes $\text{Si}(\text{N}_3)_n\text{Cl}_{4-n}$ ($n = 1-4$) was not attempted because of the explosive nature of these compounds. For the cyclization with 1,4-but-2-endiols the equilibrium mixture with $\text{SiCl}_4/\text{NaN}_3$ 1:2.5 was used.²⁰

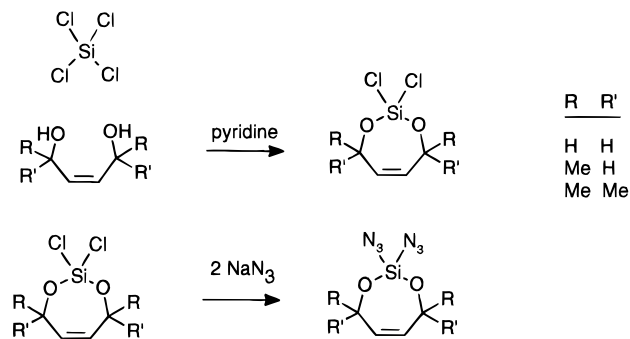
Method B starts with SiCl_4 and 1,4-but-2-endiols. The chloride–azide exchange is performed subsequently (Scheme 3). The overall yields with method A and B were 45% and

(18) (a) Sundermeyer, W. *Angew. Chem.* **1962**, *74*, 717. (b) Wiberg, N.; Raschig, F.; Sustmann, R. *Angew. Chem.* **1962**, *74*, 388–389. (c) Birkhofer, L.; Wegner, P. *Org. Synth.* **1970**, *50*, 107–110. (d) Wiberg, N.; Neruda, B. *Chem. Ber.* **1966**, *99*, 740–749.

(19) See also: (a) Wiberg, E.; Michaud, H. Z. *Naturforsch.* **1954**, *9b*, 500. (b) *Nachr. Chem. Techn.* **1970**, *18*, 26–27.

(20) For similar cyclizations of methyl- and phenyl-substituted dichloro-silanes with diols, see: (a) Kriebel, R. H.; Burkhard, C. A. *J. Am. Chem. Soc.* **1947**, *69*, 2689–2692. (b) Calas, R.; Nicou, P. C. R. *Acad. Sci. Paris* **1959**, *249*, 1011–1013. (c) Cragg, R. H.; Lane, R. D. *J. Organomet. Chem.* **1984**, *270*, 25–37. (d) Cragg, R. H.; Lane, R. D. *J. Organomet. Chem.* **1985**, *291*, 153–157.

Scheme 3. Method B



55% ($R = R' = \text{Me}$). The parent system ($R = R' = \text{H}$) and the dimethyl derivative ($R = \text{H}$, $R' = \text{Me}$) polymerize upon concentration of the solution. The tetramethyl compound ($R = R' = \text{Me}$), however, is kinetically stable and can be purified by distillation.²¹ The liquid is not explosive (when dropped on a 300 °C hot plate) and thus was a suitable precursor for chemical vapor deposition experiments.

Photo- and Thermochemical Fragmentation. The photochemical (UV, wavelength 254 nm) induced fragmentation of the tetramethyl compound ($R = R' = \text{Me}$) did not lead to the formation of SiO_2 and 2,5-dimethyl-2,4-hexadiene. Only 50% of the expected amount of nitrogen was eliminated. Elementary analysis and spectroscopic investigations indicate that nitrogen-containing, oligomeric silicon compounds were formed, probably via nitrene or diazo intermediates.^{17d}

Because our quantum chemical calculations indicated a high activation barrier the thermochemically induced fragmentation was performed under flash vacuum conditions (650 °C, 5×10^{-2} mbar, 0.1 s contact time, Figure 6). The quartz tube was loaded with sodium chloride crystals to allow removal and characterization of the deposited nonvolatile material. During pyrolysis the appearance of the sodium chloride crystals did not change; however, after removal from the quartz tube they did not dissolve in water anymore. Obviously they were coated with a thin layer of amorphous quartz. By employing ultrasound the sodium chloride was dissolved in water and the residue was analyzed. According to the elementary analysis the insoluble material was almost pure SiO_2 (C = 0.738%, N = 0.445%, H = 0.418%). The volatile products that were condensed in a cold trap are a complex mixture of C_7 and C_8 hydrocarbons according to NMR, GC-MS, and elementary analysis. Tetramethylbutadiene could not be detected even though it was found to be reasonably stable under the pyrolysis conditions. Thus tetramethylbutadiene is not an intermediate during fragmentation. In agreement with our calculations a concerted reaction therefore can be excluded.

Conclusion

4,4',7,7'-Tetramethyl-2,2-diazido-1,3,2-dioxasila-5-cycloheptene is a suitable and easily accessible precursor for the chemical vapor deposition of quartz. Thin layers of SiO_2 are used as a protective coat for a variety of materials, e.g. on metals against corrosion, semiconductors as insulating layer, optical glasses and plastics as antireflex coat, and data recording media and recorder heads against mechanical wear. If our precursor can compete with silicon monoxide²² or tetraalkoxy silanes²³ is not yet clear and will be subject of further investigations.

(21) A similar kinetic stabilization toward dimerization and polymerization was observed by the reaction of dichlorodimethylsilane with ethylene glycol which gives only dimers and polymers (ref 20a) and pinacol which yields the monomeric 1,3,2-dioxasilacyclopentane (ref 20c).

(22) *Ullmanns Encyklopädie der technischen Chemie*, 4. Aufl., Bd. 21; Verlag Chemie: Weinheim, Germany, 1979; S.481ff.

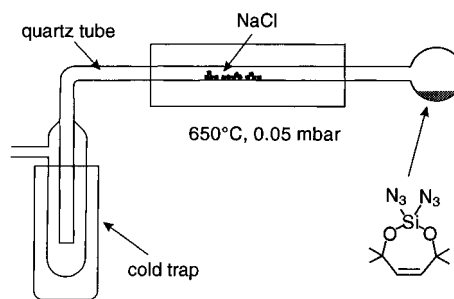


Figure 6. Flash pyrolysis apparatus for the deposition of quartz on sodium chloride.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of dry nitrogen. Solvents were dried using standard techniques and glassware was dried in an oven (120 °C) for several hours, and the apparatus was assembled hot while flushing with a stream of nitrogen. ¹H-NMR, ¹³C-NMR, and ²⁹Si-NMR spectra were recorded on a JEOL GX-400 spectrometer. Chemical shifts are reported on the δ scale relative to tetramethylsilane. Mass spectra were determined with a Varian MAT 311 A mass spectrometer at an ionizing voltage of 70 eV. A Finnigan MAT 90 with a ICIS-datasystem equipped with a Varian 3000 gas chromatograph was employed for GC-MS. The gas chromatograph was fitted with a 25 m \times 0.25 mm i.d. fused silica capillary column SE-54. Elemental analyses were performed on a Heraeus CHN-Mikromat, Si and O by the microanalytical laboratory Ilse Beetz, Kronach.

Synthesis of 4,4',7,7'-Tetramethyl-2,2-diazido-1,3,2-dioxasila-5-cycloheptene. Method A. To a cold suspension of sodium azide (3.2 g, 50 mmol) in acetonitrile (30 mL) was added silicon tetrachloride (2.3 mL, 20 mmol) via a syringe by vigorous stirring. After complete addition the mixture was allowed to warm to room temperature and was stirred for 12 h. Then a mixture of *cis*-2,5-dimethyl-3-hexene-2,5-diol (2.88 g, 20 mmol) and pyridine (3.3 mL, 40 mmol) in acetonitrile (25 mL) was added dropwise to the ice cold (−18 °C) reaction mixture. After being stirred at room temperature for 3 h, the suspension was filtered through a pad of Celite and the yellow solution was concentrated to one-half the volume. Extracting three times with pentane (20 mL), removal of the solvent, and distillation at reduced pressure (45 °C 5.0×10^{-2} mbar) afforded 4,4',7,7'-tetramethyl-2,2-diazido-1,3,2-dioxasila-5-cycloheptene as a colorless oil, yield 2.26 g (44.5%).

Method B. Silicon tetrachloride (3.45 mL, 30 mmol) was added to a solution of *cis*-2,5-dimethyl-3-hexene-2,5-diol (4.39 g, 30 mmol) and pyridine (4.9 mL, 60 mmol) in acetonitrile (60 mL) at −18 °C under vigorous stirring. After complete addition the mixture was allowed to warm to room temperature and was stirred for 12 h. The suspension was filtered through a pad of Celite, to the yellow solution was added sodium azide (4.9 g, 75 mmol), and the mixture was stirred for an additional 12 h. After being filtered through a pad of Celite, the solution was concentrated to one-half the volume and extracted three times with pentane (20 mL). The pentane was evaporated and the residue distilled under reduced pressure, yielding 2.26 g (54.8%) of the desired product: IR (neat) 2980, 2160, 1375, 1360, 1330, 1300, 1190, 1145, 1100, 1060, and 735 cm^{-1} ; ¹H-NMR (400 MHz, CDCl_3) δ 1.49 (s, 12H) 5.43 (s, 2H); ¹³C-NMR (100.6 MHz, CDCl_3) δ 31.4, 76.0 and 134.9; ²⁹Si-NMR (79.4 MHz, CDCl_3) δ −75.8; *m/e* 239 (base), 196, 181, 43, and 28. Anal. Calcd for $\text{C}_8\text{H}_{14}\text{N}_6\text{O}_2\text{Si}$: C, 37.78; H, 5.55; N, 33.04. Found: C, 37.35; H, 5.67; N, 31.99.

Synthesis of 4,4',7,7'-Tetramethyl-2,2-dichloro-1,3,2-dioxasila-5-cycloheptene. Silicon tetrachloride (2.3 mL, 20 mmol) was added to a solution of *cis*-2,5-dimethyl-3-hexene-2,5-diol (2.9 g, 20 mmol) and pyridine (3.3 mL, 40 mmol) in acetonitrile (60 mL) at −18 °C under vigorous stirring. Then the mixture was allowed to warm to room temperature and was stirred for 12 h. The precipitation of pyridinium chloride was filtered off through a pad of Celite, and the clear yellow

(23) For a review see: (a) Bradley, D. C. *Chem. Rev.* **1989**, 89, 1317–1322. For a recent publication, see: (b) Narula, C. K.; Varshney, A.; Riaz, U. *Chem. Vap. Deposition* **1996**, 2, 13–15.

solution was concentrated to one-half the volume. The solution was extracted three times with 20 mL portions of pentane, and the collected pentane fractions were evaporated. Distillation of the residue under reduced pressure afforded 2.36 g of 4,4',7,7'-tetramethyl-2,2-dichloro-1,3,2-dioxasila-5-cycloheptene as a colorless oil, yield 48.9%: IR (neat) 2990, 1375, 1360, 1300, 1185, 1140, 1060, and 760 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 1.52 (s, 12H) 5.41 (s, 2H); $^{13}\text{C-NMR}$ (100.6 MHz, CDCl_3) δ 31.6, 77.9 and 134.9; $^{29}\text{Si-NMR}$ (79.4 MHz, CDCl_3) δ -54.3; *m/e* 240, 225 (base), 182, 167, 115, and 43. Anal. Calcd for $\text{C}_8\text{H}_{14}\text{Cl}_2\text{O}_2\text{Si}$: C, 39.84; H, 5.85. Found: C, 38.90; H, 5.73.

NMR-Screening Experiments. Reaction of silicon tetrachloride with different amounts of sodium azide. The reactions were carried out in a mixture of $\text{CH}_3\text{CN}/\text{CD}_3\text{CN}$. A suspension of sodium azide in acetonitrile (6 mL) was cooled to -18°C , and silicon tetrachloride was added via a syringe. The reaction mixture was allowed to warm to room temperature and was stirred for additional 12 h. After filtration the solution was submitted to $^{29}\text{Si-NMR}$ spectroscopy (pulse delay 15 s).

Reaction of silicon tetrachloride (0.5 mL, 4.35 mmol) with 2 equiv of sodium azide (566 mg, 8.71 mmol): $^{29}\text{Si-NMR}$ (79.4 MHz, CDCl_3) δ -18.3 (6%), -31.2 (30%), -45.3 (46%), -60.0 (18%).

Reaction of silicon tetrachloride (0.5 mL, 4.35 mmol) with 2.5 equiv of sodium azide (708 mg, 10.9 mmol): $^{29}\text{Si-NMR}$ (79.4 MHz, CDCl_3) δ -31.2 (12%), -45.3 (44%), -60.0 (44%).

Reaction of silicon tetrachloride (0.5 mL, 4.35 mmol) with 3 equiv of sodium azide (849 mg, 13.1 mmol): $^{29}\text{Si-NMR}$ (79.4 MHz, CDCl_3) δ -31.2 (3%), -45.3 (30%), -60.0 (49%), -75.1 (18%).

Flash Vacuum Pyrolysis of 4,4',7,7'-Tetramethyl-2,2-diazido-1,3,2-dioxasila-5-cycloheptene. In the distillation flask of a flash vacuum pyrolysis apparatus 1.3 g (5.1 mmol) of 4,4',7,7'-tetramethyl-2,2-diazido-1,3,2-dioxasila-5-cycloheptene was evaporated within 10 h at 50°C and a pressure of 0.05 mbar. The pyrolysis was carried out in a quartz tube of 20 mm diameter and 450 mm length heated to 650°C . The tube was loaded with sodium chloride crystals. After pyrolysis the sodium chloride crystals were removed and suspended in water. The crystals did only dissolve after treatment with ultra sound. According to the elementary analysis the remaining insoluble material (yellowish-white powder) was almost pure SiO_2 . Anal. Calcd for SiO_2 : Si, 46.67. Found: Si, 46.18, C, 0.738; H, 0.418, N, 0.445. The volatile organic products generated during pyrolysis were condensed in a cold trap at -196°C . According to NMR, GC-MS, and elementary analysis (C, 83.10; H, 8.75; N, 1.44; O, 6.42; Si, 0) the colorless liquid is a complex mixture of C_7 and C_8 hydrocarbons. Tetramethylbutadiene could not be detected even though it was found to be stable under the above pyrolysis conditions.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for support.

JA9615886