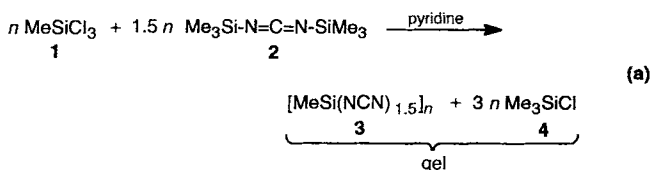


Preparation of Non-Oxidic Silicon Ceramics by an Anhydrous Sol–Gel Process\*\*

Andreas O. Gabriel and Ralf Riedel\*

The sol–gel process for the synthesis of oxidic glasses and ceramics has been the subject of intensive investigations in synthetic inorganic chemistry and is used in a wide range of technical applications.<sup>[1, 2]</sup> However, it was limited hitherto to systems containing oxygen.<sup>[2]</sup> We now report on the first anhydrous sol–gel process for the synthesis of oxygen-free silicon ceramics.

The reaction of trichloro(methyl)silane (**1**) with the carbodiimide synthetic building block bis(trimethylsilyl)carbodiimide (**2**) and a pyridine catalyst produces a transparent, dimensionally stable gel [Eq. (a)]. The reaction is performed without sol-



vents. The reaction time to the gel point can be altered by varying the amount of pyridine and by changing the reaction temperature (Figure 1). The reaction mixture also gels at room temperature and without pyridine. For example, with 0.25 equiv pyridine (with respect to **1**), the reaction time to the gel point

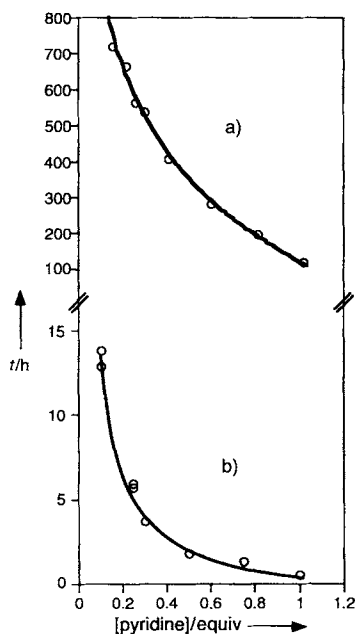


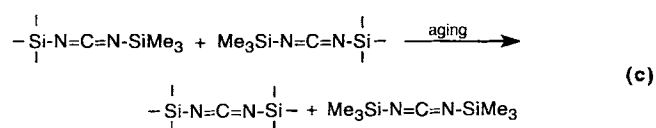
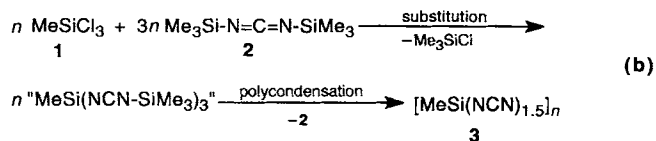
Figure 1. Dependence of the reaction time to the gel point on the pyridine concentration for the reaction of **1** with **2** without solvent a) at room temperature, and b) at reflux temperature.

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increases from 6 h (reflux temperature) to 24 days (room temperature).

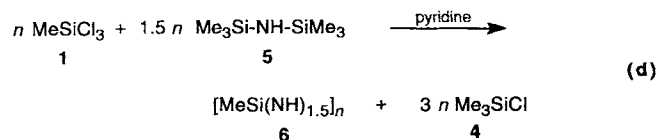
Reaction (a) proceeds completely analogously to the known aqueous sol–gel process; the carbodiimide **2** adopts the role played by water in the substitution and condensation steps [Eq. (b)]. During the aging process, the number of bonds in the gel network is increased by progressive polycondensation. The FT-IR spectra of the nonaged gels reveal the presence of trimethylsilyl end groups; these are no longer detectable by spectroscopy after the aging process [Eq. (c)]. Therefore, the



condensation reactions are not complete at the gel point, but continue during the aging process. The rate of aging is not only a function of the amount of pyridine, but also a function of the temperature: a higher pyridine content and a higher aging temperature (20–45 °C) accelerate further cross-linking. During the aging process there is no phase change to give a crystalline solid. The xerogel **3** obtained after drying ( $3 \times 10^{-2}$  mbar, 130 °C) is X-ray amorphous. Furthermore, the in-situ X-ray powder diffractograms do not show any reflections in the temperature range between room temperature and 850 °C which could indicate crystalline phases.

The controlled aging of the gel is characterized by crack-free, three-dimensional shrinkage. Thus, for a pyridine content of 0.3 equiv with respect to **1**, shrinkage is complete after about four weeks. It is irreversible, and the rate of shrinkage is likewise dependent on the temperature and the concentration of catalyst. Immediately after gelation, the gel is transparent. On aging the gel becomes cloudy. On slow evaporation of the liquid phase, it converts into the transparent xerogel **3**. The gel shrinks during the aging process to 25% of the original volume. After the liquid phase was decanted off, and the remaining liquid removed by slow evaporation, the gel shrinks linearly by a further 10%. Measurements of the porosity revealed that the gel is very dense; no micropores could be detected.<sup>[3]</sup>

In contrast, on treating **1** with hexamethyldisilazane (**5**) there was no gelation, but only precipitation of a solid, **6**<sup>[4]</sup> [Eq. (d)].



Thus, the carbodiimide group seems to be the decisive factor in the nonaqueous sol–gel process presented here. The intact carbodiimide groups of **3** were detected by FT-IR spectroscopy ( $\tilde{\nu}_{\text{as}}(\text{N}=\text{C}=\text{N}) = 2152 \text{ cm}^{-1}$ ) and by Raman spectroscopy ( $\tilde{\nu}_g(\text{N}=\text{C}=\text{N}) = 1533 \text{ cm}^{-1}$ ) not only in the freshly prepared gel, but also in the aged gel. This is in agreement with the results from the treatment of **2** with dichloro(dimethyl)silane<sup>[5, 6]</sup> as

well as tetrachlorosilane.<sup>[7]</sup> SiCl<sub>4</sub> reacts with **2** in an analogous manner to that shown in Equation (a) to give a methyl-free gel of composition SiC<sub>2</sub>N<sub>4</sub>. After calcination of this xerogel the first crystalline phases in the ternary Si-C-N system could be isolated and characterized.<sup>[7]</sup>

The thermally induced ceramization of xerogel **3** was investigated by simultaneous thermal analysis (STA) between room temperature and 1500 °C in He. This indicated the yield of ceramic to be 60%. Between 560 and 590 °C a mass loss of 20% was measured, which is accompanied by an exothermic reaction (Figure 2). The decomposition products determined in situ by

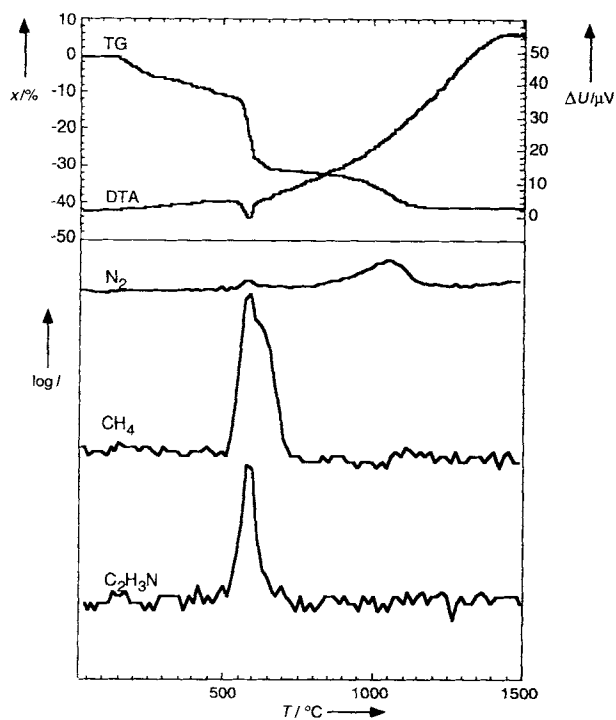


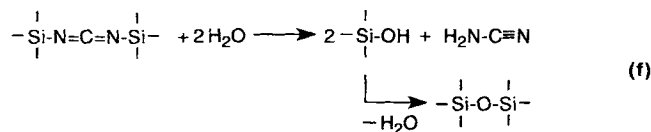
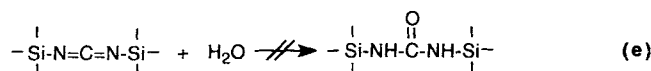
Figure 2. Thermogravimetric (TG) analysis (mass loss  $x$  [%]) and differential thermal analysis (DTA:  $\Delta U$  [ $\mu\text{V}$ ]) of dried xerogel **3**, as well as the monitoring of the pyrolysis under Ar by mass spectrometry of the product gases N<sub>2</sub>, CH<sub>4</sub>, and C<sub>2</sub>H<sub>3</sub>N. Heating rate: 2 K min<sup>-1</sup>.

mass spectrometry were identified as predominantly methane ( $m/z$  16) and acetonitrile or methyl isonitrile ( $m/z$  41), and their fragments. Between 850 and 1120 °C there was a further mass loss of about 10%, which is attributed to the cleavage of nitrogen (Figure 2).

FT-IR investigations of samples annealed at different temperatures revealed that during decomposition between 500 and 600 °C the deformation vibrations  $\gamma = 1270 \text{ cm}^{-1}$  of the Si-CH<sub>3</sub> groups were not detected after thermal treatment. After annealing of **3** above 800 °C the intensity of the carbodiimide vibrational band at  $2152 \text{ cm}^{-1}$  decreased continuously; however, it was still detectable by FT-IR spectroscopy at 1200 °C.

The thermoanalytical and spectroscopic results correlate very well with the elemental analytical data of **3**: the elemental composition of **3**, SiC<sub>2.5</sub>N<sub>3</sub>H<sub>3</sub> changes to SiC<sub>1.23</sub>N<sub>2.50</sub> and to SiC<sub>1.12</sub>N<sub>1.63</sub> after tempering at 700 and 1200 °C, respectively.

Xerogel **3** is very sensitive to hydrolysis on account of the carbodiimide groups. In contrast to organic diimides, **3** does not react with formation of a urea derivative, but with hydrolytic cleavage of the silyl groups [Eqs. (e) and (f), respectively].<sup>[8]</sup>



There is no indication of the presence of the carbonyl vibration of the urea derivative in the FT-IR spectra. After a short exposure of **3** to air, the IR spectrum displays a broad band at  $3272 \text{ cm}^{-1}$  (SiO-H and N-H), an intense band at  $1063 \text{ cm}^{-1}$  (Si-O-Si), and a band at  $1578 \text{ cm}^{-1}$  (H<sub>2</sub>N-CN). The shift of the vibrational bands at  $2152 \text{ cm}^{-1}$  (carbodiimide group) to  $2264 \text{ cm}^{-1}$  (cyanamide) points to hydrolysis in accord with Equation (f).

The anhydrous sol-gel process allows the implementation of a whole series of technologically relevant production processes, which are already known from conventional sol-gel techniques. At the moment we are working on the synthesis of silicon carbide ceramics in the form of nanospherical powders, monolithic structural parts, fibers, and membranes as well as on the coating and infiltration of porous substrates. In addition, the transfer of this novel sol-gel process to other elements is under further investigation.

### Experimental Section

All the reactions were carried out in pre-heated glass vessels in an anhydrous stream of argon. The samples for the IR (KBr) and Raman investigations were prepared and measured under inert gas. The STA measurements (Netzsch 429, mass spectrometer: Balzers QMG 420) were performed under helium with a heating rate of 2 K min<sup>-1</sup>.

**2: Method a:** Cyanamide (2.5 mol, 105 g) in anhydrous THF (150 mL) was slowly added dropwise with vigorous stirring to hexamethyldisilazane (2.5 mol, 403 g). The reaction was initiated by gentle heating, which led to the evolution of ammonia. The remaining dissolved cyanamide was subsequently added dropwise very slowly at room temperature. After the evolution of ammonia was complete, the reaction mixture was heated to reflux for about 1.5 h until no more gas was evolved under these conditions. The solid components that had formed were filtered off under inert gas, and the filtrate concentrated, followed by fractional distillation of the residue (twice) over a 30 cm Vigreux column. At 164 °C, 377 g (2.03 mol, 81% yield) **2** was obtained. – **Method b** [10]: A mixture of dicyanodiamide (42 g), hexamethyldisilazane (177 g), and ammonium sulfate (0.2 g) was heated to reflux for 8 h. Distillation (twice) over a Vigreux column at 164 °C gave 134 g (72%) **2**. The spectroscopic data correspond to those given in ref. [8, 9].

[MeSi(NCN)<sub>1.5</sub>]<sub>n</sub> (gel): **2** (20.0 g, 107 mmol) was treated with **1** (10.7 g, 71.6 mmol) under inert gas. After addition of pyridine (566 mg, 10.7 mmol), the mixture was heated to 90 °C. The gel point was reached after 13 h. The reaction mixture was aged at 45 °C. The gel point could be changed by varying the amount of pyridine added and/or the reaction temperature. At room temperature and with 10.7 mmol of pyridine, the reaction mixture gelled after 50 d. After completion of the aging process, excess liquid was decanted off, and the remaining liquid evaporated at 50 °C under inert gas, to produce a transparent, shaped xerogel. FT-IR (KBr):  $\tilde{\nu} = 2965$  (SiMe),  $2152$  (NCN),  $1270$  (SiMe),  $748 \text{ cm}^{-1}$  (SiN); Raman:  $\tilde{\nu} = 2974$  (SiMe),  $2906$  (SiMe),  $1533 \text{ cm}^{-1}$  (NCN); <sup>29</sup>Si CP/MAS-NMR (300 MHz):  $\delta = -62.3$ ; elemental analysis [11] (calcd for C<sub>2.5</sub>H<sub>3</sub>N<sub>3</sub>Si (103.16): C 29.11, N 40.73, O 0.00, Si 27.23): C 28.75, N 38.3, O 0.28, Si 26.9; (700 °C): C 19.0, N 44.8, O 0.26; pyrolytate (1200 °C): C 21.1, N 34.4, O 0.32.

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## Asymmetric Mannich Synthesis of $\beta$ -Amino Acids with Two New Stereogenic Centers at the $\alpha$ and $\beta$ Positions\*\*

Horst Kunz,\* Andreas Burgard, and Dirk Schanzenbach

Dedicated to Professor Leopold Horner on the occasion of his 85th birthday

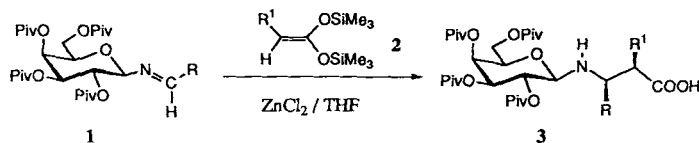
Chiral  $\beta$ -amino acids are important constituents of natural products and drugs, for example peptides,<sup>[1]</sup> antibiotics,<sup>[2]</sup> and cytostatics such as taxol.<sup>[3]</sup> In addition, they can be converted into  $\beta$ -lactams, which are a prominent class of antibiotics themselves.<sup>[4]</sup> By virtue of this background, the asymmetric synthesis of chiral  $\beta$ -amino acids has been receiving increasing attention. Apart from stereoconservative strategies starting from enantiomerically pure  $\alpha$ -amino acid derivatives,<sup>[5, 6]</sup> conjugate addition reactions of amines and amides with  $\alpha,\beta$  unsaturated carboxylic acid derivatives<sup>[5, 7]</sup> and reactions of imines with ester enolate equivalents<sup>[5, 8–12]</sup> have been employed in the stereoselective synthesis of these compounds.  $\beta$ -Amino acids containing stereogenic centers at the  $\alpha$  and  $\beta$  positions have been synthesized by a Michael addition and subsequent alkylation.<sup>[13]</sup> Alternatively, the reaction of chiral ester enolates<sup>[8, 10–12]</sup> with imines often leads directly to  $\beta$ -lactams.<sup>[11, 12]</sup> In some cases, amino acid thioesters<sup>[10]</sup> or *N*-aryl  $\beta$ -amino acid esters<sup>[8]</sup> have been isolated as intermediates.

We have found that the zinc chloride-catalyzed Mannich reaction of 2,2-disubstituted silyl ketene acetals with *N*-galactosylaldimines furnishes  $\beta$ -amino acid esters in high yield and diastereoselectivity.<sup>[9]</sup> A further advantage of this synthesis is that the auxiliary can be removed and recovered by simple acidolysis of the *N*-glycosidic bond. Unfortunately, this process can not be applied to prochiral monosubstituted silyl ketene acetals with comparable success. In the case of sterically less hindered silyl ketene acetals, zinc chloride catalyzes a rapid  $O \rightarrow C$  silyl shift before the reaction with the imine can take place.

However, a general access to  $\beta$ -amino acids with two new stereogenic centers is provided by the reaction of *N*-galactosyl-

imines **1** with bis(*O*-trimethylsilyl) ketene acetals<sup>[11,4]</sup> in the presence of zinc chloride in THF (Table 1). As a rule, yields and diastereoselectivities of these Mannich reactions between two prochiral components are high. Without exception, only two of the four possible diastereomers are formed. In most cases one of them is obtained in large excess.

Table 1. Asymmetric Mannich synthesis of  $\alpha$ -branched  $\beta$ -amino acids.



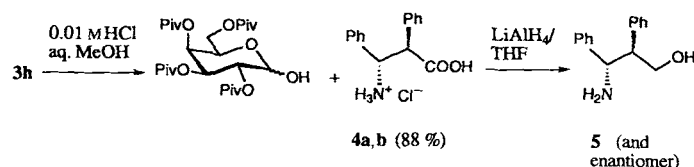
1/2	R	R <sup>1</sup>	T [°C]/t [h]	3	Yield [%]	erythro:threo [a]
a/a	Ph	Me	0/144	a	45	>20:1:0:0
b/a	3-Cl-Ph	Me	-30/48	b	94	>20:1:0:0
c/a	4-F-Ph	Me	-30/48	c	88	>20:1:0:0
d/a	4-Me-Ph	Me	-30/48	d	90	>20:1:0:0
e/a	2-Napht	Me	0/96	e	97	3:1:0:0
f/b	4-Cl-Ph	Et	-30/48	f	90	10:1:0:0
g/c	<i>n</i> -pentyl	Ph	-30/96	g	72	15:1:0:0
a/c	Ph	Ph	-30 → 20/16	h	68	8:1:0:0
f/c	4-Cl-Ph	Ph	-30/72	i	94	18:1:0:0

[a] 400 MHz <sup>1</sup>H NMR of crude product. Due to the betaine structure of the products, no satisfactory separation could be achieved by HPLC.

It is noteworthy that naphthaldimine **1e** and benzaldimine **1a** show low reactivity and only convert at about 0 °C. Nevertheless, the reaction of **1a** with the bis(silyl) ketene acetal **2a**, derived from propionic acid, to give **3a** proceeds with excellent diastereoselectivity. This also holds true for the reaction of **2a** with imines of substituted benzaldehydes. A second diastereomer was not unequivocally detected for products **3b–3d**. The *N*-galactosylimines **1b–1d** and **1f** as well as the aliphatic compound **1g** even react with the more demanding bis(silyl) ketene acetals with high diastereoselectivity. After conversion into the methyl esters with diazomethane, separation or a high degree of enrichment of the diastereomeric  $\beta$ -amino acid derivatives can be achieved.

In order to assign the configuration of the  $\beta$ -amino acids **3**, 2,3-diphenyl- $\beta$ -alanine (**4**) is released from **3h** with 1 *N* HCl in methanol. Subsequent reduction with lithium aluminum hydride yields 3-amino-2,3-diphenylpropanol (**5**), for which all four stereoisomers have been described.<sup>[15, 16]</sup>

The <sup>1</sup>H NMR spectrum of **4** shows that the two diastereomers of **3h** (ratio 8:1, Table 1) contain enantiomers of the  $\beta$ -amino acid **4**. Comparison of the optical rotation value and the <sup>1</sup>H NMR spectrum of **5** with data reported in the literature<sup>[15, 16]</sup> proves that the *erythro* compounds **4a** and **4b** have been formed (Table 2) with **4a** (2*R*,3*S*) as the favored enantiomer. Provided that no epimerization occurs during reduction, this assignment of configuration should apply to all the  $\beta$ -amino acids **3** (Table 1).



Scheme 1. Determination of configuration of the  $\beta$ -amino acids **3** by release of **4** from **3h** and subsequent reduction to **5**; only **4a** is shown.

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