

SYNTHESIS OF MONOMERIC AND OLIGOMERIC CARBODIIMIDES WITH POLYSILANE AND SILOXANE FRAGMENTS

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Summary

Bis(di- and trisilanyl)carbodiimides $R-N=C=N-R$ [$R = Me_3Si_2$, $Me_3Si-SiMePh$, $Me_3Si-Si(n-Bu)_2$, $(Me_3Si)_2SiMe$] and oligomeric carbodiimides $\{SiMe_2SiMe_2-N=C=N\}_n$, $\{SiMe_2OSiMe_2N=C=N\}_n$ have been obtained from the corresponding chlorosilanes and silver cyanamide. Alternative methods for the synthesis of these compounds using cyanamide, organogermanium- and organotin carbodiimides have been proposed. Synthesis of 1,1-di-n-butyl-1-chlorotrimethylsilane is described.

Introduction

Organosilylcarbodiimides have valuable practical properties and can be used as effective hydro- and thermostabilizers for polyurethanes, thermostabilizers for polyvinylchloride compositions, components of isolation covers, high-temperature dye-stuffs, radiation-resistant hermetic materials, active intermediates for the synthesis of not readily accessible substances, etc. [1]. Here we report on the preparation of new monomeric and oligomeric carbodiimides containing di- and trisilanyl fragments and tetramethylidisiloxane group in the molecule.

Results and discussion

Bis(di- and trisilanyl)carbodiimides (IIa–IIId) were synthesized by the reaction of corresponding chlorodi- and trisilanes with silver cyanamide [2]. This reaction is

$$2Me_3SiSiRR'Cl + Ag_2NC\equiv N \rightarrow Me_3SiSiRR'-N=C=N-SiRR'SiMe_3 + 2AgCl$$

Ia, $R = R' = Me$	IIa
Ib, $R = Me, R' = Ph$	IIb
Ic, $R = R' = n-Bu$	IIc
Id, $R = Me, R' = SiMe_3$	IIId

accompanied by the rapid conversion of the green-yellow residue of Ag_2NCN into

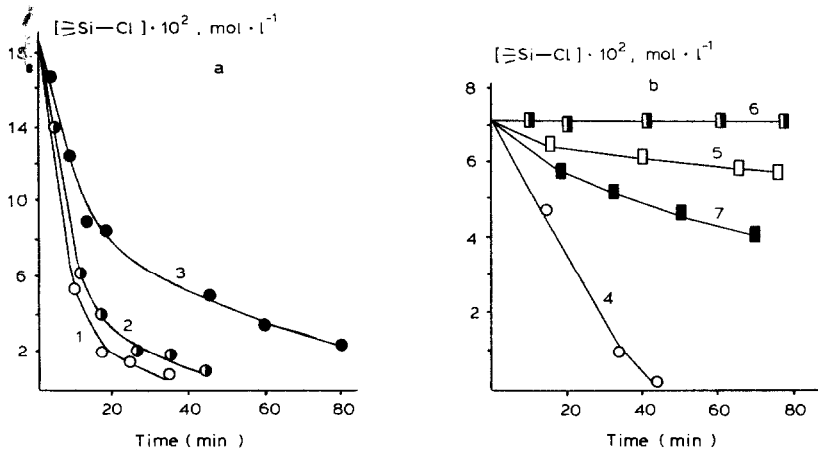
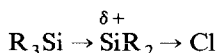


Fig. 1. Kinetic curves for the consumption of organochlorosilanes in reactions with silver cyanamide (a) and lithium trimethylsilylanolate (b) (benzene:ether 26:5, 20°C): 1, $\text{Me}_5\text{Si}_2\text{Cl} + \text{Ag}_2\text{NCN}$, 2:1; 2, $(\text{Me}_3\text{Si})_2\text{SiMeCl} + \text{Ag}_2\text{NCN}$, 2:1; 3, $\text{Me}_3\text{SiCl} + \text{Ag}_2\text{NCN}$, 2:1; 4, $\text{Me}_5\text{Si}_2\text{Cl} + \text{Ag}_2\text{NCN}$, 1:1; 5, $\text{Me}_5\text{Si}_2\text{Cl} + \text{Me}_3\text{SiOLi}$, 1:1; 6, $(\text{Me}_3\text{Si})_2\text{SiMeCl} + \text{Me}_3\text{SiOLi}$, 1:1; 7, $\text{Me}_3\text{SiCl} + \text{Me}_3\text{SiOLi}$, 1:1.

white AgCl and is complete after 30–50 min in ether or ether/benzene at 20°C. Progress of the reaction was followed by monitoring the consumption of chlorosilane and the accumulation of the corresponding carbodiimide by GLC. Kinetic curves for the consumption chlorosilane in the reaction with silver cyanamide and lithium trimethylsilylanolate are presented in Fig. 1.

Analysis of the kinetic curves (Fig. 1a) suggests that pentamethylchlorodisilane (Ia) and 2-chloroheptamethyltrisilane (Id) interact with Ag_2NCN more rapidly than trimethylchlorosilane.

It is known [3–5], that the chlorodisilanes, $\text{R}_3\text{SiSiR}_2\text{Cl}$, are less active in nucleophilic substitution reactions than chlorosilanes R_3SiCl (nucleophiles Me_3COLi , Me_3COOLi , Me_3SiOLi , $\text{Me}_3\text{COC(O)OLi}$, $\text{Me}_3\text{COOC(O)OLi}$). This fact can be explained as follows: the positive charge induced by the chlorine atom on the silicon atom is lowered by the donor R_3Si group, therefore the nucleophilic attack on the silicon atom is inhibited.



2-Chloroheptamethyltrisilane (Id) which has two donor R_3Si groups in the molecule does not react with Me_3SiOLi at room temperature. However, chlorosilanes Ia–d readily interact with Ag_2NCN , in spite of its insolubility in organic solvents. The ease of reaction with silver cyanamide can be explained in accordance with [6], either by the counterion influence (Ag^+), or by the soft nature of the resonance-stabilized nucleophilic particle $^{2-}\text{N}-\text{C}\equiv\text{N} \leftrightarrow \text{N}=\text{C}-\text{N}^{2-}$, or by a combination of these two factors.

Since silver cyanamide is an expensive and explosive reagent [1], we have developed other methods for the synthesis of polysilylcarbodiimides using cheaper and less dangerous compounds. Reaction of organochloropolysilanes with cyana-

TABLE 1
PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR THE COMPOUNDS OBTAINED

Compound	B.p. (°C/mmHg)	n_D^{20}	d_4^{20}	M_R_D		Analysis (Found) (%)			Empirical formula	Calc (%)		
				Found	calc	C	H	Si		C	H	Si
Ic ^a	87-89/1	1.4651	0.8785	78.98	78.63	52.72	10.85	22.21	C ₁₁ H ₂₇ ClSi ₂	52.64	10.84	22.38
IIa	95-96/3	1.4745	0.8372	101.76	99.10	43.65	10.10	37.00	C ₁₁ H ₃₀ N ₂ Si ₄	43.64	9.99	37.11
IIb	170-172/3	1.5390	0.9684	138.09	138.06	58.58	7.59	26.70	C ₂₁ H ₃₄ N ₂ Si ₄	59.09	8.03	26.32
IIc	168-170/3	1.4850	0.8652	156.02	154.88	58.37	11.10	23.83	C ₂₃ H ₅₄ N ₂ Si ₄	58.65	11.56	23.85
IIId	120-122/3	1.5010	0.8715	141.64	141.07	43.52	10.01	40.52	C ₁₅ H ₄₂ N ₂ Si ₆	43.00	10.10	40.22
III	-	1.4770 ^b	-	-	-	38.48	8.09	36.33	(C ₅ H ₁₂ N ₂ Si ₂) _n	38.42	7.74	35.93
		1.5130 ^c										
IV	-	1.4660 ^b	-	-	-	34.60	7.08	32.73	(C ₃ H ₁₂ N ₂ OSi ₂) _n	34.85	7.02	32.60
		1.4573 ^c										
V ^d	144-146/1	1.5022	0.9714	77.46	77.80	66.02	9.05	11.12	C ₁₄ H ₂₃ ClSi	65.97	9.10	11.02
VI	145-147/3	1.5060	0.8759	99.22	99.23	69.42	10.48	20.35	C ₁₇ H ₃₂ Si ₂	69.78	11.02	19.02

^a Cl found 14.00%, calc 14.13%. ^b The oligomers were obtained from Ag₂NCN. ^c The oligomers were obtained from H₂NCN in the presence of Et₃N. ^d Cl found 13.72%; calc 13.91%.

mide in the presence of an equimolar amount of triethylamine proved to be the most convenient. The reaction mixture was stirred in boiling ether for 5 h and yield $2\text{Me}_3\text{SiSiMe}_2\text{Cl} + \text{H}_2\text{NCN} + 2\text{Et}_3\text{N} \rightarrow \text{IIa} + 2\text{Et}_3\text{N} \cdot \text{HCl}$

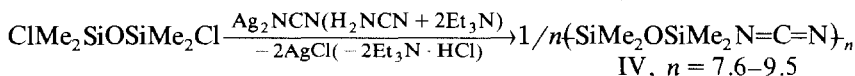
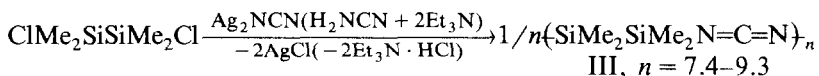
of the expected carbodiimide (IIa) was 73%. Carbodiimide yield decreased to 47%, when the reaction was carried out with pyridine.

Compound IIa was also synthesized by a transmetallation reaction of organometallic carbodiimides by a published procedure [7]. The reaction was carried out without solvents at a reactant ratio of 2:1 for 30 min. Pentamethylchlorodisilane $2\text{Me}_3\text{SiSiMe}_2\text{Cl} + \text{R}_3\text{MN}=\text{C}=\text{NMR}_3 \rightarrow \text{IIa} + 2\text{R}_3\text{MCl}$

$\text{R}_3\text{M} = \text{Et}_3\text{Ge}, n\text{-Bu}_3\text{Sn}$

does not react with lead cyanamide (PbNCN) in boiling ether or dimethylformamide.

Carbodiimides (IIa-d) are colourless liquids relatively stable to atmospheric oxygen and moisture. Their properties are presented in Table 1. Reaction of 1,2-dichlorotetramethyldisilane and 1,3-dichlorotetramethyldisiloxane with cyanamide or its silver salt gives oligomeric organosilylcarbodiimides (III, IV) in 80% yield. Compounds III and IV which probably have the cyclic structure are colourless

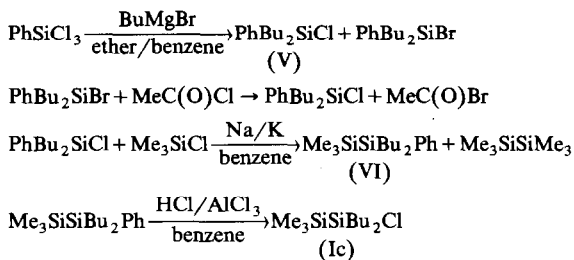


viscous liquids and are relatively stable in air. Cryoscopic determination of molecular masses in benzene shows that the degree of polymerization (n) varies from 7.4 to 9.5 and does not differ significantly from that for carbodiimides of $(\text{R}_2\text{SiN}=\text{C}=\text{N})_n$ ($n = 6.4-8.4$) [8]. The structure of the compounds II-IV synthesized were investigated by IR spectroscopy (Table 2). The compounds II-IV show an intense absorption band at $2175-2220 \text{ cm}^{-1}$ ($\text{N}=\text{C}=\text{N}$), but no band at $2260-2280 \text{ cm}^{-1}$ ($=\text{N}-\text{C}\equiv\text{N}$), confirming their carbodiimide structure.

Carbodiimide II-IV are hydrolyzed after exposure to atmospheric moisture for a long time to give $\text{H}_2\text{N}-\text{C}\equiv\text{N}$. The Si-Si bond is not oxidized by atmospheric oxygen, this is confirmed by the absence of an absorption band at $1060-1080 \text{ cm}^{-1}$ (Si-O-Si). 1,1-Di-*n*-butyl-1-chlorotrimethyldisilane (Ic) used for the synthesis of carbodiimide (IIc) was obtained according to Scheme 1. Organochloropolysilanes (Ia, Ib, Id) were obtained by standard procedures [9,10].

TABLE 2
IR SPECTRA (ν, cm^{-1}) FOR ORGANOSILICON CARBODIIMIDES

Compound	N=C=N	C-H	Me ₃ Si	Other signals
IIa	2180	2945, 2890	1240, 830	
IIb	2175	2945, 2885	1245, 860, 835	3060, 3040 (Ph), 1110 (Ph-Si)
IIc	2180	2950, 2920, 2860	1240, 850, 830	1460, 1370, 1180, 1080 (Bu-Si)
IId	2175	2950, 2890	1245, 850, 835	
III	2205	2940, 2880	1245, 820	
IV	2215	2960, 2890	1260, 830, 800	1065 (Si-O-Si)



SCHEME 1

Experimental

The IR spectra were recorded on Perkin-Elmer 577 and UR-20 spectrophotometers between KBr plates, GLC analysis of the reaction mixtures and checks on purity of the compounds obtained were performed on a Tsvet-104 gas chromatograph, equipped with 2 m stainless steel column packed with 5% SE-30 on Chromatone N-AW-DMCS.

Bis(di- and trisilanyl)carbodiimides (IIa, b, c, d)

(1) A mixture of 7.37 g (44.2 mmol) of pentamethylchlorodisilane (Ia) and 5.67 g (22.1 mmol) of silver cyanamide in 60 ml of dry ether was subjected to vigorous shaking in a sealed ampule at room temperature for 1 h. 6.10 g (42.6 mmol, 96%) of AgCl separated, the ether was removed by distillation and the residue was distilled in vacuum yielding 6.3 g (20.8 mmol, 94%) of bis(pentamethyldisilanyl)carbodiimide (IIa).

Bis(1-phenyltetramethyldisilanyl)carbodiimide (IIb), bis(1,1-dibutyltrimethyldisilanyl)carbodiimide (IIc) and bis(heptamethyltrisilan-2-yl)carbodiimide (IId) were obtained similarly in yields from 90 to 95%.

(2) A solution of 2.10 g (50.0 mmol) of cyanamide and 10.10 g (100.0 mmol) of triethylamine in 50 ml of ether was added dropwise to 16.70 g (100.1 mmol) of compound Ia in 50 ml of ether during 10 min. The reaction mixture was boiled with stirring for 1 h and 13.16 g (95.7 mmol, 95%) of hydrochloric triethylamine was filtered off. The ether was removed from the filtrate by distillation and the residue was fractionated in vacuum yielding 10.00 g (33.1 mmol, 66%) of compound IIa. Similarly, 1.20 g (4.0 mmol, 47%) of carbodiimide IIa was obtained from 2.85 g (17.1 mmol) of pentamethylchlorodisilane, 0.36 g (8.6 mmol) of cyanamide and 1.34 g (17.0 mmol) of pyridine in ether.

(3) Compound (Ia) (1.10 g, 6.6 mmol) was mixed with 2.04 g (3.3 mmol) of bis(tris-n-butylstannyl)carbodiimide and refluxed for 30 minutes. Then the reaction mixture was distilled in vacuum, and after redistillation, 0.65 g (2.15 mmol, 65%) of carbodiimide (IIa), b.p. 95–96°C/3 Torr and 1.65 g (5.07 mmol, 77%) of tributylchlorostannane, b.p. 108–110°C/3 Torr were isolated. Similarly, 2.02 g (10.4 mmol, 71%) of triethylchlorogermane, b.p. 43–45°C/3 Torr and 1.54 g (5.1 mmol, 70%) of compound IIa, b.p. 86–88°C/2 Torr were obtained, when 2.43 g (14.6 mmol) of compound Ia was treated with 2.61 (7.3 mmol) of bis(triethylgermyl)carbodiimide.

Oligomeric carbodiimides III and IV

(1) A mixture of 1.86 g (9.94 mmol) of 1,2-dichlorotetramethyldisilane, 2.55 g (9.97 mmol) of silver cyanamide and 20 ml of ether was vigorously shaken in a sealed ampule at room temperature for 6 h. The next day the ampule was opened, 2.84 g (19.81 mmol, 99%) of AgCl was filtered off, then the ether was distilled off, the residue was heated at 120–140 °C/3 Torr for 1 h and centrifuged, yielding 1.22 g (78%) of oligomeric disilanylcarbodiimide (III) in the form of a colourless transparent viscous liquid. Found: *M* 1163 (cryoscopy in benzene). Similarly, 1.43 g (74%) of oligomeric disiloxane carbodiimide (IV) was obtained when 2.26 g (11.1 mmol) of 1,3-dichlorotetramethyldisiloxane was treated with 2.85 g (11.1 mmol) of silver cyanamide. Found: *M* 1306 (cryoscopy in benzene).

(2) A mixture of 3.50 g (18.7 mmol) of 1,2-dichlorotetramethyldisilane, 0.78 g (18.6 mmol) cyanamide, 3.78 g (37.4 mmol) of triethylamine and 100 ml of ether was heated with stirring for 30 min. 4.33 g (31.5 mmol, 85%) of hydrochloric triethylamine was then filtered off. The ether was removed from the filtrate by evaporation and the residue was heated at 140 °C/3 Torr for 30 min and centrifuged. 2.00 g (69%) of compound III was obtained. Found: *M* 1455. Similarly, 3.02 g (84%) of oligomeric disiloxane carbodiimide (IV) was obtained when 4.23 g (20.8 mmol) of 1,3-dichlorotetramethyldisiloxane was treated with 0.88 g (20.9 mmol) of cyanamide and 4.21 g (41.7 mmol) of triethylamine. Found: *M* 1628.

Phenyldi-n-butylchlorosilane (V)

Phenyltrichlorosilane 192 g (0.9 mol) was quickly added with stirring and cooling in icy water to Grignard reagent which had been prepared from 45 g (1.85 mol) of magnesium, 236 g (1.72 mol) of butyl bromide in 700 ml of ether. The reaction mixture was then heated for 12 h and filtered. After the ether had been removed by evaporation, 600 ml of benzene was added to the residue and the mixture boiled for 7 d. The resulting precipitate was filtered off, and the benzene was distilled off. The residue consisted of some liquid and a small amount of solid. After filtering, the filtrate was distilled in vacuum, and a broad fraction, b.p. 136–153 °C/6 Torr was collected. GLC analysis showed that this fraction was a mixture of two compounds: PhBu₂SiCl and PhBu₂SiBr. Then the isolated fraction was boiled with a 4-fold volume excess of acetyl chloride, the mixture of MeCOCl and MeCOBr was distilled off, and the residue was distilled with the use of a deflegmator. Redistillation gave 86.8 g (0.34 mol, 38%) of phenyldi-n-butylchlorosilane (V). GLC analysis showed that the purity of the main product was 98%.

1-Phenyl-1,1-di-n-butyltrimethyldisilane (VI)

A mixture 15.0 g (0.65 mol) of sodium, 90.0 g (2.30 mol) of potassium and 400 ml of benzene (benzene had been distilled over sodium) was placed in a three-necked flask fitted with a Hershberg mixer, a reflux condenser and a dropping funnel. The mixture was heated under argon until a liquid alloy was formed. Then the mixer was actuated, and the sodium/potassium alloy was dispersed. The flask was cooled to 50 °C and a solution of 79.0 g (0.31 mol) of PhBu₂SiCl in 237.0 g (2.18 mol) of trimethylchlorosilane was slowly added dropwise with vigorous stirring. The reaction mixture started boiling immediately upon addition and continued to do so for about 1.5 h. The mixture was then boiled with stirring for 6 days. Each day (after the mixture had been allowed to settle down overnight) a 2 ml sample was taken

from the liquid phase to determine the concentration of changed chlorosilanes. This was determined by mixing the sample with 30 ml of distilled water, and formed hydrochloric acid which was generated was titrated with 0.1 N aq. KOH. It was established that after 6 d the mixture of chlorosilanes had reacted completely with Na/K alloy. The reaction mixture was then filtered, the benzene and hexamethyldisilane were removed by distillation, and the residue distilled in vacuum. The fraction with b.p. 125–157°C/3 Torr was collected. The isolated fraction was twice distilled by use of a deflegmator yielding 30.2 g (0.10 mol, 32%) of compound (VI). GLC analysis showed that the purity of the main product was 98.5%.

1.1-Di-n-butyl-1-chlorotrimethyldisilane (Ic)

To 25.4 g (86.9 mmol) of compound (VI), in 250 ml of benzene, was added 1.30 g (9.7 mmol) of anhydrous aluminium chloride. Dry HCl was bubbled through the solution for 14 h and GLC analysis of the reaction mixture showed that all the phenyldisilane (VI) was converted into chlorodisilane during this time. The benzene was removed by distillation and the residue was fractionated in vacuum yielding 17.9 g (71.4 mmol, 82%) of compound (Ic).

The kinetics of the reactions of organochlorosilanes with silver cyanamide and lithium trimethylsilanolate (Fig. 1)

Ag₂NCN (0.1–0.2 g, 0.39–0.78 mmol) and a measured amount of solvent were thermostatted at 20°C. The required amount of chlorosilane solution was added with stirring. Samples for GLC analysis were periodically taken from the liquid phase. Since the Me₃SiOLi was dissolved in a benzene/ether mixture, this solution was used in the kinetic investigation.

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