

Vinylcarbo-cyclosiloxane Reaction with Si-H-organodisiloxanes

Liviu Sacarescu, Nicolae Luchian, Mihai Marcu, Rodinel Ardeleanu and Gabriela Sacarescu
Institute of Macromolecular Chemistry "Petru Poni", 6600 Iasi, Romania

Received: 20 November 1994; accepted 26 March 1995

ABSTRACT

New cyclo-linear organosiloxanes are prepared through the hydrosilylation reaction of vinylcarbo-cyclosiloxane with organomethyl(H)disiloxanes using chloroplatinic acid as catalyst. These products are characterized by IR, ¹H-NMR spectroscopy, molecular weight, elemental analysis which confirm the predicted chemical structures.

Key Words: cyclocarbosiloxanes, cyclic organosilicon, hydrosilylation, cyclo-linear-organodisiloxanes

INTRODUCTION

In the last few years, in the field of organosilicon chemistry attention has been focussed on structurally complex polymers. Linear, cyclo-linear and spiro-cyclic polyorganosiloxanes have been obtained both by ionic polymerization and polycondensation [1].

The polyhydrosilylation reaction has seldom been used in polymer synthesis though it provides a possible method for obtaining a great variety of polymer structures. In these cases, the backbones contain, along with the siloxane bond, ethylene bridges [2]. In practice many works present the hydrosilylation as an addition reaction of unsaturated compounds to polymers with Si-H groups to obtain polycarbosiloxane structures.

Polymerization data on cyclocarbosiloxanes are scarce and most of them give information about the well-known ring-opening mechanism with different kinds of acids or bases as catalysts [3]. The synthesis of polycyclic structures containing both siloxane and hydrocarbon

segments seems to be a more challenging research field and has spectacular applications [4].

This work is our first attempt to obtain a disiloxane-cyclocarbosiloxane model compound through hydrosilylation of a cyclic vinylcarbo-siloxane compound.

EXPERIMENTAL

Materials

Bromobenzene (>95.5 % wt.), butylbromide (>93.0 % wt.) and p-tolylbromide (>95.0 % wt.) were supplied by Merck. They were freshly distilled before use.

Methyl-H-dichlorosilane (> 98% wt.) was supplied by Fluka and also distilled before use.

Apparatus

IR spectra were registered with a Perkin-Elmer 577 spectrophotometer in the 4000-200 cm⁻¹ region using KBr pellets.

¹H NMR spectra were registered with a

Jeol-60 MHz spectrometer in CDCl_3 (TMS).

Molecular weights were obtained through the cryoscopic method in benzene.

Synthesis

Organomethyl(H)disiloxanes (I,II,III)

Si-H-organochlorosilanes were synthesized via Grignard reactions from methyl(H)dichlorosilane with bromobenzene (II) butylbromide (I) and p-tolylbromide (III), respectively [5] and purified on a 20 cm Vigreux column. The Si-H-disiloxanes were obtained through aqueous hydrolysis reaction by adding Si-H-organochlorosilanes dropwise, on cold water, under vigorous stirring. When the reaction stopped, ethyl ether was added and the mixture was washed to eliminate the acidity. The solvent was distilled under normal conditions and the products, Si-H-disiloxanes, were first carefully dried on Na_2SO_4 and then distilled at 5-8 mm Hg vacuum.

Vinylcyclo-carbosiloxane (IV)

1-Vinyl-1,3,3-trimethyl-4,4-diphenyl-3,5-dioxo-1,3-disilacyclopentane.

Vinylcyclo-carbosiloxane was prepared using a previously described method [6] from benzophenone dilithium compounds with vinylmethyl-dichlorosilane-dimethyldichlorosilane mixture in anhydrous ethyl ether by the high dilution coupling technique. This product was then purified by recrystallization from ethyl alcohol-acetone solution. The vinylcyclo-carbosiloxane is a crystalline, white substance soluble both in polar and nonpolar solvents.

Bis {organomethyl (cyclocarbosiloxanethylen)} disiloxane (V, VI, VII)

Using organomethyl(H)disiloxanes and vinylcyclo-carbosiloxane dicyclo-carbosiloxandisiloxane products were synthesized through a hydrosilylation reaction.

Reaction Scheme

Vinylcyclo-carbosiloxane, (19.5 g (60 mmol)) was dissolved in 50 mL of anhydrous toluene in a 100 mL three neck round-bottom flask equipped with condenser and argon inlet. The solution was heated to 75-80°C. After 30 min., 0.8 mL (8 mmol

Pt) of a 0.01M hexachloroplatinic acid solution in isopropyl alcohol was added. After another 30 min., 60 mmol organo-H-disiloxane was added. The reaction time was determined using IR spectroscopy analysis of the Si-H group. The solution was cooled, filtered, and distilled. The colorless product was then characterized by IR, ^1H NMR, molecular weight determination and elemental analysis.

Yields: 60% (V), 55% (VI), 50% (VII).

RESULTS AND DISCUSSION

Characteristic IR absorption bands [7] are displayed in Table 1. It is obvious that the new products no longer have the $-\text{CH}=\text{CH}$ -infra-red absorption band at 950 cm^{-1} . The Si-O-Si bond absorbance around 1080 cm^{-1} is present at the same intensities both in reagents (I-IV) and products (V-VII). In the 1140 cm^{-1} region, the characteristic dental peak for Si- CH_2 - CH_2 -Si polycarbosilane chain is present but not very clearly expressed because of the Si- C_6H_5 absorption band vicinity at 1125 cm^{-1} .

^1H NMR spectra for reagents and products are shown in Table 2. The characteristic shifts for the Si- CH_2 - CH_2 -Si appear in the 4.0-6.0 ppm region [7].

Spectral analysis reveals that no side reactions occur and the hydrosilylation process has a normal course, with slight differences regarding yields and reaction times being a consequence of the steric hindrances of the bulky phenyl and p-tolyl groups at the reaction centers.

Further investigations were made by molecular weight determinations and elemental analysis (Table 3).

It is evident that the experimental results are in accordance with the calculated values. These are the reasons which made us to consider for reagents and products the structures presented in the reaction scheme.

All the products are non-coloured viscous liquids. The physico-chemical properties for both reagents and products are presented in Table 4.

Table 1. Infra-red absorption spectra (cm^{-1}).

Comp. / Assign.	I	II	III	IV	V	VI	VII
Si-CH=CH ₂				454			
Si-O-Si				550			
C-H	690	690	690	695	710	700	700
Si-CH ₃	805	780	780	780	800	780	780
pCH ₃ C ₆ H ₅			800				775
CH	875				900	910	910
Si-CH=CH ₂				950			
Si-O-Si	1015	1020	1020	980	1025	1100	1100
Si-CH ₂ -Si					1140	1150	1140
Si-C ₆ H ₅		1125				1125	1125
Si-CH ₃	1255	1260	1265	1255	1260	1265	1260
Si-CH ₃	1390	1395	1400	1350	1400	1400	1400
CH	1450				1470		
C-C	1480	1485	1500	1500	1500	1500	1500
C-C	1585	1600	1585		1580	1600	1580
Si-CH=CH ₂				1900			
Si-H	2185	2215	2195				
C-H arom.		2900	3000	3000	2950	3000	3100

Table 2. ¹H NMR Spectrum data (ppm).

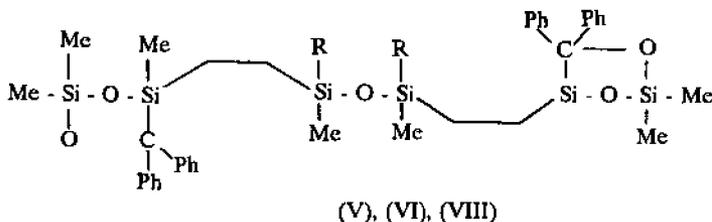
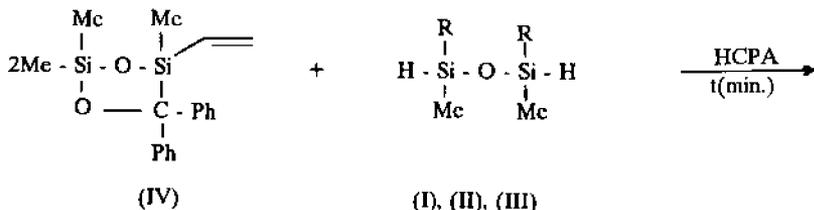
Proton / Assign.	I	II	III	IV	V	VI	VII
-CH ₃ Si-Me	0.05(s)	0.30(s)	0.30(s)	0.30(s)	0.00(s)	0.15(s)	0.15(s)
-CH ₂ -CH ₂ - bridge					4.55(s)	4.50(s)	4.50(s)
C ₆ H ₅ - Si-Ph		7.35(m)	7.15(m)			7.25(m)	7.20(m)
-CH ₃ p-Tol			2.31(d)				2.30(d)
-(CH ₂) _n -H Si-Bu	1.35(m)				1.37(m)		
-H Si-H	3.55(s)	3.50(s)	3.52(s)				
-CH=CH ₂ Si-Vi				6.02(m)			

Table 3. Molecular weight and elemental analysis data.

Comp.	Molecular weight calcd/experm.	Elemental analysis (%) calcd/experm.			
		Si	C	H	O
(I)	218/	25.68/	55.04/	11.92/	7.34/
	216.82	25.03	55.56	12.03	7.06
(II)	258/	21.70/	65.11/	6.97/	6.20/
	259.2	20.82	65.01	7.22	5.92
(III)	286/	19.58/	67.13/	7.69/	5.59/
	287.82	19.02	66.95	7.02	6.05
(IV)	326/	17.17/	66.25/	6.75/	9.82/
	324.81	17.03	66.40	6.53	9.03
(V)	870/	19.31/	63.45/	8.04/	9.19/
	859.61	19.03	63.05	7.85	8.70
(VI)	910/	18.46/	65.93/	6.81/	8.79
	904.54	18.13	65.48	6.72	8.35
(VII)	938/	17.91/	66.52/	7.03/	8.53/
	930.5	17.81	66.04	7.23	8.32

Table 4. Physico-chemical properties.

Comp.	Summary Formula	B.P. °C/mmHg	d_4^{20} g/cm ³	n_D^{20}
(I)	Si ₂ C ₁₀ H ₂₆ O	132.2	0.8125	1.4204
(II)	Si ₂ C ₁₄ H ₁₈ O	141-142.5/1	0.9751	1.4335
(III)	Si ₂ C ₁₆ H ₂₂ O	108-109/1	0.9984	1.4850
(IV)	Si ₂ C ₁₈ H ₂₂ O ₂	M.p.110-111°C		
(V)	Si ₄ C ₄₆ H ₇₀ O ₅	180-181/5	1.0334	1.4031
(VI)	Si ₄ C ₅₀ H ₆₂ O ₅	210-211/5	1.0422	1.4432
(VII)	Si ₆ C ₅₂ H ₆₆ O ₅	217-218/1	1.0451	1.4133



R = Butyl, (I); (V)
 R = Phenyl, (II); (VI)
 R = p-Tolyl, (III); (VII)

Reaction Scheme

CONCLUSION

The synthesis of polycyclic structures containing both siloxane and hydrocarbon segments are being challenged regarding polymerization method of cyclocarbosiloxanes carried through ring-opening mechanism.

The synthesis involving the formation of disiloxane-cyclocarbosiloxane model compounds through hydrosilylation of a cyclic vinyl-carbosiloxane is confirmed by the formulations obtained from experimental and spectral data.

REFERENCES

1. Mathias, L. J., Reichert, V. R., Carothers, T. W., Bozen, R. M., *Polymer Preprints*, **34**, 1, 77 (1993).

2. Zhdanov A. A., *Makromol. Chem. Suppl.*, **6**, 227 (1984).
 3. Andrianov, K. A., Delazari, N. V., Volkova, L. M., Ronsinskaya Ts. Ya., Alyavdin N. A., *Izv. Akad. Nauk SSSR, Ser. Khim.* (in Russian), 1716 (1971).
 4. Carothers, T. W., Mathias, L. J., *Polymer Preprints* **34**, 2, 538 (1993).
 5. Andrianov, K. A., Delazari, N. V., *Dokladi Akad. Nauk SSSR*, **122**, 3, 393 (1958).
 6. Luchian, N., Sacarescu, L., Rugina, T., Harabagiu, V., Cotzur, C., *Polym. Bull.*, **26**, 47 (1991).
 7. Smith, A. L., "The Analytical Chemistry of Silicones", John Wiley & Sons, Inc., P. 305 (1991).