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Cyclic organosilicon compounds

Reaction of 1,4-dilithium-1,1,4,4-tetraphenylbutane with organodichlorosilanes

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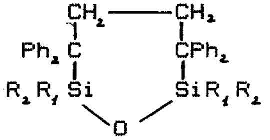
ABSTRACT

Cyclic organosilicon compounds were obtained by the coupling reaction of 1,4-dilithium-1,1,4,4-tetraphenylbutane and organochlorosilanes with general formula $R'R''SiCl_2$(R'=methyl,R''= ethyl , phenyl ,vinyl , p-tolyl).The chemical analysis,molecular weight determination , IR spectra have shown that new compounds have been formed by ring closure through a siloxane bond . The thermogravimetric analysis indicates a thermal stability of compounds up to 360°C.

INTRODUCTION

The organosilacycloalcanes are starting compounds in the synthesis of polymeric siloxane bond containing materials with interesting propreties.Different methods for the preparation of 5,6,7 or more nombered cycles were reported:addition of organohydrogensilanes to unsaturated organic compounds [1,2] or to silanes with unsaturated groups in the structure [3,6] cyclisation of dimethyl(cyclobutoxy)chlorosilane in the presence of sodium or lithium [7] , the reaction of (acetoxybutyl) methylethoxy silanes with alkalis [8,9] , thermal cyclisation of the reaction products of dimethylchlorosilane with trimethyl butenoxysilane [10] dehydration of bis[(hydroxybutyl)tetramethyl]disiloxane [11] , hydrolysis of bis-(alkyldichlorosilyl)-propane [12] or of bis-(methylchloroethoxysilyl)propane [13] with aqueous KOH solution , reaction of o-dichlorobenzene with chlorodimethyl methoxy silane and sodium [14] , reaction of 2,2,6-trimethyl-6-ethoxy-1-oxa-2,6-disilachlorohexane with acetyl chloride [15] reaction of bis-[(iodomethyl)tetramethyl]disiloxane with sodium compounds of malonic ester [16] , hydrolytic condensation of chlorodimethylethoxysilane with chloromethyl/methyl/diethoxy, silane and further processing of the reaction compounds [17]. Frequently organosilacycloalcanes are obtained by use of Grignard reagents.In this manner 1,1,3,3-tetramethyl-2-oxa-1,3- disilacycloheptane [18] and 1,1-diorgano-1-sila-2-oxa-cyclohexanes [19] were synthesized .Previously we described the coupling of 1,4-dilithium-1,1,4,4-tetraphenylbutane with diorganodichlorosilane [20] or with trichlorosilane and organotrichlorosilane [21].This paper deals with the preparation and with some physico-chemical characteristics of compounds (II a-d) resulted from the coupling reaction with dichlorodiorganosilane:



Ph= C_6H_5-
R_1= CH_3-
R_2= II_a C_2H_5-
II_b $CH_2 = CH$ -
II_c C_6H_5-
II_d p-CH_3 - C_6H_4-

EXPERIMENTAL

1,1-Diphenylethylene was prepared according to the method reported in the literature [22].1,4-Dilithium-1,1,4,4-tetraphenylbutane (I) was obtained as red crystals by stirring of 1,1-diphenylethylene in ether solution with small lithium grains. Dichloromethylethylsilane,dichloromethylvinylsilane,dichloromethyl(p-tolyl)silane and dichloromethylphenylsilane were obtained by Grignard reactions [23,24] and purified by rectification.Diethyl ether was dried over sodium wire [25] and freshly distilled before use. IR spectra were recorded by means of a Perkin Elmer model 577 spectrophotometer,within the 4000-200 cm^{-1} region. Samples were pelleted with KBr. DTA and DTG curves were registered using a MOM Paulik-Paulik-Erdey derivatograph with 9°/min,heating rate ,within a temperature range of 20-900°C.

2,7-Dimethyl-2,7-diethyl-3,3,6,6-tetraphenyl-1-oxa-2,7-disilacycloheptane.(II a)

The synthesis method was described in a previous work [20].14 g of freshly prepared 1,1-diphenylethylene,250 ml anhydrous diethylether and 1.5 g lithium were used.This mixture was stirred 20 hrs. resulting 1,4-dilithium-1,1,4,4-tetraphenylbutane as dark-red prismatic crystals.The excess of lithium was taken out and 10.8 g dichloromethylethylsilane was added dropwise to the suspension,under stirring,during 2 hrs.The reaction was continued another 130 hrs. and the white LiCl precipitate was filtered.The yellow product left after distillation of diethylether was purified from acetone-ethylic alcohol system and dried,resulting 2 g (yield:10.2%) of yellowish crystalline substance,M.p.=185°C,soluble in benzene, acetone,carbontetrachloride.
Calcd. anal. for $C_{34}H_{40}OSi_2$:C,78.46;H,7.69;Si,10.77;
mol. weight:520
Found:C,78.38;H,7.68;Si,10.56;mol. weight (cryoscopically determined in benzene):514.

2,7-Dimethyl-2,7-divinyl-3,3,6,6-tetraphenyl-1-oxa-2,7-disilacycloheptane.(II b)

To the suspension of 1,4-dilithium-1,1,4,4-tetraphenylbutane obtained from 14 g 1,1-diphenylethylene and 1.5 g lithium in 250 ml diethylether,10.6 g dichloromethylvinylsilane were added. After 130 hrs. reaction time and purification, 7.5 g (yield : 38.6%) of crystalline , yellowish product II b M.p.=118-125°C,soluble in benzene,acetone,carbon tetrachloride were obtained.
Calcd. anal. for $C_{34}H_{36}OSi_2$:C,79.07;H,6.98;Si,10.85;
mol. weight:516
Found C,78.72;H,7.04;Si,10.78;mol. weight (cryoscopically determined in benzene):522.

2,7-Dimethyl-2,3,3,6,6,7-hexaphenyl-1-oxa-2,7-disilacycloheptane.(II c)

The same procedure was used starting from 10 g 1,1-diphenylethylene,1.5 g lithium and 9 g dichloromethylphenylsilane.After 90 hrs. reaction time and purification ,7 g (yield:48.2%) of crystalline, yellowish product,M.p.=118-120°C were obtained The substance is soluble in acetone,benzene,carbon tetrachloride, diethylether.
Calcd. anal. for $C_{42}H_{40}OSi_2$:C,81.82;H,6.49;Si,9.09;
mol. weight:616
Found:C,81.32;H,6.31;Si,9.30;mol. weight (cryoscopically determined in benzene):626.

2,7-Dimethyl-2,7-di(p-tolyl)-3,3,6,6-tetraphenyl-1-oxa-2,7-disilacycloheptane.(II d)

1,4-Dilithium-1,1,4,4-tetraphenylbutane was prepared from 8 g 1,1-diphenylethylene and 1 g lithium and reacted for 130 hrs. with 4.6 g dichloromethyl(p-tolyl)silane to give after repeated purifications in acetone-ethylic alcohol system 3 g (yield: 35.8%) of substance II d.,M.p.=136-138°C.This product is soluble in acetone,benzene,carbon tetrachloride,diethylether.
Calcd. anal. for $C_{44}H_{44}OSi_2$:C,81.99;H,6.83;Si,8.67;
mol. weight:644
Found:C,81.67;H,6.71;Si,8.80;mol. weight (cryoscopically determined in benzene):635.

RESULTS AND DISCUSSION

The synthesis of the organooxasilacycloheptanes proceeds in two steps [20]:the coupling reaction of dichlorodiorganosilanes to organolithium reagent and the hydrolysis reaction of the resulting chlorodiorganosilyl groups with ring closure.The yield in solid cyclic products were between 10 and 48%. Similar results for organooxadisilacyclohexanes were obtained. The reactivity of dichlorodiorganosilanes with 1,4-dilithium-1,1,4,4-tetraphenylbutane varies as a function of the nature of the organic substituents to the silicon atom in the silane molecule. The substitution of one methyl group in the dichlorodimethyl silane with an electronoacceptor group (phenyl,vinyl,p-tolyl) determines an increasing of the yield in cyclic products.The electronoacceptor substituents makes easiest the reaction with the organolithium compound because the electropositivity to the silicon atom becames greater (the influence of the conjugation effect is greater than the induction effect -I influence of the other substituent).However,dichlorodimethylsilane reacts faster with 1,4-dilithium-1,1,4,4-tetraphenylbutane than dichlorodiphenylsilane [20].This observation was made also by Carraher and Dommeier [27] in the synthesis of some silicon polyesters. The substitution of one methyl group in dichlorodimetilsilane with an ethyl group leads to smaller quantity of product in the reaction with the organolithium compound.Similar observations were made in the polymerisation of disilacyclohexanes [26].This effect was attributed to the increased electronodonor characteristics of the ethyl group on one hand and to the steric hindrance on the other.

The ring closure of the 5-8 nombered siloxane cyclic is provided by IR spectra [3,18].

Thus the heptacyclosiloxanes asymmetric stretching vibration band of Si-O-Si bond appears in cycloheptasiloxanes at 1015 cm^{-1} (9.86) instead of 1069 cm^{-1} (9.44) for linear polysiloxanes (3.18).The organooxasilacycloheptanes synthetized by us show this band in the 1100-1015 cm^{-1} region (Table 1).As far the case of organooxasilacycloheptanes previously prepared [20],the IR C-H adsorbtion bands (table 1) occur at shorter wavelengths as compared to those of the starting hydrocarbon;an explanation of this fenomen might be the decrease of the silicon electronegativity [28].

At the same time the little shift of the caracteristic band for Si-R bond (R=CH_3,C_2H_5,CH=CH_2,C_6H_5,$C_6H_4CH_3$) in organooxasilacycloheptanes as compared with organosilanes or poly(organosiloxane) can be attributed to the inductiv effect of the other groups bonded to the silicon atom ,to the interaction of the vibrations or to the hindrances [29].

Table 1.IR Absorbtion spectra of the new substances

Substance	Frequency cm^{-1}	Assignement	Values from literature
I	500	Si-O-Si	520 [30]
	690	C-H	690-710 [31]
	780	Si-CH_3	775 [32]
	950	Si-C_2H_5	940-970 [29]
	1000	Si-C_2H_5	1010-1020 [29]
	1025	Si-O-Si	1020-1100 [29]
	1245	Si-CH_3	1240-1280 [33]
	1400	Si-CH_2-	1390 [32]
	1435	Si-CH_3	1390-1440 [32]
	1585	C-C	1590 [32]
	2080	C_6H_5mono-substit.	1750-2000 [32]
	2860	C-H	2850-3000 [34]
	2930	C-H	2962 [31]
	3000	C-H aromatic	3000-3100 [29, 35]

II	454	Si-CH=CH_2	454 [36]
	525	Si-O-Si	520 [30]
	690	C-H	690-710 [31]
	730	Si-CH=CH_2	730 [33]
	780	Si-CH_3	775 [32]
	910	CH_2	950 [37]
	1015	Si-O-Si	1020-1100 [29]
	1250	Si-CH_3	1240-1280 [33]
	1400	Si-CH_2-	1390 [32]
	1435	Si-CH_3	1390-1440 [32]
	1480	C-C	1475-1525 [38]
	1580	Si-CH=CH_2	1595 [37]
	2940	C-H	2962 [31]
	3000	C-H aromatic	3000-3100 [29, 35]
III MePh	540	Si-O-Si	520 [30]
	690	C-H	690-710 [31]
	730	Si-C_6H_5	700-740 [39]
	780	Si-CH_3	775 [32]
	1025	Si-O-Si	1020-1100 [29]
	1250	Si-CH_3	1240-1280 [33]
	1395	Si-CH_2-	1390 [32]
	1425	Si-C_6H_5	1428-1440 [29]
	1480	C-C	1475-1525 [38]
	1585	C-C	1580-1600 [40]
	2930	C-H alif.	2962 [31]
	3000	C-H arom.	3000-3100 [29, 35]
IV Me-pTol.	495	CH_2 from heterocycle	490-500 [41]
	550	Si-O-Si	520 [30,33]
	695	C-H	690-710 [31]
	775	$pCH_3C_6H_4$	800 [42]
	910	CH_2	950 [37]
	1015	C-H	1037[43,44]
	1100	Si-O-Si	1020-1100 [29]
	1250	Si-CH_3	1240-1280 [33]
	1380	Si-CH_2	1390 [32]
	1440	Si-CH_3	1440-1390 [32]
	1485	C-C	1475-1525 [38]
	1580	C-C	1580-1600 [40]
	2920	C-H alif.	2962 [35,45]
	3010	C-H arom.	3000-3100 [29, 35]
V 1,1,4,4-tetraphenylbutane	710	C-H	690-710 [31]
	760	CH_2	740 [43]
	1040	C-H	1037 [43,44]
	1260	CH_2	1300 [31]
	1460	CH_2	1467 [31]
	1500	C-C	1475-1525 [38]
	1600	C-C	1580-1600 [40]
	2900	C-H alif.	2962 [31]
	3010	C-H arom.	3000-3100 [29, 35]

DTA and DTG curves of compounds II a-d show that they are stable up to temperatures between 360 and 400 °C. Heating beyond these temperatures causes weight losses in three steps. The first and the second steps are transformation reactions by the splitting of two and four phenyl groups respectively from the 1,1,4,4-tetraphenylbutanediyl-1,4 chain , with the formation of double bonds. In tab. 2 the transformation temperatures t_1 and t_2 and the decomposition temperature t_3 are given together with the weight losses.

Table 2 .Starting temperatures t_1 and t_2 for the transformation reactions,decomposition temperature t_3 and C_6H_5 group losses

Substance	Temperature C			Phenyl group losses		
	t_1	t_2	t_3	No.of groups	%exp.	%calcd.
I	400			2	29	29.6
	410	520	715	3	43.26	43.86
				4	59.2	59.2
II	400			2	29.5	29.84
		518	720	4	60.5	59.68
III	370			2	24.5	25
	400			3	38.0	37.5
		410	655	4	49.5	50.0
IV	360			2	24	23.9
	450			3	35.5	35.87
		500	680	4	47.5	47.80

The synthesized compounds were heated for two hours at 400°C then IR spectra were registered (tab. 3) .The presence of 1665 cm^{-1} (compound I) and 1660 cm^{-1} (compounds II,III,IV) bands characteristic for C=C bond and of 730 cm^{-1},1420 cm^{-1} bands characteristic for $Si-C_6H_5$ bond (compound III) demonstrates that the rearrangement of the molecules takes place by the breaking of the $C-C_6H_5$ bonds.

Table 3 .IR Absorbtion spectra of the new combinations before and after a 400 °C heating

Substance	Cold sample Frequency (cm^{-1})	Heated sample Frequency (cm^{-1})	Assignement
I	-	600 * *	C-H alchene
	690	690	C-H
	780	785	$Si-CH_3$
	950	950	$Si-C_2H_3$
	1025-1000	1000-1100	C-H;Si-O-Si
	1245	1250	$Si-CH_3$
	1400	1380	$Si-CH_2-$
	1435	1440	$Si-CH_3$
	1585	1585	C-C
	-	1655	C=C
	2930	2940	C-H
	3000	3020	C-H arom.
II	470	470	$Si-CH=CH_2$
	-	595 * *	C-H alchene
	690	695	C-H
	730	730	$Si-CH=CH_2$
	780	780	$Si-CH_3$
	910	915	CH_2
	1015	1010-1015	Si-O-Si
	1250	1255	$Si-CH_3$
	1400	1385	$Si-CH_2-$
	1435	1435	$Si-CH_3$
	1480	1480	C-C

	1580	1585	Si-CH=CH$_2$
	-	1650 "	C=C
	2940	2940	C-H
	3000	3000	C-H arom.
III	690	690	C-H
	730	730 *	Si-C$_6$H$_5$
	780	775	Si-CH$_3$
	1025	1005-1115	Si-O-Si; C-H
	1250	1260	Si-CH$_3$
	1395	1380	Si-CH$_2$-
	1425	1420	Si-C$_6$H$_5$
	1480	1480	C-C
	1585	1585	C-C
	-	1650	C=C
	2930	2920	C-H
	3000	3005	C-H arom.
IV	-	605 *	C-H alchene
	695	690	C-H
	775	775	pCH$_3$-C$_6$H$_5$
	910	910	CH$_2$
	1015	1015;1025	C-H
	1100	1010-1100	Si-O-Si
	1250	1250	Si-CH$_3$
	1380	1385	Si-CH$_2$-
	1440	1435	Si-CH$_3$
	1485	1485	C-C
	1580	1585	C-C
	-	1650 *	C=C
	2920	2900 *	C-H
	3010	2995	C-H arom.

* - strong
**- very strong

From these data and from those previously reported [20] one can conclude that the second substituent to silicon atom in organo-oxasilacycloheptanes influences the thermal stability of the tetraphenylbutanediyl chain. These compounds are ranged in the following series in function of the first transformation temperature t_1:

$$IV < III < I=II$$

The analytical data, the molecular weight values together with the IR data of the new compounds support the proposed structures.

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