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Abstract

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SYNTHESIS AND SPECTRA OF TRIMETHYLALKYL-(PHENYL, CHLORO)-1-OXA-2,6-DISILACYCLOHEXANES

Recently, interest has increased in various heterocyclic compounds. Among carbocyclosiloxanes there have been described methyldiphenyl-1-oxa-2,5-disilacyclopentanes ([1], [2]), tetramethyl-1-oxa-2,6-disilacyclohexane ([3]), C-substituted tetramethyl-1-oxa-2,6-disilacyclohexanes ([4]), tetramethyl-1-oxa-1,7-disilacycloheptane ([5]), 2,2,4,4-tetramethyl-3-oxa-2,4-disilabicyclo-(3,2,2)-nona-6,8-diene ([6]), and

$$\mathrm{CF_2}\begin{matrix}\mathrm{CF_2C_6H_4Si(CH_3)_2}\\ \\ \mathrm{CF_2C_6H_4Si(CH_3)_2}\end{matrix}\mathrm{O} \qquad (7)$$

In the present work, new trimethylalkyl-(phenyl, chloro)-1-oxa-2,6-disilacyclohexanes were obtained in 60–80% yield by hydrolysis of bis-(alkylchlorosilyl)-propanes with an aqueous solution of potassium hydroxide

$$\mathrm{Cl(CH_3)_2SiCH_2CH_2CH_2Si(CH_3)(R)Cl} \xrightarrow{\mathrm{H_2O,\ KOH}}$$

$$\longrightarrow \begin{matrix} & & \mathrm{CH_2} & & \\ & \diagup & & \diagdown & \\ & \mathrm{CH_2} & & \mathrm{CH_2} & \\ & | & & | & \\ \mathrm{(CH_3)_2Si} & & & \mathrm{Si-(CH_3)} & \\ & \diagdown & & | & \\ & & \mathrm{O} & \mathrm{R} & \end{matrix} \qquad \mathrm{R = CH_3\ (I),\ C_3H_7\ (II),\ C_4H_9\ (III),}$$

$$\mathrm{C_6H_5\ (IV),\ Cl\ (V).}$$

On heating an ether solution of 1-dimethylchlorosilyl-3-methyldichlorosilylpropane with sodium bicarbonate, a bicyclic compound was obtained according to the equation

$$Cl_2(CH_3)Si(CH_2)_3Si(CH_3)_2Cl \xrightarrow{NaHCO_3}$$

```
                 CH2                       CH2
            /           \            /            \
          CH2            CH2       CH2             CH2
→          |              |         |               |
       (CH3)2Si           Si   —    O     —         Si     Si − (CH3)2      (VI)
            \             /                         \         /
                 O       CH3               CH3        O
```

Bis-(alkylchlorosilyl)-propanes were obtained by the reactions

$$CH_3SiCl_3 + RMgBr \rightarrow CH_3(R)SiCl_2, \quad (a)$$

$$CH_3RSiCl_2 + CH_2{=}CHCH_2MgBr \rightarrow CH_3(R)ClSiCH_2CH{=}CH_2, \quad (b)$$

$$CH_3(R)ClSiCH_2CH{=}CH_2 + HSi(CH_3)_2Cl \xrightarrow{H_2PtCl_6}$$

$$\rightarrow Cl(CH_3)(R)SiCH_2CH_2CH_2Si(CH_3)_2Cl, \quad (c)$$

$$R = CH_3,\ C_3H_7,\ C_4H_9,\ C_6H_5,\ Cl.$$

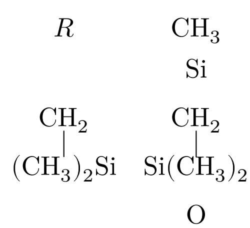
The properties of the newly synthesized substances are presented in Table 1. In the IR absorption spectra of carbocyclosiloxanes I–VI, of interest is the shift of the frequencies of the Si–O–Si vibrations in comparison with the frequencies of these vibrations in the case of hexaalkyldisiloxanes, hexamethylcyclotrisiloxane

Table 1

Nos.	Formula	bp, °C/mm	n_D^{20}	d_4^{20}	Yield, %	MR found	MR calculated	Mol. wt. found	Mol. wt. calculated	Found, % C	Found, % H	Found, % Si	Found, % Cl	Calculated, % C	Calculated, % H	Calculated, % Si	Calculated, % Cl
I	$(CH_3)_2Si{-}CH_2{-}CH_2CH_2SiO(CH_3)_2^*$	146	1,4250	0,8737	79,4	51,43	51,48	171	174	47,24	10,30	31,49	–	48,25	10,36	32,20	–
II	$(CH_3)_2Si{-}CH_2CH_2CH_2SiO(CH_3)(C_3H_7)$	61/2	1,4360	0,8796	68,0	60,18	60,77	199	202	52,80	10,88	27,79	27,45	52,42	10,94	27,75	–

Nos.	Formula	bp, °C/mm	n_D^{20}	d_4^{20}	Yield, %	MR found	MR calculated	Mol. wt. found	Mol. wt. calculated	Found, % C	Found, % H	Found, % Si	Found, % Cl	Calculated, % C	Calculated, % H	Calculated, % Si	Calculated, % Cl
III	[illegible]	75/21	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	55,51	[illegible]	[illegible]	[illegible]	55,51	11,00	25,94	—
VI	[illegible]	98/21	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	236,4	61,29	[illegible]	[illegible]	—	60,97	8,54	23,73	—
V	[illegible]	67/25	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	28,88	18,20
IV	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	320	334,7	[illegible]	[illegible]	[illegible]	—	43,06	9,03	33,57	—
VIIA	$CH_2=CH-CH_2(C_3H_7)(CH_3)SiCl$	163–164	1,4481	[illegible]	[illegible]	46,95	47,85	—	—	—	—	16,32	[illegible]	—	—	17,23	24,82
VIII	$CH_2=CH-CH_2(C_7H_{15})(CH_3)SiCl$	[illegible]	[illegible]	[illegible]	[illegible]	51,70	52,50	—	—	53,68	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	15,88	20,01
XI	$Cl(CH_3)_2SiCH_2CH_2Si(CH_3)_2Cl$	118–119/41	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—	—	37,40	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	24,42	31,0
X	$Cl(CH_3)_2Si(CH_2)_3Si(CH_3)Cl_2$	118–119/30	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—	—	29,00	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	22,51	42,71
IX	$Cl(CH_3)_2Si(CH_2)_3Si(CH_3)(C_3H_7)Cl$	113–114/2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—	41,48	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	21,78	28,01
XII	$Cl(CH_3)_2Si(CH_2)_3Si(CH_3)(C_7H_{15})Cl$	123–124/2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—	44,13	[illegible]	[illegible]	25,39	44,21	8,84	20,64	26,19

and cyclosiloxanes of the type



$R = CH_3,\ C_2H_5,\ C_6H_5.$ (XIII)

For carbocycloxiloxanes I–IV the frequency of the Si—O—Si vibrations is 990 (for V, ν(Si—O—Si) = 1000 cm^{-1}) and 646 cm^{-1}, instead of 1060–1070 and 520–550 cm^{-1} for hexaalkyldisiloxanes or 1016 and 606 cm^{-1} for hexamethylcyclotrisiloxane.

Fig. 1. Infrared absorption spectra of cyclosiloxanes

For cyclosiloxanes of type XIII one of the Si—O—Si vibration frequencies is

equal to 1018 cm^{-1}. For compound VI, ν(Si—OSi) lie near 990 (ring) and 1080 cm^{-1} (linear Si—OSi bond). The vibration frequencies that may be assigned to various groups bonded to the silicon atom, for compounds I–VI, coincide with the frequencies and assignments from work (8): Si—CH_3 1255–1258 cm^{-1} (I–VI); Si$(CH_2)_3$Si 900–907, 931–934, 1020–1022, and 1091–1095 cm^{-1} (I–VI); Si—C_3H_7-*n* 1213 cm^{-1}; Si—C_4H_9-*n* 1198 cm^{-1}; Si—C_6H_5 1118 cm^{-1} (see Fig. 1).

Experimental Part

Methylpropylallylchlorosilane (VII). The Grignard reagent, prepared from 81 g (0.67 mole) of allyl bromide, was added to 105 g (0.67 mole) of methylpropyldichlorosilane in 150 ml of ether. The mixture was heated for 5 h, the precipitate was filtered off, and the filtrate was distilled on a column; 30.4 g of VII was obtained, b.p. 163-164°, yield 34%.

VIII was obtained analogously.

1,3-Bis-(dimethylchlorosilyl)-propane (IX). 52.5 g (0.39 mole) of dimethylallylchlorosilane, 36.8 g (0.42 mole) of dimethylchlorosilane, and 1 g of 0.1 N H_2PtCl_6 solution in *iso*-C_3H_7OH were heated in a three-necked flask equipped with a stirrer, thermometer, and efficient reflux condenser. At 65° a vigorous reaction began, and the temperature rose to 123°. The mixture was boiled for 3 h at 131° and fractionated on a column; 61.6 g of IX was obtained, b.p. 118-119°/141 mm, yield 68%.

Compounds X, XI, XII were obtained analogously.

2,2,6-Trimethyl-6-butyl-1-oxa-2,6-disilacyclohexane (III). To a cooled solution of 14 g (0.25 mole) of KOH in 100 ml of water, at 5°, 22.9 g (0.1 mole) of 1-dimethylchlorosilyl-3-methylbutylchlorosilylpropane in 200 ml of ether was added; the mixture was stirred for 1 h, the ether layer was separated, washed with water, and dried over Na_2SO_4; on fractionation, 2.5 g of III was isolated, b.p. 76-78°/2 mm, yield 69.4%.

Compounds I-IV were obtained analogously.

2,2,6-Trimethyl-6-chloro-2,6-disilacyclohexane (V). To a mixture of 9.91 g (0.07 mole) of KOH, 20 ml of acetone, and 20 ml of ether, 8.8 g of $Cl_2CH_3Si(CH_2)_3Si(CH_3)_2Cl$ and 5 drops (0.12 ml) of water were added, and the mixture was stirred for 6 h at room temperature. On the following day the precipitate was filtered off, and from the filtrate 4.5 g of V was isolated with b.p. 75-80°/28 mm, yield 58.4%; the redistilled product had b.p. 67°/25 mm.

Bicyclic siloxane (VI). To 7.4 g (0.088 mole) of $NaHCO_3$, 40 ml of ether, and 0.18 ml of water, with stirring, 11 g (0.044 mole) of $Cl_2(CH_3)Si(CH_2)_3Si(CH_3)_2Cl$ was added over 30 min; vigorous evolution of CO_2 was observed. Then 2 g of Na_2SO_4 was added, and the mixture was stirred for 1 h at room temperature and 1 h at 35°. The precipitate was

separated, and from the filtrate 4.6 g of VI was isolated, b.p. 150–153°/27 mm, yield 62.5%; the redistilled product had b.p. 142°/21 mm.

The IR spectra of I–VI were investigated on two spectrophotometers: VIKS M-3 with an NaCl prism (700–1500 cm^{-1}) and IKS-14 with a KBr prism (400–700 cm^{-1}); the substances were recorded as a thin layer between tightly pressed salt windows.

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Note: Figure translations are in progress. See original paper for figures.