# OPTICALLY ACTIVE MENTHOXYETHYL-

## AND METHOXYPROPYLALKYLALKOXY(CHLORO)SILANES

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In a previous paper we obtained the menthyl esters of chlorosilylpropionic and chlorosilylbutyric acids [1]. It seemed of interest to synthesize some organosilicon compounds, containing the ether menthoxy group in the organic radical, suitable for obtaining optically active polymers.

When methyldiethoxysilane or triethoxysilane was heated with methyl vinyl ether in the presence of an 0.1 N solution of  $H_2PtCl_6$  in isopropyl alcohol the corresponding  $\beta$ -menthoxyethylethoxysilanes were obtained in yields of 66 and 16%, respectively, according to the scheme

 $\mathrm{CH}_{2} = \mathrm{CHOC}_{10}\mathrm{H}_{19} + \mathrm{HSi} \ (\mathrm{CH}_{3})_{n} \ (\mathrm{OC}_{2}\mathrm{H}_{5})_{3 - n} \rightarrow \mathrm{C}_{10}\mathrm{H}_{19}\mathrm{OCH}_{2}\mathrm{CH}_{2}\mathrm{Si} \ (\mathrm{CH}_{3})_{n} \ (\mathrm{OC}_{2}\mathrm{H}_{5})_{3 - n} \ n = 0.1$ 

The low yield of menthoxyethyltriethoxysilane can be explained by the side disproportionation reaction, since, together with the desired product, a substantial amount of tetraethoxysilane is formed. We were unable to obtain the menthoxyethylchlorosilanes by the reaction of menthyl vinyl ether with hydrochlorosilanes in the presence of  $H_2PtCl_6$  and in the absence of an inhibitor; here the main reaction was polymerization of the starting ether. When alkyl(aryl)chlorohydrosilanes are reacted with allyl menthyl ether the reaction goes in 30-40 min and the yield reaches 70-75%.

 $\begin{array}{l} \operatorname{Cl}_{3\_n}\operatorname{Si}(\mathbf{R})_n \operatorname{H} + \operatorname{CH}_2 = \operatorname{CH}_2\operatorname{H}_2\operatorname{OC}_{10}\operatorname{H}_{19} \rightarrow \operatorname{C}_{10}\operatorname{H}_{19}\operatorname{OC}_{12}\operatorname{CH}_2\operatorname{CH}_2\operatorname{CH}_2\operatorname{Si}_{3\_n}(\mathbf{R})_n \\ \operatorname{R} = \operatorname{CH}_3, \ n = 0, \ 1, \ 2; \ \operatorname{R} = \operatorname{C}_2\operatorname{H}_5, \ \operatorname{C}_6\operatorname{H}_5, \ n = 1 \end{array}$ 

However, together with addition, the formation of cleavage products is observed when phenyldichlorosilane is reacted with menthyl allyl ether, and the yield of the main product is only 25%. The purity of the starting allyl menthyl ether exerts an important effect on the reaction course. The presence of menthol in the ether leads to the formation of menthoxy derivatives and a complex mixture of products. We were unable to obtain the  $\gamma$ -menthoxypropylmethylethoxysilanes by the reaction of chloropropylmethylethoxysilanes with  $C_{10}H_{19}ONa$ . Always, together with replacement of the chlorine, a slight transetherification of the ethoxy groups was observed, and the obtained reaction products had a higher coefficient of refraction and density than the  $\gamma$ -menthoxypropylmethylethoxysilanes obtained by the reaction of hydroethoxysilanes with menthyl allyl ether, or by the etherification of the appropriate menthoxypropylchlorosilanes. The products obtained by the last two methods were identical.

 $\begin{array}{c} \operatorname{CH}_3 \left(\operatorname{C}_2\operatorname{H}_5\operatorname{O}\right)_2 \operatorname{SiH} + \operatorname{CH}_2 = \operatorname{CHCH}_2 \operatorname{OC}_{10}\operatorname{H}_{19} \xrightarrow{\operatorname{H}_2\operatorname{PtCl}_4} \\ \xrightarrow{\operatorname{C}_2\operatorname{H}_3\operatorname{OH}, \ (\operatorname{C}_2\operatorname{H}_5\operatorname{O})_2 \operatorname{SiCH}_2\operatorname{CH}_2\operatorname{CH}_2\operatorname{CH}_{2}\operatorname{OL}_{10}\operatorname{H}_{19} \xleftarrow{\operatorname{C}_2\operatorname{H}_3\operatorname{OH}, \ (\operatorname{C}_2\operatorname{H}_5), \operatorname{N}} \\ \xrightarrow{\operatorname{C}_2\operatorname{H}_3\operatorname{OH}, \ (\operatorname{C}_2\operatorname{H}_5\operatorname{O})_2 \operatorname{SiCH}_2\operatorname{CH}_2\operatorname{CH}_2\operatorname{CH}_2\operatorname{CH}_{19} \xleftarrow{\operatorname{C}_2\operatorname{H}_3\operatorname{OH}, \ (\operatorname{C}_3\operatorname{H}_3), \operatorname{N}} \\ \end{array}$ 

The properties of the synthesized compounds are given in Table 1. The ultraviolet and infrared spectra, and also the optical rotation dispersion curves in the range 608-302 nm, were taken for all of the obtained compounds. The obtained optical rotation dispersion curves (r. d.) were processed using the Druid equation. The optical rotation constants of the synthesized compounds are given in Table 2.

The r. d. curves of all of the investigated compounds are described by the Druid equation in the wavelength range 589-334 nm. All of the compounds in chloroform solution have negative specific rotation values, lying in the range 40-60°. The value of the rotation constant A of the Druid equation is quite sensitive to change in the structure of the ethers, while the value of  $\lambda_0$  lies close to 170 nm for all of the ethers,

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TAB	LE 1. Properties of Synthesize	od Co:	spunodu												
	Compound	%				W	н		Found	%			Calcula	ted, %	
No.	Formula	,bləiY	Boiling point, C(p, mm of Hg)	<sup>n</sup> 20	$d_4^{20}$	found.	calc., %	U	н	si	IJ	υ	H	ŝ	0
I	C <sub>10</sub> H <sub>19</sub> OCH2CH2CH2Si(CH3)2Cl	33,4	102-105(0,5)	1,4615	0,9429	84, 84	85,14	62,54 62,70	11,06	9,54 9,54	11, 99	61,92	10,75	9, 64	12,20
II	C <sub>10</sub> H <sub>19</sub> OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Si (CH <sub>3</sub> ) Cl <sub>2</sub>	65,18	124 - 126(1,5)	1,4650	1,0175	84,61	84,76	53,74	9,24	9,32	22, 82 22, 74	53,99	9,06	10,6	22, 79
III	C <sub>10</sub> H190CH2CH2CH2Si (C2H5) Cl2	72,31	126-128(1)	1,4680	1,0136	89,25	89,41	55,62	0,52	8,35 8,35	21,13	55,35	9,29	8,62	21,81
ΙΛ	$C_{10}H_{19}OCH_2CH_2CH_2Si(C_6H_5)Cl_2$	25,17	166—169(0,5)	1,5103	1,084	103,1	104,48	60,70 60,70	200 200 200 200 200 200 200 200 200 200	7,42	19,18	61,09	8,09	7, 51	19,00
Λ	C <sub>10</sub> H <sub>19</sub> OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> SiCl <sub>3</sub>	73, 63	121-125(1,5)	1,4701	1, 0960	84,50	84,32	47,61	7,64	. 8 . 54 . 54	31,93	47,04	7, 59	8,45	32, 08
	C <sub>10</sub> H <sub>19</sub> OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Si (CH <sub>3</sub> ) 2OC <sub>2</sub> H <sub>5</sub> C <sub>10</sub> H <sub>19</sub> OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Si (CH <sub>3</sub> ) (OC <sub>2</sub> H <sub>5</sub> ) 2	57,10 65,56	140 - 143(2,5) 133 - 137(1,5)	1,4501 1,4476	$0,8944 \\ 0,9221$	90,54 95,91	91,07 96,51	67,77 65,46	12, 15	8 8 9 30 9 30 9 30 9	R	67,88 65,76	12, 07 11, 58	9,36 8,48	11
VIII	C <sub>10</sub> H <sub>19</sub> OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	61,88	152-156(1)	1,4420	0,Ò374	102,19	101, 95	65, 67 63, 91	11,58	*,25 *,22	ł	63,28	11,18	7, 78	I
IX	[C <sub>10</sub> H <sub>19</sub> OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Si (CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> O	<u>5</u> 9,6	200-205(0,5)	1,4615	!	1		67,54 67,54	11,74	10,60	1	68,36	11,87	Ι <b>ΰ</b> , 65	I
XIX	C <sub>10</sub> H <sub>19</sub> OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Si (CH <sub>3</sub> ) <sub>2</sub> OC <sub>10</sub> H <sub>19</sub> C <sub>10</sub> H <sub>19</sub> OCH <sub>2</sub> CH <sub>2</sub> SiCH <sub>3</sub> (OC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	65, 58	160-166(0,5) 138-139(3)	1,4635 1,4438	$0,9294 \\ 0,9181$	91,48	91,86	65,11 65,11	11,98	21.0 9 1 1 0 1 0 1 0 8	11	$73,40 \\ 64,50$	12,20 11,46	6,81 8,88	11
IIX	C <sub>13</sub> H <sub>19</sub> OCH <sub>2</sub> CH <sub>2</sub> Si (OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	16,5	134135(2)	1,4390	0,9388	97,10	97, 30	62,76 63,05	10,95	8,45	1	62,37	11,05	8,10	1

Compounds
Synthesized
<b>Properties of</b>
ABLE 1.

	Compound	Mol.	Mol. wt.				1		ц Ц
No.	Formula	found	calcu- lated	–ر¢]ی	<i>а</i> [м]–	[M],66	-A·10-5	۸», nm	c,g/1001
I II IV VV VI VII VIII IX XX XII XIII	$\begin{array}{l} C_{10}H_{19}O(CH_2)_{3}Si(CH_3)_2Cl\\ C_{10}H_{19}O(CH_2)_{3}Si(CH_3)Cl_2\\ C_{10}H_{19}O(CH_2)_{3}Si(C_{3}H_{3})Cl_2\\ C_{10}H_{19}O(CH_2)_{3}Si(C_{3}H_{3})Cl_2\\ C_{10}H_{19}O(CH_2)_{3}SiCl_3\\ C_{10}H_{19}O(CH_2)_{3}Si(CH_3)_{2}OC_{2}H_{5}\\ C_{10}H_{19}O(CH_2)_{3}Si(CH_3)_{2}OC_{2}H_{5}\\ C_{10}H_{19}O(CH_2)_{3}Si(CH_3)_{2}OC_{4}H_{3}\\ (C_{10}H_{19}O(CH_2)_{3}Si(CH_3)_{2}OC_{4}H_{5})_{3}\\ (C_{10}H_{19}O(CH_2)_{3}Si(CH_3)_{2}OC_{4}H_{5})_{3}\\ (C_{10}H_{19}O(CH_2)_{2}Si(CH_3)_{2}OC_{10}H_{19}\\ C_{10}H_{19}O(CH_2)_{2}Si(CH_3)_{2}OC_{10}H_{19}\\ C_{10}H_{19}O(CH_2)_{2}Si(CH_3)_{2}OC_{10}H_{19}\\ C_{10}H_{19}O(CH_2)_{2}Si(OC_{4}H_{5})_{3}\\ C_{10}H_{19}O(CH_2)_{2}Si(OC_{4}H_{5})_{3}\\ CH_{2}=CHCH_{2}OC_{10}H_{19} \end{array}$	290,0 306,9 314,5 373,9 345,7 315,2 334,5 336,0 524,2 320,8 340,7	290,9 311,4 325,46 373,5 331,9 300,5 330,5 360,6 527,0 410,6 316,6 346,6	60,26 59,94 52,72 44,70 52,48 46,92 38,52 42,98 63,83 57,88 55,25 50,17 87,73	175,3 186,7 171,5 166,9 174,2 140,8 127,3 154,9 337,6 237,6 174,9 173,9 172,3	520,5 557,7 510,6 505,5 522,00 440,4 440,4 478,88 1014,6 735,4 543,55 538,22 515,6	56,2 58,8 48,1 52,4 54,5 47,0 39,4 48,8 106,4 76,9 56,8 55,3 51,3	162 170 200 176 174 164 212 180 170 175 179 180 160	3,52 4,84 5,00 3,82 3,60 3,15 4,59 5,26 4,84 4,56 4,25 4,10 4,57

TABLE 2. Optical Rotation Constants of Silicon-Containing Menthyl Ethers (chloroform, 23°)

characterizing the contribution made by the optically active menthyl group.  $[\alpha]_D$  decreases when the  $Cl_3Si$ group is inserted in allyl menthyl ether [compound (V)];  $[\alpha]_D$  increases when the chlorine is replaced by the methyl group [compounds (I) and (II)]. The values [M] and A suffer a slight deviation from the corresponding values for allyl menthyl ether, with some increase in the effective volume of the substituent (replacing the  $CH_3$  group by either  $C_2H_5$  or the  $C_6H_5$  group) causes the  $[\alpha]$ , [M] and A in this series to decrease somewhat [compounds (II), (III) and (IV)]. High values of  $[\alpha]$ , [M] and A are observed for dimer (IX), due to the presence of two menthyl groups in the molecule, with a retention of the value of  $\lambda_0$ , general for the entire investigated series (~170 nm). From a comparison of compounds (IX) and (X), where the menthoxy group is attached directly to the silicon, it can be seen that an increase in the rotation is caused more by the entire grouping  $C_{10}H_{19}O(CH_2)_3Si$  than by the presence of the second menthyl group. In the case of (X) the values of  $[\alpha]_D$  and [M]\_D are smaller than for (IX).

It is interesting to compare compounds (VI)-(VIII), (XI) and (XII), where the effect of varying the number of ethoxy groups and the distance between the menthoxy group and the silicon atom on  $[\alpha]_D$  can be followed. A comparison of (VI) and (X) reveals that replacing the menthoxy group by ethoxy lowers  $[\alpha]$ , [M] and A, in which connection an accumulation of ethoxy groups leads to an even greater decrease in  $[\alpha]$ . Approach of the menthyl group to the silicon atom [compare the pairs (XII) and (VII), and (XI) and (VII) reveals that  $[\alpha]$ , [M] and A increase sharply. A change in the environment around the silicon atom, with the  $CH_2CH_2OC_{10}H_{19}$  grouping being present, is practically without effect on [M], A and  $\lambda_0$  [(XI), (XII)], whereas sharp changes in  $[\alpha]$ , [M] and A are observed when the  $C_{10}H_{19}$  group is further removed by one  $CH_2$  group, i.e. when the  $CH_2CH_2OC_{10}H_{19}$  grouping is present [compounds (VII) and (VIII)].

### EXPERIMENTAL

The starting *l*-menthyl allyl ether was obtained as described in [2]]from allyl bromide and  $l - C_{10}H_{19}ONa$ , bp 90-90.5° (1.5 mm);  $n_D^{20}$  1.4561;  $d_4^{20}$  0.8713 [ $\alpha$ ] -87.78°. Literature data [2]: bp 103-104° (13 mm);  $d_4^{19}$  0.8763, 0.8830; [ $\alpha$ ] -98.3°. *l*-Menthyl vinyl ether was obtained as described in [3], bp 109-113° (35 mm);  $n_D^{20}$  1.4558;  $d_4^{20}$  0.8694,  $\alpha_D^{21}$  -5.83°, [ $\alpha$ ]<sub>D</sub> -68.2°. Literature data [3]: bp 201-202°; 79° (8 mm);  $n_D^{20}$  1.4550;  $d_4^{20}$  0.8695.

 $\frac{\gamma-\text{Menthoxypropylmethyldichlorosilane}}{1000}$  In the mixture of 15 g of freshly distilled menthyl allyl ether and 0.2 g of an 0.1 N solution of  $H_2PtCl_6$  in isopropanol was added about 5 g of HSi(CH<sub>3</sub>)Cl<sub>2</sub>. Slight warming up was observed. The mixture was heated up to 60°, where the temperature rose sharply up to 140°. The remainder of the HSi(CH<sub>3</sub>)Cl<sub>2</sub> (a total of 15.3 g) was added slowly. The reaction mixture was heated at this temperature for 40 min. Fractional distillation gave 16.8 g of (II); bp 124-126° (1.5 mm);  $n_D^{20}$  1.4650. (D-(V) were obtained in a similar manner.

 $\frac{\gamma-\text{Menthoxypropylmethyldiethoxysilane} (VII)}{\rho}$ . A mixture of 8.55 g of menthyl allyl ether, 6.97 g of HSi(CH<sub>3</sub>)(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> and 0.2 g of an 0.1 N solution of H<sub>2</sub>PtCl<sub>6</sub> in isopropanol was heated up to 60°, where the temperature rose sharply up to 150°. The reaction mixture was heated for 3.5 h. Fractional distillation gave 12.3 g of (VII); yield 85.5%; bp 126-140° (1.5 mm). After redistillation, bp 131-134° (1.5 mm); nD<sup>20</sup> 1.4461; d<sub>4</sub><sup>20</sup> 0.9193. Found %: C 65.21; H 11.74; Si 8.24. MR 95.90. Compounds (XI) and (XII) were obtained in a similar manner. To a solution of 4.13 g of absolute  $C_2H_5OH$  and 4.83 g of triethylamine in 50 ml of ether, with stirring, was slowly added 5.15 g of (II). The mixture was refluxed for 1 h, and the precipitate was filtered. From the filtrate by fractional distillation we isolated 3.58 g of (VII), bp 137-138° (1.5 mm);  $n_D^{20}$  1.4476;  $d_4^{20}$  0.9221. Found %: C 65.46; H 11.40; Si 8.36. MR 95.91. Compounds (VI) and (VIII) were obtained in a similar manner.

<u>Reaction of  $(CH_3)_2ClSiH$  with Menthyl Allyl Ether</u>. To a mixture of 14.3 g of  $HSi(CH_3)_2Cl$  and 0.3 g of a 0.1 N solution of  $H_2PtCl_6$  in isopropanol was slowly added 25.5 g of menthyl allyl ether, containing about 30% of menthol [bp 72-76° (1 mm);  $n_D^{20}$  1.4600]. The reaction mixture was heated, in which connection the temperature rose sharply up to 140°, after which the heating was continued for another 20 min. Fractional distillation gave: a) 12.7 g (33.4%) (I) bp 110-122° (1 mm); after redistillation, bp 102-105° (0.5 mm);  $n_D^{20}$  1.4615;  $d_4^{20}$  0.9429. b) 8.9 g (X); bp 160-166° (0.5 mm);  $n_D^{20}$  1.4635;  $d_4^{20}$  0.9294.

Reaction of  $HSi(C_6H_5)Cl_2$  with  $CH_2=CHCH_2OC_{10}H_{19}$ . To a mixture of 19.48 g of  $CH_2=CHCH_2OC_{10}H_{19}$  and 0.3 g of 0.1 N H<sub>2</sub>PtCl<sub>6</sub> solution was added about 4 g of  $HSi(C_6H_5)Cl_2$ . The mixture was heated up to 80°, where the temperature rose sharply up to 130°. Then the remainder of the chloride was added (a total of 19.9 g). The mixture was heated for 3.5 h at 205°. Fractional distillation gave: a) 4.5 g C<sub>6</sub>H<sub>5</sub>Si(OC<sub>10</sub>H<sub>19</sub>)Cl<sub>2</sub>; bp 136-138° (0.5 mm); nD<sup>20</sup> 1.5058; d<sub>4</sub><sup>20</sup> 1.0998. Found %: C 55.9 H 9.23; Cl 21.01; Si 8.48. MR 89.93. C<sub>16</sub>H<sub>24</sub>SiOCl<sub>2</sub>. Calculated %: C 58.0; H 7.30; Si 8.47; Cl 21.39. MR 89.60. b) 13.08 g of (IV); yield 25.63%; bp 166-169° (0.5 mm); nD<sup>20</sup> 1.5103; d<sub>4</sub><sup>20</sup> 1.0840.

 $[C_{10}H_{19}OCH_2CH_2CH_2Si(CH_3)_2]_2O$  (IX). To a mixture of 3.15 g of NaHCO<sub>3</sub>, 2.36 g of urea and 100 ml of ether was added 6.39 g of (l) in drops. The reaction mixture was stirred for 3 h. The filtrate was washed with water and then dried over Na<sub>2</sub>SO<sub>4</sub>. Fractional distillation gave 3.5 g of (IX); bp 200-205° (0.5 mm); nD<sup>20</sup> 1.4615.

Determination of Optical Rotation. The compounds were taken as 3-5% solutions in chloroform, using a polarimeter tube 1 dm long and an SPU-E spectropolarimeter. The study was made at 23° in the wavelength range 302-608 nm.

#### CONCLUSIONS

1. Nine new optically active menthoxypropylalkyl(ethoxy)chlorosilanes and menthoxyethylethoxysilanes were obtained by the reaction of alkylhydrochlorosilanes and methylhydroethoxysilanes with menthyl allyl and menthyl vinyl ethers. Menthoxypropylmethylethoxysilanes were isolated when the menthoxypropyl-methylchlorosilanes were etherified.

2. All of the obtained compounds possess a negative rotation and give smooth negative optical rotation dispersion curves, which are satisfactorily described by the Druid equation in the wavelength range 302-608 nm.

#### LITERATURE CITED

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