

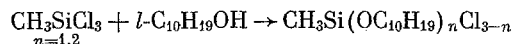
SYNTHESIS OF OPTICALLY ACTIVE METHYLMENTHOXYCHLOROSILANES AND MENTHYL ESTERS OF METHYLCHLOROSILYLPROPIONIC AND METHYLCHLOROSILYLISOBUTYRIC ACIDS

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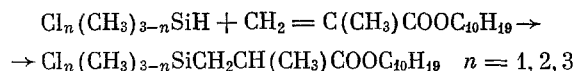
The stereochemistry of organosilicon compounds, and especially of the optically active compounds, is attracting much attention in recent years [1]. The optical activity in such compounds can be due to an asymmetrical silicon atom, as well as to optically active organic groups, attached to the silicon atom. The latter compounds have remained relatively unstudied, whereas they can serve as the components of disymmetrical catalysts [2] and as the starting materials for the preparation of various optically active organosilicon heat stable polymers, representing interest for the creation on their basis of supports for disymmetrical catalysts and adsorbents. An optically active aminopolysiloxane, obtained by the hydrolysis of 2-methylbutyltrichlorosilane [3], is described in the literature.

The purpose of the present paper was to obtain some optically active organosilicon monomers and polymers, containing the menthoxy group attached directly to the silicon atom, and also in the organic radical, and to study the effect of the structure of the molecule on the optical rotation. Of the first type of compounds we synthesized sundry methylmenthoxychlorosilanes by the reaction of methyltrichlorosilane with *l*-menthol in the presence of urea. When the reaction is run using equimolar ratios of the reactants, both the mono- and the dimethoxyderivatives are formed according to the scheme

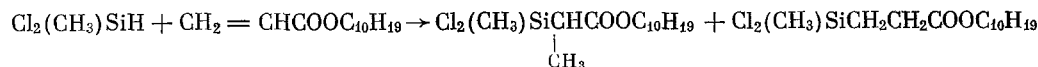


When the conditions for the hydrolysis of the methylmenthoxychlorosilanes were studied it proved that reaction with sodium bicarbonate gave, besides hydrolysis of the chlorine, also substantial cleavage of the menthoxy group. When the hydrolysis is run with the calculated amount of water in the presence of triethylamine the menthoxy group is not attacked, and only the chlorine is hydrolyzed to give methylmenthoxypolysiloxanes. However, the obtained methylmenthoxypolysiloxanes are both hydrolytically and heat unstable. Almost complete cleavage of the menthoxy group is observed when they are heated in the air at 200° for 1 h or when they are refluxed with water.

To synthesize optically active organosilicon monomers, containing the methoxy group in the organic radical, we studied the addition of methylchlorohydrosilanes to the menthyl esters of the acrylic and methacrylic acids in the presence of H_2PtCl_6 . Previously it had been established [4-9] that the addition of silane hydrides to methyl methacrylate goes with the formation of only the β -adduct, whereas with methyl acrylate, depending on the starting silane hydride, both the α - and the β -isomers were obtained. When the reaction of methylchlorohydrosilanes with menthyl methacrylate was studied it was found that the addition goes in the first 3-4 h, with the formation of the menthyl esters of methylchlorosilylisobutyric acid according to the scheme



Long heating of the reaction mixture with excess chlorosilane complicates the reaction, and the formation of products containing the Si-OC bond is observed. The reaction of methyldichlorosilane with menthyl acrylate gave two isomers, indicating that the presence of the bulky menthoxy group does not change the course of the reaction.



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TABLE 1. Properties of Synthesized Compounds

No.	Compound	Yield, %	bp, °C (p. mm of Hg)	n_D^{20}	d_4^{20}	MR		Found, %				Calculated, %			
						found	calculated	C	H	Si	Cl	C	H	Si	Cl
I	$\text{CH}_3\text{SiCl}_2(\text{OC}_{10}\text{H}_{19})$	34, 13	97-97.5 (1)	1.4554	1.0280	70.90	69.88	—	10.64	10.66	25.6	—	10.63	10.42	26.32
II	$\text{CH}_3\text{SiCl}(\text{OC}_{10}\text{H}_{19})_2$	8, 34	160-164 (1)	1.4629	1.0287	109.9	110.88	64, 80	9, 38	7.46	8.66	64, 81	10.63	7.21	9.11
III	$\text{Cl}(\text{CH}_3)_2\text{SiCH}_2\text{CH}(\text{CH}_3)\text{COOC}_{10}\text{H}_{19}$	49, 5	140-143 (3)	1.4622	0.9812	89.49	89.87	60, 10	9, 38	8.48	11.71	60, 24	9.31	8.79	11.12
IV	$\text{Cl}_2(\text{CH}_3)\text{SiCH}_2\text{CH}(\text{CH}_3)\text{COOC}_{10}\text{H}_{19}$	52, 0	140-145 (3)	1.4679	1.0552	89.40	89.43	53, 42	8, 12	8.30	7.89	53, 31	8.30	7.89	21.20
V	$\text{Cl}_3\text{SiCH}_2\text{CH}(\text{CH}_3)\text{COOC}_{10}\text{H}_{19}$	44, 5	112-114 (1)	1.4693	1.1482	89.31	88.998	45, 93	7, 15	7.95	27.29	46, 72	7.00	7.80	29.56
VI	$\text{Cl}(\text{CH}_3)_2\text{SiCH}_2\text{CH}_2\text{COOC}_{10}\text{H}_{19}$	29, 37	109-117 (1, 5)	1.4600	0.9760	85.40	86.226	50, 7	9, 57	8.48	11.83	59, 06	9.57	9.20	11.60
VII	$\text{Cl}_2(\text{CH}_3)\text{SiCH}_2\text{CH}_2\text{COOC}_{10}\text{H}_{19}$	23, 63	112-116 (1)	1.4640	1.0603	84.70	84.79	53, 00	8, 16	8.78	21.30	51, 63	8.04	8.61	21.80
VIII	$\text{Cl}_2(\text{CH}_3)\text{SiCH}_2\text{CH}_2\text{COOC}_{10}\text{H}_{19}$	29, 55	140-144 (1)	1.4635	1.0597	84.62	84.79	53, 26	8, 37	8.32	21.68	51, 63	8.04	8.61	21.80
IX	$\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{COOC}_{10}\text{H}_{19}$	32, 2	113-115 (1, 5)	1.4689	1.1451	83.99	84.25	45, 41	6, 38	8.75	23.64	45, 14	6.70	8.14	30.77
X	$\text{HO}(\text{CH}_3)_2\text{SiCH}_2\text{CH}(\text{CH}_3)\text{COOC}_{10}\text{H}_{19}$	80, 0	—	—	—	—	—	63, 99	10, 14	9.45	5.55*	63, 94	10.75	9.34	5.59*
XI	$[\text{O}(\text{CH}_3)_2\text{SiCH}_2\text{CH}(\text{CH}_3)\text{COOC}_{10}\text{H}_{19}]_x$	89, 78	—	—	—	—	—	62, 72	9, 88	9.03	—	63, 34	9.86	9.34	—

* Amount of OH groups, %.

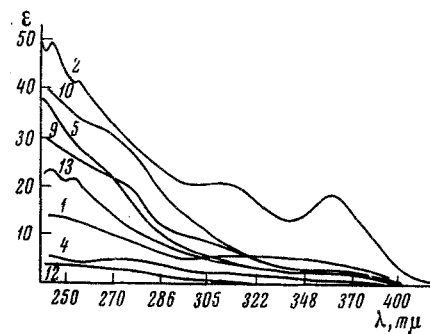
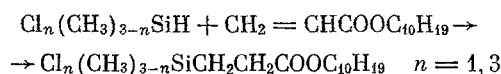


Fig. 1. Optical rotation dispersion curves.

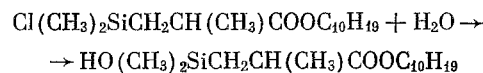
The structure of the obtained compounds was established by the NMR method. For the α -isomer the CH_3 doublet, $\delta = 1.35 \cdot 10^{-6}$, with a coupling constant $J = 7$ Hz, is characteristic, while for the β -isomer the $\text{Cl}_2(\text{CH}_3)\text{SiCH}_2$ triplet, $\delta = 2.56 \cdot 10^{-6}$, is characteristic. The other lines were not identified due to superimposition of the spectrum of the menthyl substituent.

Only the β -adducts were isolated when dimethylchlorosilane and trichlorosilane were reacted with menthyl acrylate.

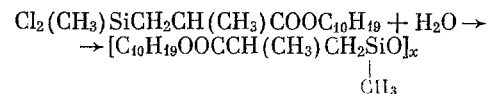


The structure of all of the synthesized compounds was also confirmed by the infrared spectra.

The silanol is formed in 80% yield when the menthyl ester of dimethylchlorosilylisobutyric acid is hydrolyzed in the presence of urea, while the formation of the disiloxane is not observed.



The hydrolysis of the methylester of methyldichlorosilylisobutyric acid under the same conditions leads to the formation of a polymer with a low molecular weight.



The properties of the synthesized compounds are given in Table 1. The values of the specific rotation at 589.3 and 313 $m\mu$ (maximum value) are given in Table 2. The strong absorption in the vicinity of 300 $m\mu$, which can be seen from the given ultraviolet spectra (Fig. 2), makes it difficult to measure the rotation dispersion (r.d.) at $\lambda < 300$ $m\mu$. The corresponding values of the molecular rotation $[\text{M}]_D$ and $[\text{M}]_{313}$ and the constants A and λ_0 of the Drude monomial equation, which in a certain wavelength range are described by the r.d. curves, are also given in Table 2. The constants were calculated graphically by the Heller method in the coordinates $1/[\text{M}]\lambda^2$ vs. $1/\lambda^2$. The obtained series of compounds makes it possible to ascertain the effect of the chlorosilyl group in the investigated compounds on the optical rotation of the menthoxy group [compounds (I), (II),

TABLE 2. Optical Rotation Constants of Organosilicon Compounds (Chloroform, 23°)

No.	Formula	Mol. wt.	$[\alpha]_D$	$[\alpha]_{25}$	$-[M]_D$	$-[M]_{25}$	$\lambda_0, m\mu$	Wavelength range, $m\mu$	C, g/100 ml
I	$CH_3SiCl_2(OC_{10}H_{19})$	269, 26	62, 99	274, 5	169, 4	738, 4	157	577-366	4, 71
II	$CH_3SiCl(OC_{10}H_{19})_2$	389, 02	78, 33	340, 5	304, 7	1324, 6	158	546-312	4, 02
III	$Cl(CH_2)_2SiCH_2CH(CH_3)COOC_{10}H_{19}$	318, 92	52, 89	290, 1	168, 7	734	155	492-334	3, 90
IV	$Cl_2(CH_3)SiCH_2CH(CH_3)COOC_{10}H_{19}$	339, 36	51, 42	224, 1	174, 3	769, 7	172	589-334	5, 27
V	$Cl_3SiCH_2CH(CH_3)COOC_{10}H_{19}$	359, 76	34, 29	101, 6	123, 4	365, 6	162	589-366	6, 19
VI	$Cl(CH_2)_2SiCH_2CH_2COOC_{10}H_{19}$	304, 9	55, 1	163, 2	168, 0	497, 7	163	589-365	4, 34
VII	$Cl_2(CH_3)SiCH(CH_3)COOC_{10}H_{19}$	325, 26	49, 11	169, 2	159, 7	550, 4	132	589-366	—
VIII	$Cl_2(CH_3)SiCH_2CH_2COOC_{10}H_{19}$	325, 26	45, 72	137, 7	148, 9	448, 6	149	589-407	4, 36
IX	$Cl_3SiCH_2CH_2COOC_{10}H_{19}$	345, 8	38, 33	160, 7	132, 4	555, 3	151	589-334	3, 57
X	$HO(CH_2)_2SiCH_2CH(CH_3)COOC_{10}H_{19}$	300, 56	53, 93	274, 5	162, 1	825	168	546-365	2, 96
XI	$[(H_{10}C_{10}O)OCCH(CH_3)CH_2Si(CH_3)-O]_x$	284, 46	65, 14	289, 2	187, 6	822, 7	164	546-334	4, 06
XII	$[(H_{10}C_{10}O)_2Si(CH_3)_2-O]_x$	360, 9	57, 08	253, 4	206, 0	914, 5	172, 5	607-334	3, 21
XIII	$[(H_{10}C_{10}O)_2Si(CH_3)-O]_x$	244, 36	32, 23	152, 4	69, 09	326, 7	183, 9	577-334	3, 82

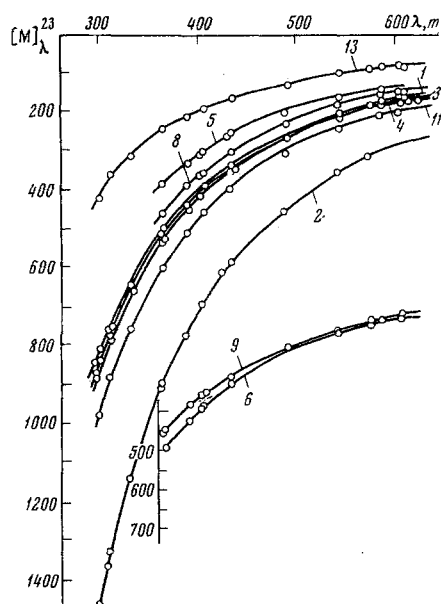


Fig. 2. Ultraviolet spectra of investigated compounds.

(XII) and (XIII)], and the effect of the new asymmetric atom appearing in the group attached to the chlorosilyl moiety [compounds (III)-(V), (VII) and (X)]. From an examination of the data on the optical rotation (see Table 2 and Fig. 1) it can be seen that in compounds (I) and (II) the chlorosilyl group reduces the specific rotation when compared with organic alkyl menthyl ethers, for which $[\alpha]_D \approx -95$ to -92° , however $[\alpha]_D$ for (II) is hardly different from the $[\alpha]_D$ for dimethoxy formal $[CH_2 \cdot (OC_{10}H_{19})_2: [\alpha]_D - 77.94^\circ]$. $[\alpha]_D$ is smaller in the polymethylmethoxysiloxanes than in the chloromethylmethoxysilanes. In compounds (III)-(IX) an increase in the chlorine content lowers $[\alpha]$. From Table 2 it can be seen that the maximum values of the molecular rotation $[M]_{313}$ show greater change than $[M]_D$, depending on the number of menthyl groups and the presence of an asymmetric atom in the molecule. The obtained data on the r. d. make it possible to draw some conclusions regarding the relationship between the constants of the equation and the structure. All of the compounds have a negative rotation and give smooth negative r. d. curves, which are satisfactorily described by the Drude equation, valid in the indicated wavelength range, with the constants A and λ_0 . As was to be expected, the dispersion constant shows little change and lies in the range 150-170 $m\mu$ for all of the compounds, while the rotation constants show greater change. The small changes in $[\alpha]$ and A in the series (III)-(V), when compared with (VI), (VIII) and (IX), show that the contribution of the asymmetric β -carbon atom, formed in the synthesis, to the total rotation is apparently small. A comparison of $[\alpha]$ and A for (IV) and (VII) reveals that approach of the $Cl_2(CH_3)Si$ group toward the asymmetric center lowers both $[\alpha]$ and A. Removal of the menthyl group away from the ester molecule makes it possible to estimate the degree of asymmetric synthesis. A comparison of the optical rotation of dimer (XII) and polymer (XIII) with the corresponding chlorosilanes re-

veals an important reduction in the negative rotation. In contrast, the hydrolysis of compounds (III) and (IV), containing a new asymmetric center, gives hydrolysis products [(X) and (XI)] that have a high negative specific rotation. It is interesting that in the previously investigated poly(2-methylbutyl)siloxane the $[\text{M}]_{\text{D}}$ (52.7) is also greater than for the monomer ($[\text{M}]_{\text{D}}$ 12.7), whereas the values of A nearly coincide ($A \cdot 10^{-5} = 19.2$ and 19.6) [2].

EXPERIMENTAL

Methylmenthoxydichlorosilane (I) and Methylmenthoxychlorosilane (II). With stirring, a solution of 19.8 g of *l*-menthol ($[\alpha]_{\text{D}} - 50.3^\circ$) in 150 ml of ether was added to a mixture of 19 g of CH_3SiCl_3 and 8.2 g of urea. The mixture was stirred for 40 min, and the precipitate was filtered. Fractional distillation gave 12.5 g of (I), bp $97-97.5^\circ$ (5 mm); n_{D}^{20} 1.4554; d_4^{20} 1.028 and 4.12 g (II), bp $160-164^\circ$ (2 mm); n_{D}^{20} 1.4629; d_4^{20} 1.0287.

Menthyl Ester of Dimethylchlorosilylisobutyric Acid (III). With stirring, 10.3 g of $\text{Cl}(\text{CH}_3)_2\text{SiH}$ was added to 24.5 g of freshly distilled menthyl methacrylate and 0.5 ml of 0.1 N $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ solution in isopropyl alcohol. The reaction mixture was heated at 120° for 1.5 h. Fractional distillation gave 15.15 g (49.5%) of (III), bp $140-143^\circ$ (3 mm); n_{D}^{20} 1.4622; d_4^{20} 0.9808.

Compounds (IV)-(IX) were obtained in a similar manner (see Table 1).

Menthyl Ester of Dimethylhydroxysilylisobutyric Acid (X). With stirring, 1.5 ml of water was added to a solution of 2.23 g of (III) in 50 ml of ether and 4 g of urea. The mixture was stirred at room temperature for 1.5 h, the precipitate was separated, and the ether was distilled from the filtrate until the weight remained constant. We obtained 1.67 g of (X); n_{D}^{20} 1.4649; d_4^{20} 0.9772.

(XI) was obtained in a similar manner by the hydrolysis of (IV).

The optical rotation was studied in chloroform solution at concentrations of approximately 4-5%, at 23° , in a polarimeter tube with a length of either 0.5 or 1 dm, using an SPU-E spectropolarimeter equipped with a double monochromator, in the wavelength range 302-612 $\text{m}\mu$.

The NMR spectra were taken on a "Hitachi H-60" spectrometer, with an operating frequency of 60 MHz, in chloroform solution. Tetramethylsilane was used as the internal standard.

The authors wish to thank B. Lavrukhin for taking the NMR spectra.

CONCLUSIONS

1. The reaction of methylhydrochlorosilanes with the menthyl esters of acrylic and methacrylic acid gave seven new optically active menthyl esters of chlorosilylpropionic and chlorosilylisobutyric acid. The mono- and dimethoxychloromethylsilanes were isolated when methyltrichlorosilane was etherified with *l*-menthol.

2. All of the obtained compounds have a negative rotation and give smooth negative rotation dispersion curves, which are satisfactorily described by the Drude equation in the wavelength range 302-612 $\text{m}\mu$.

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