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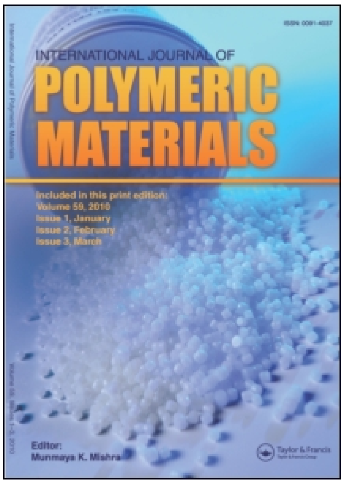

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Synthesis and Properties of Thienylorganosilanes and -Siloxanes

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(Received February 15, 1992)

By acidolysis reaction of thienylmethyldichlorosilane and 2,5-bis(dimethylchlorosilyl)thiophene synthesis has been conducted of acetoxysilanes which at further partial hydrolytic condensation at reduced temperatures led to the formation of corresponding acetoxysiloxanes.

By hydrolytic condensation of methylthienyldichlorosilane in the presence of an acceptor of chlorine hydride-pyridine, dihydroxysiloxanes were obtained.

Roentgenostructural analysis of 1,3-dihydroxy-1,3-dimethyl-1,3-dithienylsiloxane has shown that both atoms of oxygen of the compound molecule participate in the formation of hydrogen bonds being the donors and the acceptors at the same time.

Heterofunctional condensation of dichloro- and dihydroxysiloxanes led to the formation of six- and eight-membered organosiloxanes with one or two methylthienylsiloxy bonds in the cycle.

Studies of biological activity of the synthesized compounds have shown that their bactericidal properties prevail over those of the known bactericide "Cineb." Oligomethylthienyl(diphenyl)siloxane might be used as a basis for oil- and benzo-resistant lubricants, as to α,ω-diacetoxythienylmethylsiloxanes, they exert influence on the kinetics of vulcanization of rubber mixtures on the basis of carbon elastomers preventing thus their premature vulcanization.

KEY WORDS Thienylorganosilanes, thienylorganosiloxanes.

INTRODUCTION

It is known,[1] that thienylorganochlorosilanes under hydrolysis in the strong-acid media are not stable, due to the fact that in the presence of evolving chlorine hydride at room temperature, thienyl group tends to cleave off from the silicon atom, hindering thus the formation of high molecular thienyl-containing compounds.

With this in view, synthesis of new thienyl-containing acetoxyderivatives of organosilicon monomers becomes of special interest, for, at their hydrolysis, acetic acid may in the least extent affect the thienyl group at the silicon atom.

EXPERIMENTAL SECTION

Synthesis of thienyl-containing acetoxysilanes. 1 mole of thienyl-containing silane was poured into a four-neck flask equipped with mechanical stirrer, thermometer, dropping funnel and condenser. The flask was heated over oil bath at 40–50°C in the mixture and 0.4 mole of freshly distilled acetic oxide was added from dropping funnel, at constant stirring, at a rate of 2–3 drops per sec. until 10 ml of it was added to the flask. Then, temperature was raised to 60–70°C until complete evaporation of acetyl chloride. The flask was then heated to 120–130°C in the mixture to remove excess of acetyl oxide, reaction mass was distilled under vacuum.

Synthesis of thienyl-containing dihydroxysilanes and siloxanes

0.2 mole of aniline was poured into a three-neck flask, equipped with a mechanical stirrer, dropping funnel and reflux condenser; 250 ml of dry ether and 0.2 mole of water were added. The obtained mixture was cooled to $-20°C \div 20°C$ and 0.1 mole of thienylmethyldichlorosilane in 100 ml of ether was added dropwise.

After complete adding of the whole chlorosilane reaction mixture was stirred and refluxed for 1 hr. Muriatic aniline residue formed during reaction was filtered over Buchner filter, and solvent was removed in the vacuum under water-jet pump. The residue was dissolved in toluene and left at −5°C for 24 hr to give crystals.

Heterofunctional condensation of α,ω-dihydroxydiorganosiloxanes with diorganodichlorosilanes or -siloxanes

To a mixture of 0.2 mole of pyridine in 100 ml of absolute ether, 0.1 mole of α,ω-dihydroxydiorganosiloxane and dichlorodiorganosiloxane or -silane were added dropwise and synchronously, at room temperature. The mixture was heated for 5 hr at 30°C, cooled, residue was filtered, ether layer was washed for several times by distilled water and dried over Na_2SO_4. After evaporation of ether, the residue was distilled under vacuum or recrystallized from hexane.

Hydrolysis of methylthienyldiacetoxysilane

a) To a mixture of 72 g of water and 120 ml of ethyl ether, at −3°C 24 g of methylthienyldiacetoxysilane in 60 ml of ether was added and mixed at room temperature for 3 hr; ether layer wash washed and the residue dried. White powdery compound was obtained; recrystallization of it from toluene yielded 30.3 g (47.5%) of trimethyltrithienylcyclotrisilane (XXVIII); recrystallization from hexane yielded 16.8 g (19%) of tetramethyltetrathienylcyclotetrasiloxane (XXIX).

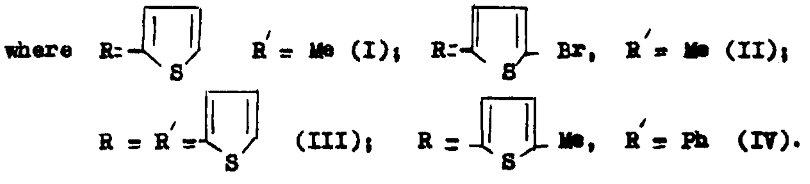
b) Likewise, from 24 g of methylthienyldiacetoxysilane in 60 ml of ether, 108 g of water and 120 ml of sulfuric ether 13.82 g of the compound XXVIII with the yield of 33% and 20.76 g of the compound XIX with the yield of 37% were obtained.

c) Likewise, from 24 g of thienyldiacetoxysilane in 60 ml of ether, 108 g of water and 120 ml of sulfuric ether, 17.89 g of the compound XXVIII and 41.74 g of the compound XXIX were obtained with the yields of 28% and 49% correspondingly.

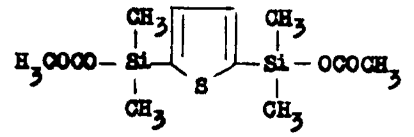
RESULTS AND DISCUSSION

By interaction of thienyl-containing dichlorosilanes and acetyloxide, corresponding organothienyldiacetoxysilanes have been synthesized:

$$RR'\,SiCl_2 + 2(CH_3CO)_2O \rightarrow RR'\,Si(OCOCH_3)_2 + 2CH_3COCl$$

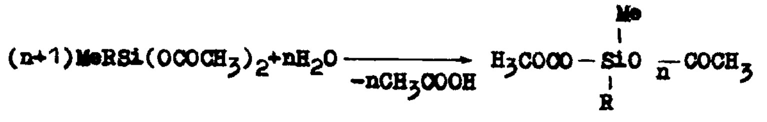


Acetylation of 2,5-bis(dimethylchlorosilyl)thiophene yielded 2,5-bis(dimethylacetoxysilyl)thiophene:



(V).

Partial hydrolytic condensation of diacetoxymethylthienylsilane at various temperatures led to the formation of α,ω-diacetoxysiloxanes:



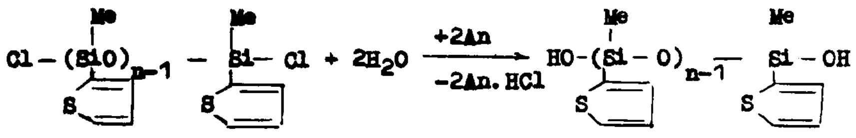
$$(n+1)MeRSi(OCOCH_3)_2 + nH_2O \xrightarrow[-nCH_3COOH]{} H_3COCO-\left(\overset{Me}{\underset{R}{Si}}O\right)_n-COCH_3$$

with n=2 (VI); 8 (VII); 11 (VIII).

Physico-chemical characteristics of the synthesized compounds are presented in Table I.

IR spectra of the obtained thienylacetoxysilanes and -siloxanes show strong absorbtion bands at 705 and 1220 cm^{-1}, moderate bands at 1500, 1520 and 1800 cm^{-1}, and weak band at 3035 cm^{-1} characteristic for C—S bands; absorbtion bands in the region of 1700–1770, 1190–1250, 925–770 characteristic for C═O bonds, and intense absorbtion bands at 1000–1100 cm^{-1} speak in favor of the presence of Si—O—Si bonds in the compounds (VI-VIII).

Methylthienyldihydroxysilane and α,ω-dihydroxymethylthienylsiloxanes were obtained by hydrolysis reaction of methylthienyldichlorosilane and α,ω-dichloromethylthienylsiloxanes at low temperatures in the presence of an acceptor of HCl—aniline.



where n=1 (IX); 2 (X); 3 (XI); 10 (XII)

The obtained compounds IX and X are colorless crystalline ones, compound XI is easy mobile liquid, and XII—oily substance.

TABLE I

Physico-chemical characteristics, elemental analysis and yields of thienyl-containing acetoxysilanes and -siloxanes

								Element composition					
				MR		M		Found			Calcd		
NN	bp, °C Merc. col. pressure, mm	n_D^{20}	d_4^{20}	Found	Calcd	Found	Calcd	S	Si	Formula	S	Si	Yield
I.	115–116(2)	1,4915	1,1821	60	59,78	200	224	11,2	11,80	$C_9H_{12}O_4SSi$	11,94	11,8	96
II.	118(1)	1,515	1,441	67	66,70	325	323	9,89	8,57	$C_9H_{11}BrO_4SSi$	9,90	8,66	98,7
III.	181(1)	1,552	1,423	70	69,30	310	313	20,68	8,78	$C_{12}H_{12}O_4S_2Si$	20,51	8,97	92,4
IV.	157(1)	—	—	—	—	319	320	10,21	8,77	$C_{15}H_{16}O_4SSi$	10,0	8,75	99,2
V.	114(1)	1,486	1,146	79	79,23	314	316	10,35	17,62	$C_{12}H_{20}O_4SSi_2$	10,12	17,72	97,1
VI.	182(2)	1,499	1,275	91	91,36	389	396	16,23	14,69	$C_{14}H_{18}O_5S_2Si_2$	16,16	14,56	40,3
VII.	—	—	—	—	—	1240	1238	20,77	18,34	$C_{44}H_{54}O_{11}S_8Si_8$	20,64	18,11	56,2
VIII.	—	—	—	—	—	1668	1664	21,42	18,67	$C_{59}H_{72}O_{14}S_{11}Si_{11}$	21,15	18,50	42,9

Structures of the synthesized compounds were verified by IR and PMR spectra and that of 1,3-dihydroxy-1,3-dimethyl-1,3-dithienyldisiloxane by roentgenostructural analysis.

PMR spectra of the compounds IX–XII are characterized by the peaks at 0.34 ppm for Me groups and at 7.16–7.70 ppm for a thienyl group.

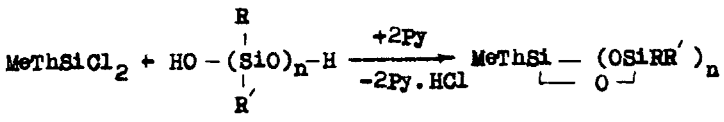
Roentgenostructural studies showed that crystals of the compound X were monowedged: $a = 11854$ (2), $b = 21{,}436$ (3), $c = 6{,}3322$ (4) Å, $V = 1522{,}7$ (6) Å, $m = 302$. $\alpha_{calcd} - 1{,}32$ g/cm^3, $Z = 4$. $C_{10}H_{14}O_3S_2Si_2$ is a spatial p^21/b group.

Roentgenograms of the compound X revealed statistical disbalance of thienyl rings due to coexistance of molecules (in approximately 1:1 ratio) with different orientations of thienyl fragments arranged around the Si—C bonds at 180° in relation to each other (Figure 1). There are seven hydrogen bonds of O—H. . .O with silanol groups in the crystals.

Molecules of the compound X in the crystals are pooled into symmetric centre dimers around the centres of symmetry (0.5; 0.5; 0) by hydrogen bonds of O(I)—HO(I). . .O(2) /distances 0. . .0.2, 702 (7) Å, H. . .O 2.14 (6) Å, angle of OHO 150 (6) Å/. Dimer, in its turn, is packed in endless columns, extended along orientation on behalf of H bonds of O(2)—HO(2). . .O(I) /distances 0. . .0.2, 741 (7) Å, H. . .O 2.14 (6) Å, angle OHO 162 (6) Å (Figure 2).

Thus, the data of roentgenostructural analysis testify that both oxygen atoms of the compound X participate in the formation of hydrogen bonds being the donors and the acceptors at the same time.

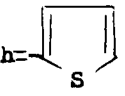
Thienyl-containing organocyclosiloxanes with different organic radicals at the silicon atom were obtained by the method of heterofunctional condensation. Six- and eight-membered organocyclosiloxanes with one methylthienylsiloxy ring in the cycle were synthesized by the authors, by interaction of methylthienyldichlorosilane and 1,3-dihydroxytetra- and 1,5-dihydroxyhexaorganosiloxanes in the absolute ether medium in the presence of pyridine:



$$MeThSiCl_2 + HO-(\underset{R'}{\overset{R}{SiO}})_n-H \xrightarrow[-2Py.HCl]{+2Py} MeThSi-(OSiRR')_n$$

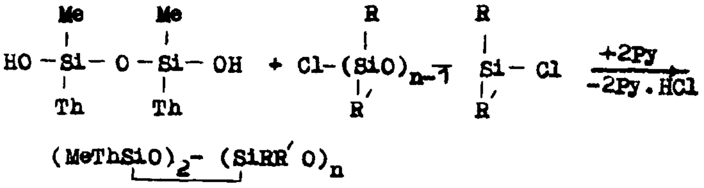
where at n=2; R=R′=Me (XIII); R=Me, R′=Vin (XIV);
R=Me, R′= $-CH_2Cl$ (XV); R=Me, R′=Ph (XVI);
R=R′=Ph (XVII)
at n=3; R=R′=Me (XVIII); R=Me, R′=Vin (XIX);
R=Me, R′=Ph (XX); R=R′=Ph (XXI);

Th=



Organocyclosiloxanes with two methylthienylsiloxane bonds in the cycle were obtained in similar conditions by interaction of 1,3-dihydroxy-1,3-dimethyl-1,3-

dithienyldisiloxane and different alkyl(aryl)dichlorosilanes and 1,3-dichlorotetraalkyl(aryl)disiloxanes. The reaction proceeds according to the scheme:



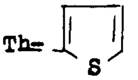
$$HO-\underset{Th}{\overset{Me}{Si}}-O-\underset{Th}{\overset{Me}{Si}}-OH + Cl-(\underset{R'}{\overset{R}{Si}}O)_{n-1}\underset{R'}{\overset{R}{Si}}-Cl \xrightarrow[-2Py\cdot HCl]{+2Py} (MeThSiO)_2-(SiRR'O)_n$$

where at n=1: R=Me, R′=Ph (XXII); R=R′=Ph (XXIII);

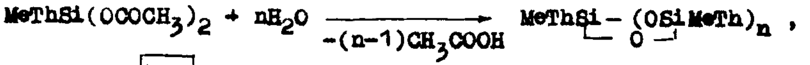
n=2: R=R′=Me (XXIV); R=R′=Ph (XXV);

R=Me, R′=Ph (XXVI); R=Me, R′=Vin (XXVII).

Th=



Study of the reaction of hydrolytic condensation of methylthienyldichlorosilane in strong acid medium has shown that the yield of methylthienylcyclosiloxanes is insignificant due to thienyl group tearing off from the silicon atom. Thus, hydrolytic condensation of methylthienyldiacetoxysilans was conducted at different temperatures. As a result, a mixture of six- and eight-membered methylthienylcyclosiloxanes with total yield of 70% was obtained. Hence, the reaction proceeds mainly by the following scheme:



$$MeThSi(OCOCH_3)_2 + nH_2O \xrightarrow[-(n-1)CH_3COOH]{} MeThSi-(OSiMeTh)_n-O ,$$

where Th=

n=2 (XXVIII); 3 (XXIX).

Low temperature conditions (−3°C) of reaction led to the formation of a six-membered cycle mainly (XXVIII), while at room temperatures, eight-membered cycle was preferentially obtained.

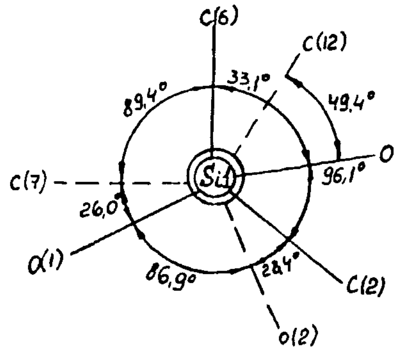


FIGURE 1 Newman projection along the line of Si(1). . .Si(2) atoms linked with atoms of si(1) and Si(2).

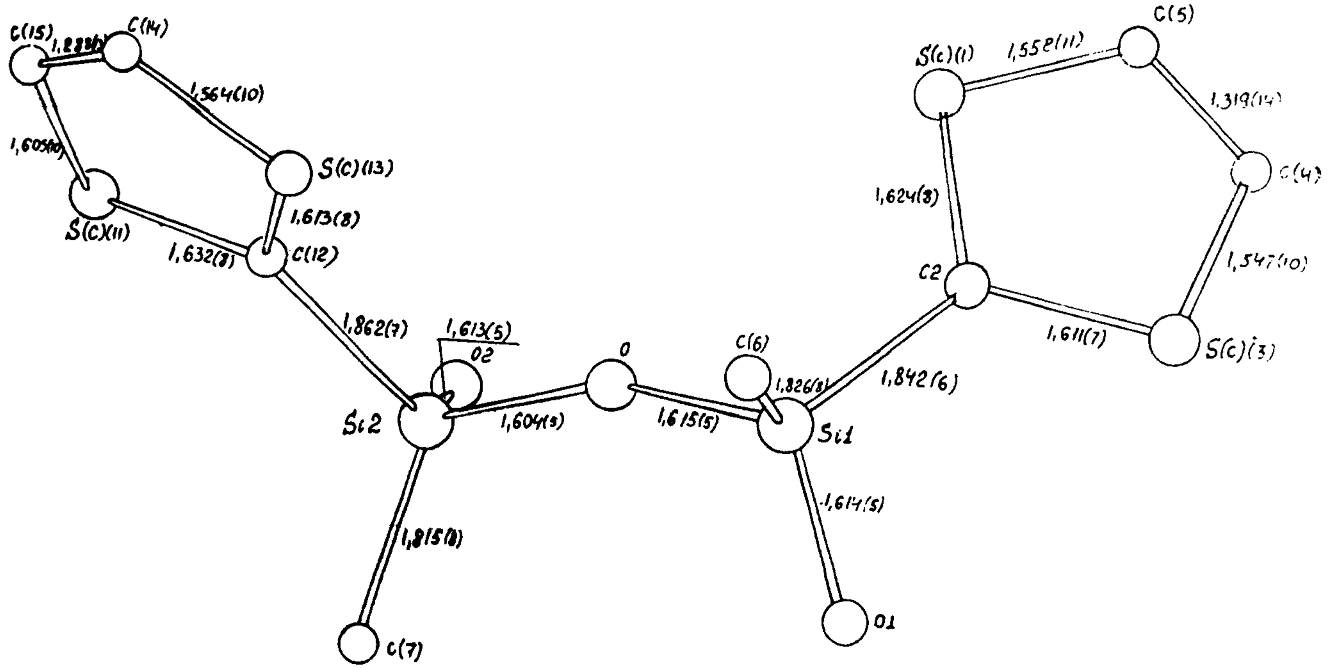


FIGURE 2 Structure of the molecule of the compound XXIII. Sulfur atom in each of the thienyl substituents occupies two positions with probability of 1/2.

TABLE II

Physico-chemical characteristics, element composition and yields of thienyl-containing organocyclosiloxanes

NN	Yield %	bp, °C Merc. col. pressure, mm	mp	n_D^{20}	d_4^{20}	MR		M		Element composition, %				
										Found			Calculated	
						Found	Calcd	Found	Calcd	S	Si	Formula	S	Si
XIII	63,2	78,1(1)	—	1,4608	1,0735	74	74,59	283	290	11,24	28,81	$C_9H_{18}O_3SSi_3$	11,03	28,96
XIV	39,7	110(1)	—	1,4425	1,046	82	82,57	300	314	10,2	26,81	$C_{11}H_{18}O_3SSi_3$	10,19	26,75
XV	43,4	131(2)	—	1,503	1,1828	85	84,26	361	559	8,7	24,1	$C_9H_{16}O_3ClSSi_3$	8,91	23,39
XVI	44,7	194(1)	—	1,535	1,1249	115	114,23	410	414	7,53	19,96	$C_{19}H_{22}O_3SSi_3$	7,72	20,28
XVII	61,3	236(10⁻²)	162–163	1,5898	1,210	150	150,68	529	538	5,38	14,6	$C_{28}H_{26}O_3SSi_3$	6,94	15,61
XVIII	62,0	146(1)	—	—	—	—	—	371	364	8,81	30,73	$C_{11}H_{24}O_4SSi_4$	8,79	30,76
XIX	40,8	160(3)	123–125	1,4695	1,108	105	105,71	421	400	8,1	27,5	$C_{14}H_{24}O_4SSi_4$	8,0	28,0
XX	59,5	—	169–170	—	—	—	—	—	550	5,90	20,42	$C_{26}H_{30}O_4SSi_4$	5,81	20,36
XXI	48,2	—	177–178	—	—	—	—	742	736	4,29	15,20	$C_{41}H_{36}O_4SSi_4$	4,34	15,21
XXII	64,0	—	122–123	—	—	—	—	415	420	16,34	22,27	$C_{12}H_{18}O_3S_2Si_3$	16,24	21,31
XXIII	61,5	—	129–130	—	—	—	—	436	428	15,19	20,71	$C_{22}H_{22}O_3S_2Si_3$	15,23	20,60
XXIV	37,9	145(2)	—	1,4705	1,1035	113	113,8	424	432	13,97	25,84	$C_{14}H_{24}O_4S_2Si_4$	14,81	25,92
XXV	16,0	200–204 (10⁻²)	140–142	1,562	1,1434	190	191,18	671	680	9,28	16,04	$C_{34}H_{32}O_4S_2Si_4$	9,41	16,4
XXVI	51,8	—	132–133	—	—	—	—	536	528	12,19	16,01	$C_{24}H_{28}O_4S_2Si_4$	12,12	15,90
XXVII	46,2	—	126–128	—	—	—	—	462	456	14,13	24,61	$C_{16}H_{24}O_4S_2Si_4$	14,03	24,56
XXYIII	47,5	—	37–38	—	—	—	—	430	426	22,4	20,50	$C_{15}H_{18}O_3S_3Si_3$	22,53	19,71
XXIX	49,0	—	81–82	—	—	—	—	557	568	23,6	18,9	$C_{20}H_{24}O_4S_4Si_4$	22,53	19,71

In PMR spectra of the compounds XIII–XXIX resonance signals characteristic to methyl groups were observed at 0.35 ppm, and those characteristic to thienyl groups were seen in the region of 7.16–7.70 ppm. Compound XV revealed chemical shift in the region of 3.45 ppm for chloromethyl groups, and the compounds XIV, XIX and XXVII in the region of 5.35 showed shifts characteristic for vinyl groups.

Physico-chemical characteristics of the synthesized compounds are given in Table II.

RESULTS

By the reaction of acidolysis of thienyl-containing dichlorosilanes corresponding acetoxysilanes have been synthesized for the first time.

Hyrolytic condensation of thienylmethyldichlorosilanes and diacetoxysilanes yielded, correspondingly, α,ω-dihydroxymethylthienylsiloxanes and thienylmethylcyclosiloxanes. By the method of heterofunctional condensation of methylthienyldichlorosilane (or siloxane) with dihydroxyorganosiloxanes, six- and eight-membered organocyclosiloxanes, with one or two methylthienylsiloxy rings in the cycle, have been synthesized.

Roentgenostructural analysis of 1,3-dihydroxydimethyldithienylsiloxane verified that both oxygen atoms of the molecule participate in the formation of hydrogen bonds, being the donors and the acceptors at the same time.

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