SYNTHESIS OF ORGANOSILICON LACTONES BASED ON VINYLACETIC ACID

V. F. Mironov and N. S. Fedorov

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6-Membered ring organosilicon lactones, with various substituents on the silicon atom, are prepared.

In a previous paper we disclosed a synthesis of 7-membered ring organosilicon lactones [1], the equations being:

$$(CH_3)_3SiO_2CCH_2CH=CH_2+HSi(CH_3)_2CH_2Cl \xrightarrow{H_2PtCl_6} \rightarrow (CH_3)_3SiO_2CCH_2CH_2CH_2Si(CH_3)_2CH_2Cl \xrightarrow{H_2O} \rightarrow ClCH_2(CH_3)_2SiCH_2CH_2CH_2COOH \xrightarrow{Na_2CO_3} (CH_3)_2CH_2SiCH_2CH_2CH_2C(=O)O \quad (1)$$

Continuing research along those lines, we found that replacement of the $ClCH_2SiH(CH_3)_2$ in this reaction by other hydrosilanes containing if only one chlorine atom at the silicon atom, at once led to formation of 6-membered ring lactones of a new type:*

$$(CH_3)_3SiO_2CCH_2CH=CH_2+HSiR_nCl_{3-n} \xrightarrow{H_2PtCl_6} \rightarrow [(CH_3)_3SiCl+HR_nCl_{2-n}SiO_2CCH_2=CH_2] \rightarrow (CH_3)_3SiCl+R_nCl_{2-n}SiCH_2CH_2CH_2C(=O)O \quad (80–90\%), \quad (2)$$

where R = CH_3–, C_2H_5–, C_6H_5– and n = 0, 1, 2. Reaction (2), giving 80–90% yields of silalactones, proceeds through two stages, each of which we were able to effect separately.

Thus in the absence of Spaier catalyst (H_2PtCl_6) trans-silylation is the sole reaction, instead of reaction 2:**

$$(CH_3)_3SiO_2CCH_2CH=CH_2 + H(CH_3)_2SiCl \rightarrow (CH_3)_3SiCl+H(CH_3)_2SiO_2CCH_2CH=CH_2. \quad (3)$$

Here the formation of the dimethylsilyl ester of vinylacetic acid was demonstrated by its synthesis according to the equation:

$$HSi(CH_3)_2Cl + CH_2=CHCH_2COOH \xrightarrow{(C_2H_5)_2NC_6H_5} (CH_3)_2HSiO_2CCH_2CH=CH_2. \quad (4)$$

In the presence of H_2PtCl_6, the dimethylsilyl ester of vinylacetic acid, prepared by the reactions of Eqs. 3 and 4, readily further cyclizes to the silicolactone

$$H(CH_3)_2SiO_2CCH_2CH=CH_2 \xrightarrow[85\%]{H_2PtCl_6} (CH_3)_2SiCH_2CH_2CH_2C(=O)O \quad (5)$$

It should be mentioned that the analogous dimethylsilyl esters of acrylic and methacrylic acids are not cyclized to silicolactones, and that at room temperature, in the absence of H_2PtCl_6, they give polymers:

$$H(CH_3)_2SiO_2CCR=CH_2 \xrightarrow{\text{room temp.}} \left[-\overset{CH_3}{\underset{CH_3}{Si}}-O\overset{O}{C}-CHCH_2- \right]_n \quad (6)$$

where R = H, Me. Our unsuccessful attempts to add hydrochlorosilanes to trimethylsilyl esters of acrylic or methacrylic acids, which led only to formation of polymer and trimethylchlorosilane, become understandable:

$$(CH_3)_3SiO_2CCR=CH_2+HSiR'Cl_2 \xrightarrow{H_2PtCl_6} [(CH_3)_3SiCl+ +HR'ClSiO_2CCR=CH_2] \rightarrow (CH_3)_3SiCl+ \left[-\overset{Cl}{\underset{R'}{Si}}-O\overset{O}{C}-\underset{R}{CH}-CH_2- \right]_n \quad (7)$$

where R = H, CH_3; R' = CH_3–, C_2H_5.

At the same time, hydroalkylalkoxysilanes and $ClCH_2Si(CH_3)_2H$ readily add to these esters.

$$(CH_3)_3SiO_2CCR=CH_2+HSi(R')(OC_2H_5)_2 \xrightarrow{H_2PtCl_6} \rightarrow (CH_3)_3SiO_2CCRHCH_2SiR'(OC_2H_5)_2, \quad (8)$$

where R = H, CH_3; R' = CH_3, C_2H_5 .

EXPERIMENTAL

Dimethylsilyl ester of vinylacetic acid (I). A mixture of 23.6 g (0.25 mole) $HSi(CH_3)_2Cl$, 37.3 g (0.25 mole) diethylaniline, and 250 ml dry ether was stirred, and 21.5 g (0.25 mole) vinylacetic acid added. The precipitate of diethylaniline hydrochloride was filtered off, and washed with fresh ether. Distillation of the filtrate gave 22.2 g I. Compound II and III were prepared similarly (see table).

Si-dimethyl-4-silavalerolactone (IV). a) 200 ml dry benzene was heated to boiling, and 0.1 ml 0.1 M solution of H_2PtCl_6 added, followed by 6.6 g I over a period of 2 hr. The benzene was distilled off and the residue distilled to give 5.5 g IV.

b) A 3-necked flask was fitted with reflux condenser, dropping funnel, and thermometer. In it were placed 17 g (0.17 ml) dimethylchlorosilane and 0.1 ml 0.1 M H_2PtCl_6 solution in iso-PrOH, the mixture heated to boiling, and 25 g (0.16 mole) trimethylsilyl ester of vinylacetic acid added over a period of 2 hr [1], when the temperature of the reaction mixture rose from 35° to 73°. After slowly distilling off the trimethylchlorosilane, the residue was vacuum-distilled,

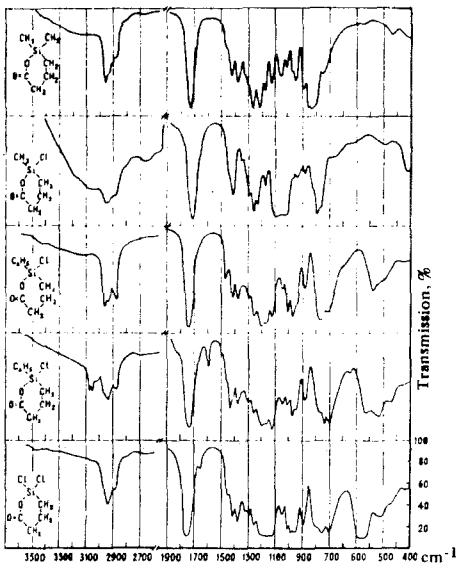
*5-Membered ring lactones of the type $R_2SiCH_2CH_2C(=O)O$ are mentioned in patents [2], a thesis [3], and an article [4].

**Evidently, trans-silylation is general for trimethylsilylesters of carboxylic acids, as we have noted in other cases.

Physical Constants and Analytical Data of Compounds Synthesized

Compound number	Compound	Bp, °C (mm pressure)	n_D^{20}	d_4^{20}	MR_D		Found, %				Calculated, %				Yield, %
					Found	Calculated	C	H	Si	Cl	C	H	Si	Cl	
I	$H_2C=CH-CH_2-C(=O)-O-Si(CH_3)(CH_3)-H$	67—68 (80)	1.4140	0.9059	39.78	40.06	50.08 49.67	8.20 8.20	19.71 19.63	—	49.95	8.38	19.47	—	70
II	$H_2C=CH-C(=O)-O-Si(CH_3)(CH_3)-H$	57—58 (110)	1.4111	0.9155	35.29	35.32	46.56	7.59	21.24	—	46.12	7.74	21.56	—	70
III	$H_2C=C(CH_3)-C(=O)-O-Si(CH_3)(CH_3)-H$	51—52 (43)	1.4175	0.9061	40.07	40.06	49.65 50.02	8.42 8.23	19.59 19.38	—	49.95	8.38	19.47	—	66
IV	$O=C(-O-)-CH_2CH_2CH_2Si(CH_3)(CH_3)$	69—70 (1,5)	1.4640	1.0495	37.94	38.22	49.78 49.82	8.56 8.33	19.89 19.77	—	49.95	8.38	19.47	—	76.6
V	$O=C(-O-)-CH_2CH_2CH_2Si(Cl)(C_2H_5)$	106—107 (3)	1.4802	1.2041	42.19	42.43	40.65 40.52	6.48 6.57	15.94 15.69	20.1 20.2	40.32	6.20	15.71	19.86	86.4
VI	$O=C(-O-)-CH_2CH_2CH_2Si(Cl)(CH_3)$	96—97 (2)	1.4753	1.2505	37.10	37.78	36.56	5.71	16.84	21 46	36.46	5.51	17.05	21.55	87.5
VII	$O=C(-O-)-CH_2CH_2CH_2Si(Cl)(C_6H_5)$	158—159 (2.5)	1.5460	1.2630	56.85	57.43	53.26 53.11	5.13 5.12	12.33 12.29	15.8 15.9	52.96	4.89	12.38	15.65	81
VIII	$O=C(-O-)-CH_2CH_2CH_2Si(Cl)(Cl)$	99—100 (1.5)	1.4859	1.4088	37.72	37.34	—	—	15.19 14.42	—	25.94	3.26	15.17	38.34	70

to give 17.5 g IV, as a viscous colorless oil. Found: M 138; 135. Calculated M 144.2. Compounds V–VIII were synthesized similarly.



IR spectra of compounds prepared

The table gives physical constants and analytical data for all the compounds prepared. The figure gives their IR spectra.

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State Scientific Research Institute for the Chemistry and Technology of Heteroorganic Compounds of the Elements, Moscow

LETTERS TO THE EDITOR

REACTION OF PYRAZINE DI-N-OXIDE WITH ACETIC ANHYDRIDE AND BENZENESULFONYL CHLORIDE

A. S. Elina and I. S. Musatova

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Previously American workers, who had studied the reaction of N-oxides of the pyrazine series with acetic anhydride, reported that di-N-oxides of pyrazine unsubstituted in the ring, unlike N-oxides of pyridine and quinoline, do not react with acetic anhydride [1]. Those authors did not find any change in UV spectrum for samples of the reaction mixture, and finally recovered the starting pyrazine di-N-oxide (I). Continuing a study of rearrangements of N-oxides of 6-membered ring aromatic diazines, we investigated the reaction of I with acetic anhydride and benzenesulfonyl chloride. The reaction of I with acetic anhydride was followed by paper chromatography, using the system 5% acetic acid-BuOH. When I was boiled with acetic anhydride and a sample of the reaction solution chromatographed, the spot of the starting di-N-oxide I (R_f 0.13, in UV light dark-violet spot) was observed to gradually decrease, and after 6 hr boiling, it was hardly visible. Also, after 2 hr boiling the chromatogram showed new spots, one with R_f (0.36–0.37, dark-violet in UV light) corresponding to pyrazine mono-N-oxide, and three other spots due to unknown substances (R_f 0.49–0.51, azure; R_f 0.67–0.69, azure; brown spot at start). Only a very inconsiderable amount of I (up to 1%) was recovered from the solution of reaction products. Removal of the acetic anhydride left an oily mixture of products, whose composition is being studied. Previously one of us showed that quinoxaline di-N-oxide reacts with benzenesulfonyl chloride at room temperature to give the benzenesulfonate of 2-chloroquinoxaline 1-N-oxide [2]. Under the same conditions the di-N-oxide of pyrazine does not react, unlike that of quinoxaline; it reacted with benzenesulfonyl chloride only when heated (75–100° for 8 hr). The reaction led to the isolation of the benzenesulfonate of compound I (30.8%) (bp 139–141°. Found: N 10.77; S 11.84%. Calculated for $C_4H_4N_2O_2 \cdot C_6H_6O_3S$. N 10.36; S 11.84%) and a substance mp 131–132° (8.7%), containing covalently linked chlorine. A solution of this compound in 2.5 N NaOH was heated for a short time; after cooling and acidifying the solution gave a color reaction with $FeCl_3$, characteristic of a cyclic hydroxamic acid. In view of these results the compound, mp 131–132°, was tentatively assigned a structure 2-chloropyrazine 1-N-oxide. Found: Cl 27.51; N 21.6%. Calculated for $C_4H_3ClN_2O$: Cl 27.19; N 21.46%. The study of this reaction is being continued.

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Ordzhonikidze All-Union Scientific Research Chemical and Pharmaceutical Institute, Moscow