SYNTHESIS OF ORGANOSILICON LACTONES BASED ON VINYLACETIC ACID

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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:

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

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:

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

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

At the same time, hydroalkylalkoxysilanes and 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.

MeOH). Found: N 10.51, 10.60%. Calculated for $C_{18}H_{16}N_2$. N 10.76%. Ie. $R_1=R_2=CH_3$, $R_3=H$, yield 69%, mp 96° (ex MeOH). Found: N 14.02, 14.16%. Calculated for $C_{13}H_{14}N_2$. N 14.13%. If. $R_1=H$, $R_2=C_6H_5$, $R_3=CH_3$, yield 78%, mp 167° (ex EtOH). Found: N 10.44, 10.53%. Calculated for $C_{18}H_{16}N_2$. N 10.76%. Ig. $R_1=R_2=R_3=CH_3$ (perchlorate), mp 194–195° (ex glacial AcOH). Found: Cl 11.51, 11.52%. Calculated for $C_{14}H_{16}N_2 \cdot HClO_4$. Cl 11,34%.

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ELEMENTARY CELL PARAMETERS OF OME 1-ORGANYLSILATRANES

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With a view to discovering the most suitable objects for investigating the crystal structure of silatranes synthesized by M. G. Voronkov

Elementery Cell Parameter of 1-Organylsilatranes $RSi(OCH_2CH_2)_3N$

R	a, Å	b, Å	c, Å	β	N
CH_3—	7.54	9.73	14.16	126.6°	4
CH_3CH_2—	9.33	16.45	6.65		4
$(CH_3)_2CH$—	9.52	17.12	6.85		4
$CH_2=CH$—	9.61	30.53	6.62		8
C_6H_5—	13.09	18.37	10.02		8
C_6H_5O—	13.64	8.41	10.83		4

and G. I. Zelchan [1–3], we have determined by X-ray analysis the parameters and translation groups of the elementary cells of 1-methyl-, 1-ethyl-1-isopropyl-, 1-vinyl-, 1-phenyl-, and 1-phenoxysilatranes.

The numbers of molecules (N) in the elementary cells of the crystals were calculated from the parameters. The elementary cells of the crystals of all the compounds investigated are simple. The table gives numerical values of the parameters of the elementary cells.

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