4-SILALACTONES AND 4-SILALACTAMS

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A general method for the preparation of organosilicon lactones and lactams in which a silicon atom attached to two carbon atoms is present in the 8-position to the heteroatom O or N has been developed. A new reaction with acyloxysilanes has been observed for a number of silicon compounds containing a chloromethyl radical, which consists in the replacement of the chlorine by the acyl radical.

In a preliminary communication [1], we recently described a method for preparing six-membered silalactones and silalaetams starting from methacrylic acid. It has also proved suitable for the synthesis of seven-membered silalactones and silalaetams starting from vinylacetic acid:

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\begin{align*}
\text{CH}_3\text{C} &= \text{CHCH}_2\text{COCH}_2\text{Si(SiCl)}_3 + \text{CH}_2\text{Cl}_2, \\
\end{align*}
\]

In all the stages of this scheme except the last, the reactions with vinylacetic acid derivatives, like those with methacrylic acid derivatives, take place readily and with high yields.

However, in the cyclization stage, the seven-membered 4-silalactone, unlike the six-membered compound, is formed in low yield (21%). This is due to the fact that under the reaction conditions the partial dimerization and polymerization of the silalactone takes place. At the same time, the seven-membered silalaetam is formed in good yield (70%). When acryllic acid was used in the scheme given above, in the first stage a reaction unexpectedly took place which led directly to the formation of a six-membered 3-silalactone.

Since when this reaction was carried out in the absence of Speier's catalyst the bulk of the starting materials was recovered and \((\text{CH}_3)_2\text{SiCl}_3\) and \(\text{H}(\text{CH}_3)_2\text{SiCH}_2\text{CCH}=\text{CH}_2\) were formed in very small amounts, the synthesis of the 4-silalactones may also take place by a different route.
The latter reaction also takes place with other starting materials.

2CICH3C—O—Si(CH3)3 + CH3SICICH3Cl→

CH3 O

→ CICH3C—O—Si(TH3)3 +

CH3 O

→ CICH3C—OCH3Si(TH3)3OCCH3Cl + 2(CH3)3SiCl

In this case, a reaction first takes place at the Si—CH3 bond and then at the C—Cl bond. However, the replacement in the last two schemes of the second component by CICH3Si(CH3)3 or by CH3Si(CH3)2H and of CICH3Si(CH3)2Cl by CH3Si(CH3)2Cl3 under otherwise the same conditions, is accompanied by no reaction of any kind. Likewise, there is no reaction between (C6H5)2SiO2CCl3 and CICH3Si(CH3)2OC2H5.

Thus, while the transsilylation reaction is a general one, the possibility of the occurrence of the new reaction depends strongly on the structure of the features of the starting materials. In conclusion, so far as concerns the properties of the lactones, it must be noted that the six-membered lactone obtained from acrylic acid, in contrast to the lactone synthesized from methacrylic acid, is capable of dimerizing on standing. This capacity for dimerizing is shown by the seven-membered lactone to an even greater extent.

EXPERIMENTAL

A description of the synthesis of six-membered silalactones from methacrylic acid has been published previously [1]. The spectra of these compounds and those described below are given in Figs. 1 and 2.

Trimethylsilylethyl (chloromethyl)dimethylsilylethylbutoxide (CIC2H5)2Si(TH3)2COO(CH3)3 (I). Over 2 hr, 26 g (0.16 mole) of (CIC2H5)2SiOCCH3CH2CH2Cl was added to a boiling mixture of 18 g (0.16 mole) of CICH3Si(CH3)2SH and 0.5 ml of a 0.1 M solution of H2PtCl6 in isopropanol. The temperature of the reaction mixture rose to 100°C. Vacuum distillation yielded 35.5 g (81%) of I with bp 81-85°C (3 mm); nD20 1.4451; d43 1.0157. (The substance was subjected to additional purification by redistillation over a small amount of Na2CO3.) Found, %: C 53.45; H 8.61; Si 17.85; N 3.85; d20 1.4450.

C1H13Si—(TH3)2—O (II). A mixture of 44 g (0.16 mole) of I and 60 ml of water was stirred vigorously with heating to 80°C for 2 hr. The organic layer was separated off, dried, and distilled in vacuum to give 30.7 g (82%) with bp 82-84°C (2 mm); nD20 1.4728; d43 1.0328. Found, %: C 52.85; 52.84; H 9.00; 8.96; Si 17.48; 17.93; MR2 43.30. Calculated for C13H18SiO5, %: C 53.13; H 8.82; Si 17.70; MR2 43.83.

We also obtained 2 g (7.98%) of dimer III with bp 160-162°C (2.5 mm) by solidifying in the receiver into a colorless crystalline mass; mp 90-97°C. Found, %: C 53.18, 53.16; H 8.96; 8.79; Si 16.05, 16.14; mol wt. 274. Calculated for C26H32Si2O6P, %: C 53.13; H 8.84; Si 17.70; mol wt. 316.55.

γ-(Chloromethyl)dimethylsilylbutoxychloride (CIC2H5)2SiOCI (IV). A mixture of 8 g (0.04 mole) of II and 4.89 g (0.04 mole) of thionyl chloride was heated in the water bath for 1 hr and then distilled in vacuum. This gave 8.3 g (94%) of IV with bp 99-100°C (4 mm); nD20 1.4700; d43 1.0971. Found, %: C 39.84, 39.32; H 6.67, 6.74; Si 12.88; Cl 33.06; 32.86; MR2 57.77. Calculated for C13H14SiClO, %: C 36.42; H 6.61; Si 13.17; Cl 33.29; MR2 54.28.

γ-(Chloromethyl)dimethylsilylbutyramide (CICH3)2Si—(CH3)3—N—H (V). A solution of 2.06 g of sodium methoxide in 10 ml of absolute methanol was added to 7.4 g of V. The reaction mixture was boiled for 2 hr. The precipitate of sodium chloride that separated out was filtered off, and the methanol was distilled off from the filtrate. Vacuum distillation of the residue yielded 4.07 g (70%) of VI with bp 160-162°C (3 mm); nD20 1.4451; d43 1.0157. (The substance was subjected to additional purification by redistillation over a small amount of Na2CO3.) Found, %: C 43.37, 43.32; H 8.66, 8.72; Si 21.02, 21.01; C1 13.23, 13.36. Calculated for C26H32SiO6P, %: C 43.39; H 8.38; Si 21.85; N 3.85; d20 1.4450.

4-Chloroacetoxy(chloroacetoxy)methylene(dimethyl)silane—CICH3—COOCH3H(C2H5)2SiO2CCl3 (VIII). a) A 250-ml Claisen flask was used as a 1 d~ 1.2844. Found, %: C 32.12, 32.21; H 4.66, 4.77; D 38.50; MR2 55.83. Calculated for C13H18SiO5, %: C 32.45; H 4.63; Si 10.83; C1 27.23, 27.13; MR2 55.83. Found, %: C 53.18, 53.16; H 8.96; 8.79; Si 16.05, 16.14; mol wt. 274. Calculated for C26H32Si2O6P, %: C 53.13; H 8.84; Si 17.70; mol wt. 316.55.

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1,2-Bis(chloroacetoxy)methylene(dimethyl)silane—CICH3—COOCH3H(C2H5)2SiO2CCl3 (IX). Hydrolysis of VIII. A mixture of 29.7 g (0.1 mole) of VIII was added to 500 ml of a saturated aqueous solution of ammonia. The yield of V was 34.28 g (72%), bp 146-148°C (2 mm). Colorless liquid crystallizing on standing (mp 28-29°C). Found, %: C 39.84, 39.52; H 6.67, 6.69; Si 21.02, 21.01; C1 13.23, 13.29. Calculated for C13H14SiClO, %: C 43.39; H 3.82; Si 18.5; d20 1.38.5.