TRANSSILYLATION REACTIONS IN ESTERS AND ETHERS OF THE SILANOLS. SYNTHESIS OF OXASILACYCLOALKANES

V. F. Mironov, N. S. Fedotov, and V. L. Kozlikov

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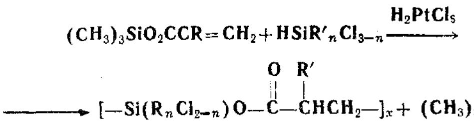
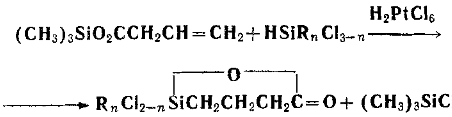
An equilibrium reaction of the exchange of silyl radicals taking place between organylchlorosilanes and acyloxy- and alkoxysilanes has been found. In the case of alkenyloxytrimethylsilane and chloro-H-silanes, in addition to the transsilylation reaction, intramolecular hydrosilyation takes place, leading to the formation of oxasilacycloalkanes.

As already reported [1, 2], in attempts to add chloro-H-silanes to trimethylsilyl esters of acrylic and methacrylic acid in the presence of H_2PtCl_6, in addition to a polymer, trimethylchlorosilane was invariably formed in high yield (~ 90%).



$$(CH_3)_3SiO_2CCR{=}CH_2 + HSiR'_nCl_{3-n} \xrightarrow{H_2PtCl_5} [-Si(R_nCl_{2-n})O-\overset{\overset{\large O}{\|}}{C}-\overset{\overset{\large R'}{|}}{C}HCH_2-]_x + (CH_3)_3SiCl \quad (1)$$

The performance of a similar reaction with a silyl ester of vinylacetic acid also led to the formation of trimethylchlorosilane and silalactone.

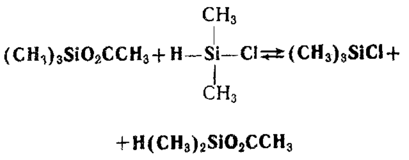


$$(CH_3)_3SiO_2CCH_2CH{=}CH_2 + HSiR_nCl_{3-n} \xrightarrow{H_2PtCl_6} R_nCl_{2-n}\underbrace{SiCH_2CH_2CH_2C}_{O}{=}O + (CH_3)_3SiCl \quad (2)$$

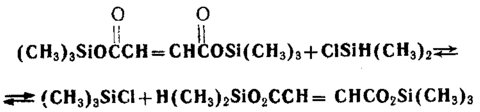
In the absence of a hydrosilylation catalyst, Reaction (2) takes place with the formation of trimethylchlorosilane and a silyl ester of vinylacetic acid.

$$(CH_3)_3SiO_2CCH_2CH{=}CH_2 + HSiR_nCl_{3-n} \rightleftarrows R_nHCl_{2-n}SiO_2CCH_2CH{=}CH_2 + (CH_3)_3SiCl \quad (3)$$

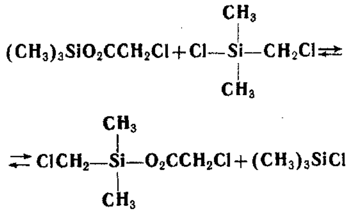
In the present work, we have established on the basis of several examples that this new* reaction, which we have called the transsilylation reaction, is a general one for various silyl esters of any carboxylic acids.



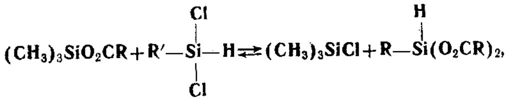
$$(CH_3)_3SiO_2CCH_3 + H-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-Cl \rightleftarrows (CH_3)_3SiCl + H(CH_3)_2SiO_2CCH_3 \quad (4)$$



$$(CH_3)_3SiO\overset{\overset{O}{\|}}{C}CH{=}CH\overset{\overset{O}{\|}}{C}OSi(CH_3)_3 + ClSiH(CH_3)_2 \rightleftarrows (CH_3)_3SiCl + H(CH_3)_2SiO_2CCH{=}CHCO_2Si(CH_3)_3 \quad (5)$$



$$(CH_3)_3SiO_2CCH_2Cl + Cl-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-CH_2Cl \rightleftarrows ClCH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-O_2CCH_2Cl + (CH_3)_3SiCl \quad (6)$$



$$(CH_3)_3SiO_2CR + R'-\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{Si}}-H \rightleftarrows (CH_3)_3SiCl + R-\overset{\overset{H}{|}}{Si}(O_2CR)_2,$$

where

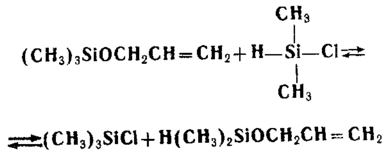
$R{=}CH_3;\ CH_2CH_2Cl;\ CH_2{-}CH{=}CH_2;\ R'{=}CH_3;\ C_2H_5.$ (7)

The performance of reactions (4–7) has shown that the transsilylation reaction is an equilibrium one. The equilibrium can be displaced in one direction or the other by eliminating one of the components from the reaction zone.

In reactions (1) and (2), for example, the equilibrium is shifted completely to the right as a consequence of the cyclization or polymerization of the H-silyl esters formed. In reactions (4–7) it can be displaced by distilling off the low-boiling component.

In addition, we have observed that the transsilylation reaction takes place successfully not only with esters but also with silyl ethers of various alcohols. For example:

$$(CH_3)_3SiOCH_2CH_2Cl + ClSi(CH_3)_2CH_2Cl \rightleftarrows (CH_3)_3SiCl + ClCH_2(CH_3)_2SiOCH_2CH_2Cl \quad (8)$$



$$(CH_3)_3SiOCH_2CH{=}CH_2 + H-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-Cl \rightleftarrows (CH_3)_3SiCl + H(CH_3)_2SiOCH_2CH{=}CH_2 \quad (9)$$

The occurrence of the latter reaction in the presence of a hydrosilylation catalyst disturbs the equilibrium because of the cyclization of the dimethylallyloxysilane. When other chloro-H-silanes are used as well, the transsilylation reaction takes place with the subsequent intramolecular silylation of the H-silyl ethers. Under these conditions, trimethylchlorosilane is formed with a yield of about 90%.

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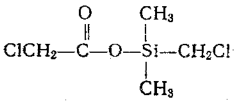
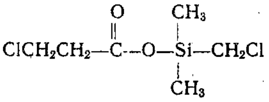
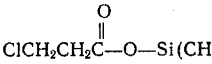
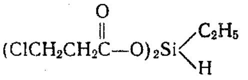
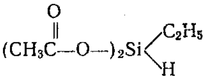
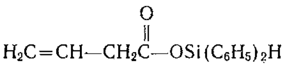
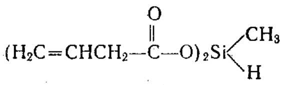
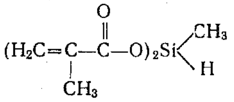
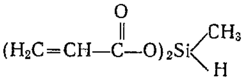
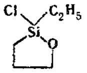
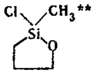
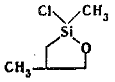
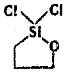
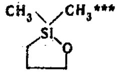
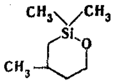
*Independently of us, a similar reaction for acetoxysilanes has been observed by N. F. Orlov [3] and for allyloxysilanes by Götz [5]. The transsilylation reaction is also characteristic of other classes of organosilicon compounds. For example, M. G. Voronkov [4] has observed it for siloxanes and E. D. Babich [6] for silazanes $(R_3Si)_2X + ClSiR'_3 \rightleftarrows R_3SiCl + R_3SiXSiR'_3$, where X = 0 or NH.

Physical Constants, Yields, and Analytical Data for the Compounds Synthesized

Compound	Formula	Bp, °C (pressure, mm)	n_D^{20}	d_4^{20}	MR_D		Found, %				Calculated, %				Yield, %
					found	calculated	C	H	Si	Cl	C	H	Si	Cl	
I	 $ClCH_2-\overset{\overset{O}{\parallel}}{C}-O-\overset{CH_3}{\underset{CH_3}{Si}}-CH_2Cl$	72 (4)	1.4549	1.2081	45.37	45.07	29.69 29.38	5.10 4.87	14.08 —	35.58 —	29.58	5.03	13.95	35.25	53.0
II	 $ClCH_2CH_2-\overset{\overset{O}{\parallel}}{C}-O-\overset{CH_3}{\underset{CH_3}{Si}}-CH_2Cl$	55 (1)	1.4530	1.1744	50.03	49.56	32.97 33.39	5.58 5.58	12.97 12.71	32.9 33.27	33.03	6.03	13.04	33.0	69.0
III	 $ClCH_2CH_2\overset{\overset{O}{\parallel}}{C}-O-Si(CH_3)_3$	54 (4)	1.4250	1.0287	45.29	44.85	39.79	7.08	15.43	19.70	39.88	7.25	15.53	19.62	82.6
IV	 $(ClCH_2CH_2\overset{\overset{O}{\parallel}}{C}-O)_2Si{<}^{C_2H_5}_{H}$	124 (1)	1.4560	1.2371	60.07	59.91	35.37 34.95	5.12 5.41	10.46 10.14	25.95 25.58	35.17	5.16	10.64	25.95	81.7
V	 $(CH_3\overset{\overset{O}{\parallel}}{C}-O-)_2Si{<}^{C_2H_5}_{H}$	174 (760)	1.4073	1.0642	41.33	40.78	—	—	—	—	—	—	—	—	86.0
VI	 $H_2C{=}CH-CH_2\overset{\overset{O}{\parallel}}{C}-OSi(C_6H_5)_2H$	135—136 (1,5)	1.5602	1.1097	78.13	77.72	71.50 71.06	5.78 5.66	— —	— —	71.60	6.01	10.46	—	49.3
VII	 $(H_2C{=}CHCH_2-\overset{\overset{O}{\parallel}}{C}-O)_2Si{<}^{CH_3}_{H}$	42—43 (2,5)	1.4237	1.0045	54.41	53.96	50.74 50.41	6.80 6.77	13.35 13.21	— —	50.44	6.58	13.10	—	79.0* 57.0
VIII	 $(H_2C{=}\underset{CH_3}{C}-\overset{\overset{O}{\parallel}}{C}-O)_2Si{<}^{CH_3}_{H}$	69—71 (3)	1.4447	1.0387	54.42	54.78	49.94 50.54	6.49 6.84	13.39 13.04	— —	50.44	6.58	13.10	—	58.0
IX	 $(H_2C{=}CH-\overset{\overset{O}{\parallel}}{C}-O)_2Si{<}^{CH_3}_{H}$	55—56 (3)	1.4388	1.0799	45.31	45.04	46.70 46.70	5.6 5.7	15.3 14.85	— —	45.16	5.41	15.08	—	73.0
X	$ClCH_2(CH_3)_2SiOCH_2CH_2Cl$	191—192 (753)	1.4479	1.1172	44.93	45.32	32.00 32.42	6,52 6,68	—	—	32.09	6.48	—	—	84.0*
XI		82 (4)	1.4760	1.1331	37.97	37.53				23.5 23.4	39.86	7.35	18.64	23.52	67.0
XII	 **	100—102 (30) mp 63—64	—	—	—					25.8 26.1	35.15	6.65	20.55	25.94	80.0
XIII		73—75 (13) mp 27—29	—	—	—					23.50 23.60	—	—	—	23.52	85.0
XIV		136—146 (20) mp 57—58	—							44.4 44.7	22.94	3.85	17.86	45.14	62.0
XV	 ***	101—103 (760),	1.4110								51.66	10.41	24.17		77.5
XVI		137—138 (750)	1.4280	0.8766	42.34	42.80	57.9 58.6	11.2 10.8	—	—	58.26	11.17			80.0

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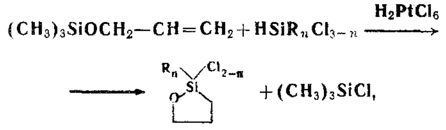
* Yield on transsilylation.

** According to the literature [5], bp 140-200° C

*** According to the literature: bp 103° C (740); n_D^{25} 1.4415; d_4^{25} 0.9178 [7]; bp 95°C; n_D^{26} 1,4170 [8].

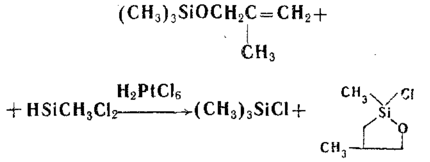


(10)

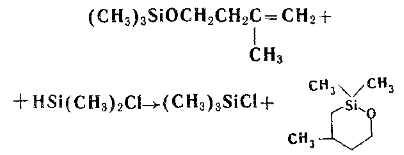
where

$R = CH_3;\quad C_2H_5;\quad C_6H_5;\quad Cl;\quad n = 0, 1, 2.$

It is curious to note that dimethylallyloxysilane could not be converted into a cyclic product in the presence of H_2PtCl_6: a high-molecular-weight substance was formed exclusively. Ethers of trimethylsilanol and other unsaturated alcohols also undergo the transsilylation reaction with chloro-H-silanes, and in the presence of H_2PtCl_6 they undergo the subsequent intermolecular hydrosilylation reaction. In this way a number of new oxasilacycloalkanes have been obtained.



(11)



(12)

EXPERIMENTAL

Chloromethyldimethylsilyl chloroacetate (I). A mixture of 33.3 g (0.2 mole) of trimethylsilyl chloroacetate and 30 g (0.2 mole) of chloromethyldimethylchlorosilane was heated to the boil for 30 min. Then the trimethylchlorosilane (identified and purity determined on a KhL-4 chromatograph) was slowly distilled off from the reaction mixture at 57–60° C, and the residue was fractionated in vacuum. The yield of I was 21.4 g (53 %).

Compounds II, IV, V, VI, and VII were obtained analogously. The initial ester III and compounds VIII and IX were prepared by the reaction of the corresponding acids and organylchlorosilanes in the presence of diethylaniline by the procedure described previously [1].

2-Chloro-2-ethyl-1, 2-oxasilacyclopentane (XI). A flask fitted with a fractionating column was charged with a mixture of 29.8 g (0.23 mole) of ethylchlorosilane, 1 g of trimethylallyloxysilane, and 0.2 ml of a 0.1 N solution of H_2PtCl_6 in isopropanol. From a dropping funnel, the remaining 29.1 g of trimethylallyloxysilane was added to the reaction mixture heated to the boil, the trimethylchlorosilane formed being continuously distilled off, by 57–60° C (15 g). This gave 21 g (67%) of XI in the form of a colorless viscous oil. 4.7 g of trimethylallyloxysilane and 4.6 g of ethyldichlorosilane were also isolated.

Compounds XI–XVI were obtained analogously. Compounds XI–XV polymerized on storage.

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