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Abstract

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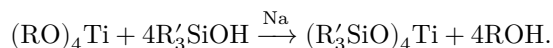
SYNTHESIS OF TETRAKIS-(TRIALKYL(ARYL)SILOXY)-TITANIUMS BY THE TRANSESTERIFICATION METHOD OF TETRAALKOXYTITANATES

(Presented by Academician A. N. Nesmeyanov, 2 VI 1957)

The only monomeric titanium-organosilicon compound of the type $(R_3SiO)_4Ti$, tetrakis-(trimethylsiloxy)-titanium— $\{(CH_3)_3SiO\}_4Ti$ —was first obtained in 1955 in 18% yield by the reaction of trimethylsilanol with titanium tetrachloride in the presence of ammonia ⁽¹⁾, and in 1957 by the reaction of sodium trimethylsilanolate with titanium tetrachloride ⁽²⁾.

We have studied the possibility of synthesizing tetrakis-(trialkyl(aryl)siloxy)-titaniums by the transesterification reaction of alkyl orthotitanates with trialkyl(aryl)-silanols in the presence of metallic sodium as a catalyst ⁽³⁾.

The reaction proceeds in good yield according to the following scheme:



The tetrakis-(trialkyl(aryl)siloxy)-titaniums obtained are colorless, relatively mobile liquids or crystals. They are stable in dry air and readily dissolve in organic solvents.*

The tendency toward hydrolysis decreases with an increase in the radical bonded to silicon.

Experimental part

Starting reagents. Alkyl orthotitanates were obtained by the method of A. N. Nesmeyanov ⁽⁴⁾ and had constants corresponding to the literature data. Trimethylsilanol was obtained by hydrolysis of hexamethyldisilazane ⁽⁵⁾; the remaining silanols were prepared by hydrolysis of the alkoxy derivatives with acetic acid in the presence of several drops of sulfuric acid. The constants of the silanols corresponded to the most reliable literature data.

Method of syntheses. All syntheses, with the exception of the synthesis of tetrakis-(triphenylsiloxy)-titanium, were carried out in a distillation flask with a

reflux condenser. An equimolecular mixture of alkyl orthotitanate and trialkylsilanol was heated in the presence of $\sim 0.01\%$ Na until the evolution of alcohol ceased. The residue was subjected to fractional vacuum distillation. The physical constants, yield, and analytical data of the tetrakis-(trialkyl-(aryl)siloxy)-titaniums obtained are presented in Table 1.

Analysis. The determination of silicon was carried out by wet ashing of a weighed portion of the substance with a mixture of oleum and nitric acid. The precipitate of silicic acid

* Tetrakis-(triphenylsiloxy)-titanium is very sparingly soluble. It can be recrystallized only from boiling xylene.

Table 1

Tetrakis-(trialkyl(aryl)siloxy)-titaniums

Compound	Pressure,		d_4^{20}	n_D^{20}	Yield, %	Si,	Si,	Ti,	Ti,
	b.p., mm Hg	m.p., °C				% calc.	% found	% calc.	% found
$[(CH_3)_3SiO]_4Ti \cdot 11H_2O$	—	—	0.9038	1.4300	50.0	27.76	27.4	11.84	11.81; 11.94
$[(C_2H_5)_2CH_2SiO]_3Ti$	—	—	0.9244	1.4545	90	21.74	21.61; 21.22	9.27	9.55; 9.57
$[(C_2H_5)_3SiO]_4Ti$	3.5	99– 101	—	—	98	19.61	19.54; 19.67	8.36	8.15; 8.71
$[(n-C_3H_7)_2CH_2SiO]_4Ti$	—	—	0.9056	1.4582	83	17.86	17.60; 17.39	7.61	7.82; 8.04
$[(C_6H_5)_3SiO]_4Ti$	—	~ 480	—	—	85	9.69	9.58; 9.58	4.16	4.40; 4.70

* Literature data (1): b.p. $106.0^\circ/7$ mm, $d_4^{20} = 0.9078$, $n_D^{20} = 1.4278$.

was filtered off and calcined at 900° . Titanium was determined in the filtrate by precipitation with ammonia. The precipitate was likewise calcined at 900° .

1. **Synthesis of tetrakis-(trimethylsiloxy)-titanium.** Into a flask with a reflux condenser were placed 5 g (0.022 g-mol) of ethyl orthotitanate, b.p. $140^\circ/6$ mm, and 13 g (0.145 g-mol) (65% excess) of trimethylsilanol, b.p. $98.5-100^\circ/760$ mm, $n_D^{20} = 1.3886$, $d_4^{20} = 0.8120$, and 0.01 g of Na. The mixture was slowly heated until the temperature of the distilling vapors reached 100° . Vacuum distillation of the residue gave 4.5 g (50.5%) of tetrakis-(trimethylsiloxy)-titanium, b.p. $110^\circ/10$ mm, $n_D^{20} = 1.4275$, $d_4^{20} = 0.9004$.

2. **Synthesis of tetrakis-(methyldiethylsiloxy)-titanium.** On heating 14.2 g (0.12 g-mol) of methyldiethylsilanol, b.p. 64°/30 mm, $n_D^{20} = 1.4204$, $d_4^{20} = 0.8503$, and 6.8 g (0.03 g-mol) of ethyl orthotitanate in the presence of 0.005 g of sodium, 4.9 g (89%) of ethyl alcohol, b.p. 79-81°, was obtained. Vacuum distillation gave 14.0 g (90.2%) of tetrakis-(methyldiethylsiloxy)-titanium, b.p. 183-186°/6.5 mm. After a second distillation the product had the constants presented in Table 1.
3. **Synthesis of tetrakis-(triethylsiloxy)-titanium.** A mixture of 13.0 g (0.1 g-mol) of triethylsilanol, b.p. 75°/24 mm, $n_D^{20} = 1.4340$, $d_4^{20} = 0.8645$, 6.8 g (0.01 g-mol) of butyl orthotitanate, b.p. 165-167°/4 mm, $n_D^{20} = 1.4905$, $d_4^{20} = 0.998$, and 0.001 g of sodium was heated until the temperature of the distilling vapors reached 118°. 7 g distilled over. On fractionation under vacuum, 10 g (98%) of tetrakis-(triethylsiloxy)-titanium was obtained, b.p. 192-196°/4 mm, m.p. 99-101°.
4. **Synthesis of tetrakis-(methyldi-*n*-propylsiloxy)-titanium.** From 14.6 g (0.1 g-mol) of methyl-*n*-propylsilanol, b.p. 80°/17 mm, $n_D^{20} = 1.4275$, $d_4^{20} = 0.8436$, 5.7 g (0.025 g-mol) of ethyl orthotitanate, and 0.01 g of sodium, under analogous conditions there was obtained 13.0 g (83%) of tetrakis-(methyldi-*n*-propylsiloxy)-titanium, b.p. 186-188°/3 mm, $n_D^{20} = 1.4570$, $d_4^{20} = 0.9044$.
5. **Synthesis of tetrakis-(triphenylsiloxy)-titanium.** Into a 250 cm³ flask were placed 11.6 g (0.04 g-mol) of triphenylsilanol, m.p. 153°, 2.3 g (0.01 g-mol) of ethyl orthotitanate, 0.01 g of sodium, and 100 ml of benzene. The contents were heated to the boiling point of the solvent for 6 h. The precipitated fine-crystalline solid was filtered off. 10 g (85%) of tetrakis-(triphenylsiloxy)-titanium was obtained; after recrystallization from boiling *o*-xylene it had m.p. ~480°.

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Note: Figure translations are in progress. See original paper for figures.

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