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# CHEMISTRY

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## Abstract

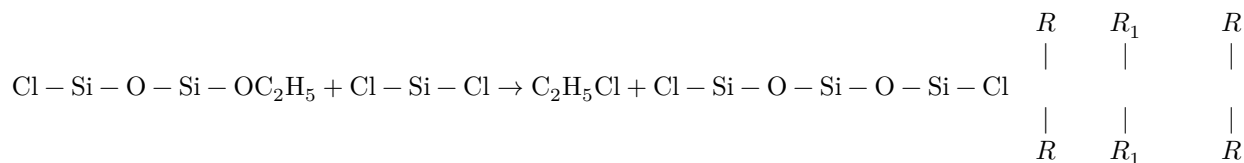
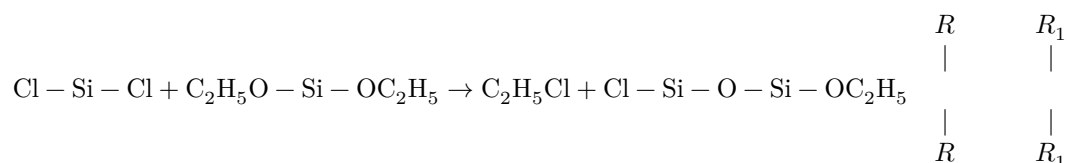
## Full Text

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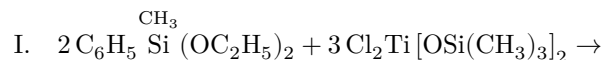
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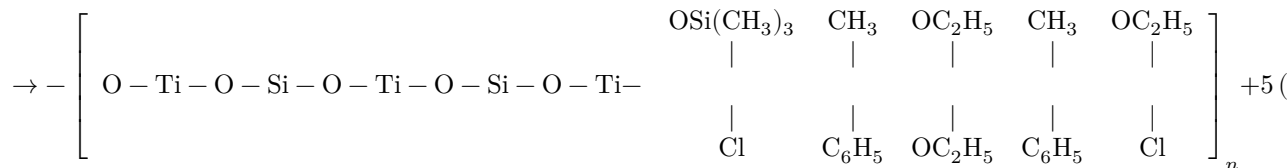
# ON THE HETEROFUNCTIONAL CONDENSATION REACTION OF BIS(TRIMETHYLSILOXY)DICHLOROTITANE WITH PHENYLMETHYLDIETHOXSILANE

The heterofunctional condensation reaction of alkyl-(aryl)-halosilanes with alkyl-(aryl)-alkoxysilanes, proceeding according to the equation



and so on, has been studied in a number of examples and is used for the synthesis of both monomers and polymers (<sup>1-3</sup>). It was of definite interest to study the heterofunctional condensation reaction between alkyl-(aryl)-alkoxysilanes and bis(trimethylsiloxy)dichlorotitanane. If this reaction proceeded according to the indicated scheme, one might expect the formation of linear polytitanorganosiloxanes. Condensation experiments of bis(trimethylsiloxy)dichlorotitanane with phenylmethyldiethoxysilane at 150° showed that, in the course of the reaction, not ethyl chloride but trimethylchlorosilane is liberated, and a polymer is formed whose chemical composition corresponds to that written in equation I:

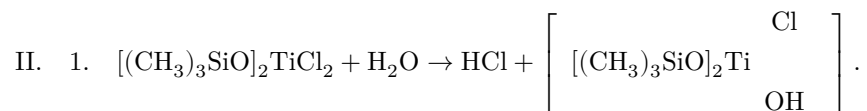




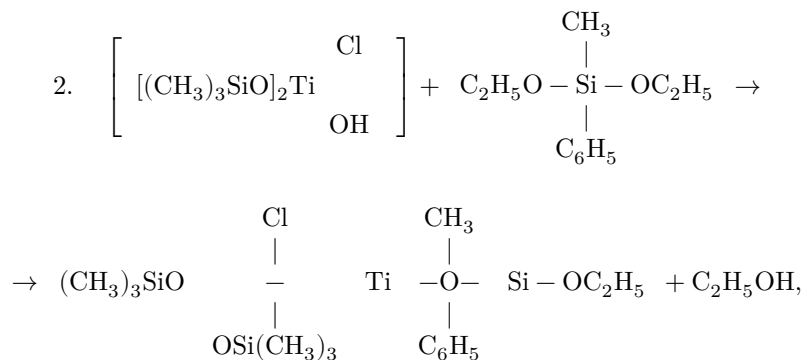
The polymer obtained by this reaction, readily soluble in benzene and toluene, is a highly elastic product at room temperature; on heating it can readily be drawn into threads, which become brittle under the action of atmospheric moisture.

Such a sharply different course of the reaction from the heterofunctional condensation of alkyl-(aryl)-halosilanes with alkyl-(aryl)-ethoxysilanes was the reason for a more thorough study of it. Investigation of this reaction showed that not only phenylmethyldiethoxysilane but also dimethyldibutoxysilane reacts with bis(trimethylsiloxy)dichlorotitanium with liberation only of trimethylchlorosilane, and not butyl chloride, and with formation of a polymer. The chemical composition of the polymer obtained and the trimethylchlorosilane liberated, in amounts close to those given in equa-

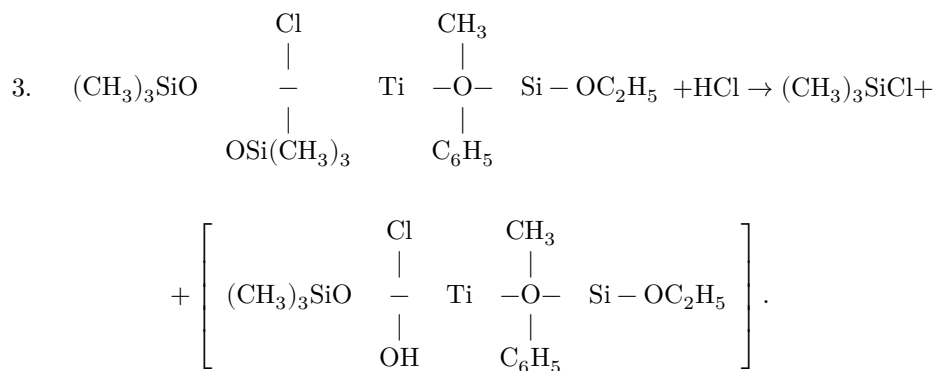
compound I, shows that this reaction proceeds in a very complex manner. To study the reaction, investigations were carried out which showed that the reaction is caused by moisture, which interacts with bis-(trimethylsiloxy)-dichlorotitanium with evolution of hydrogen chloride:



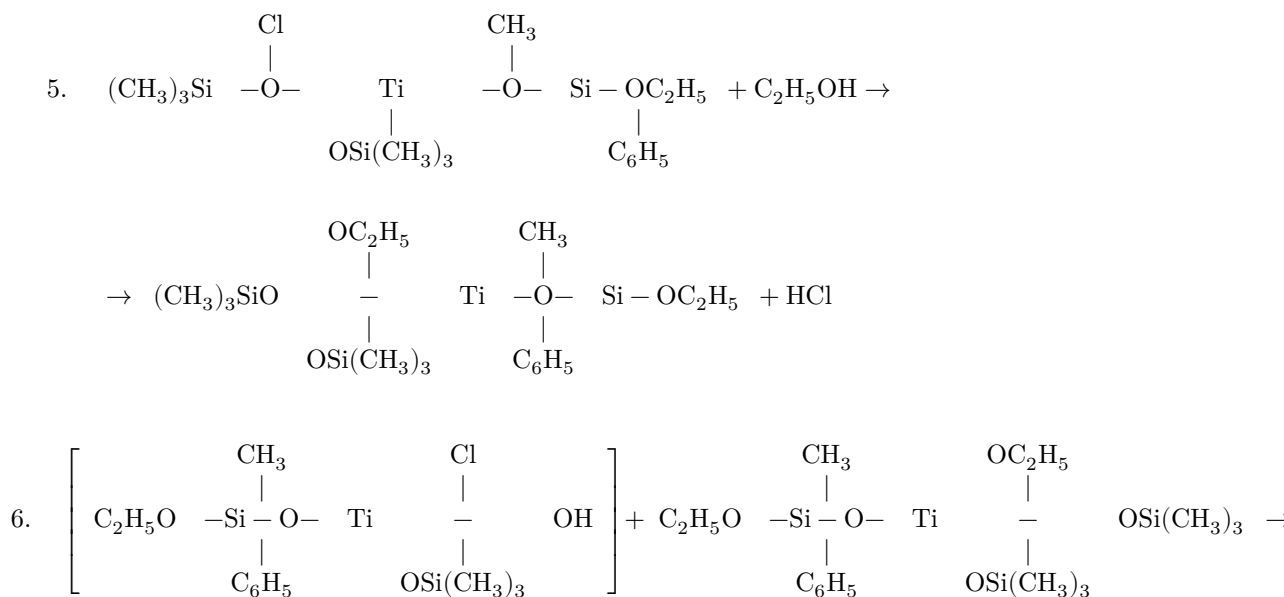
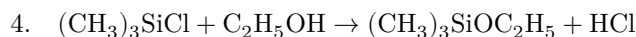
The initial reaction product reacts with phenylmethyldiethoxysilane with evolution of alcohol:

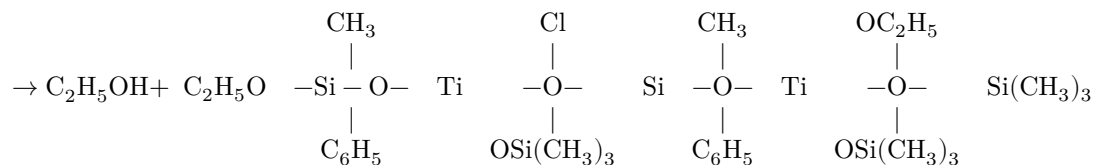


and hydrogen chloride reacts with the trimethylsiloxane group bound to titanium, with formation of trimethylchlorosilane:

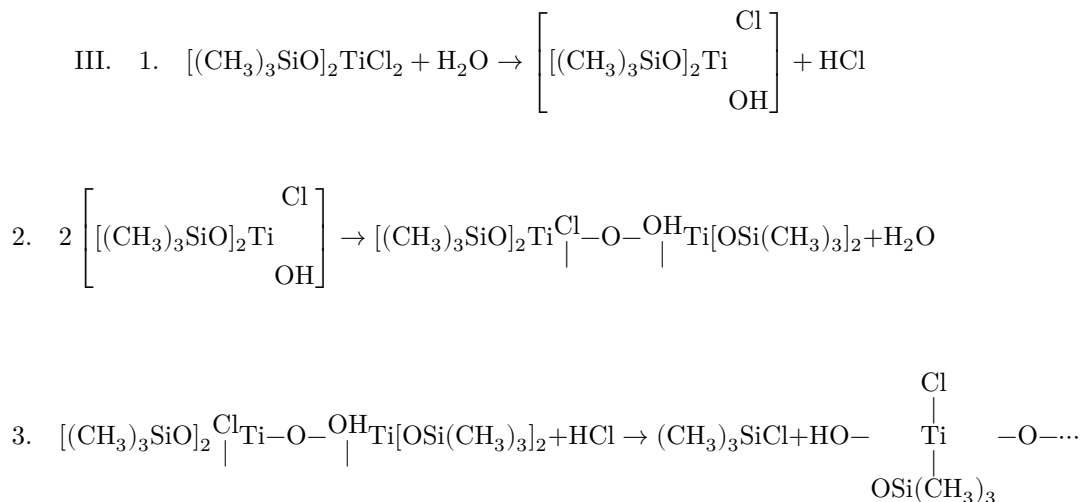


The alcohol reacts, as is shown by the composition of the polymer and of the low-molecular-weight derivatives obtained, with trimethylchlorosilane, with formation of trimethylethoxysilane, which was also isolated in small amounts:

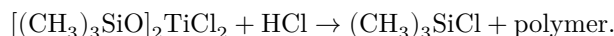




The alcohol and hydrogen chloride liberated in the course of the reaction react further with formation of trimethylchlorosilane, trimethylethoxysilane, and a polymer of the composition given above. To confirm these reactions, experiments were carried out with bis-(trimethylsiloxy)-dichlorotitanium with small amounts of water and hydrogen chloride. In the reaction of bis-(trimethylsiloxy)-dichlorotitanium with water, 0.01 mole of water was taken per mole of bis-(trimethylsiloxy)-dichlorotitanium. The reaction was accompanied by formation of trimethylchlorosilane (about 50%) and of a nonvolatile polymer, insoluble in organic solvents, containing about 50% inorganic portion. This experiment shows that bis-(trimethylsiloxy)-dichlorotitanium is converted into a polymer even in the presence of an insignificant amount of water. This may be represented by the following reaction scheme:



To confirm reaction (III)3, the interaction of bis-(trimethylsiloxy)-dichlorotitanium with hydrogen chloride was investigated, and it was found that under the action of hydrogen chloride trimethylchlorosilane and a polymer are formed:





I fraction: 58°; 6.7 g of trimethylchlorosilane; found Cl 33.06%, 33.25%; calculated Cl 32.6%. Literature data: b.p. 57°.

II fraction: 64–120°; 1.9 g of a mixture of trimethylchlorosilane and trimethylbutoxysilane.

III fraction: 122–124.5°; 3.0 g of trimethylbutoxysilane; found  $n_D^{20}$  1.3919;  $d_{20}^4$  0.7779. Literature data:  $n_D^{20}$  1.3925;  $d_{20}^4$  0.7774. B.p. 124.5°.

**III. Reaction of bis(trimethylsiloxy)dichlorotitanium with water.** A Favorskii flask with a very high dephlegmator was charged with 8.3 g (0.028 mole) of bis(trimethylsiloxy)dichlorotitanium (b.p. 73°/3 mm, Cl 24.6%) in 45 ml of dry dioxane and 0.0044 g of H<sub>2</sub>O (0.00028 mole) in 5 ml of dioxane. The mixture was heated, and after an hour liquid began to distill at a temperature of 60°; 4.6 g (66% of theory) with 32.5% Cl was distilled. For trimethylchlorosilane: b.p. 57°, Cl 32.6%. After removal of the dioxane, a dry gray powder remained in the flask (3.9 g), insoluble in organic solvents, containing 55.0% inorganic part and 15.7% chlorine. The trimethylchlorosilane obtained (2.12 g) was hydrolyzed, washed, dried, and after distillation 1 g (65% of theoretical) of hexamethyldisiloxane was isolated at 100°,  $n_D^{20}$  1.3740. Literature data: b.p. 100°,  $n_D^{20}$  1.3722.

**IV. Reaction of bis(trimethylsiloxy)dichlorotitanium with hydrogen chloride.** Dry hydrogen chloride was passed for 4 h through 11.1 g (0.037 mole) of bis(trimethylsiloxy)dichlorotitanium. The transparent solution of bis(trimethylsiloxy)dichlorotitanium turned yellow and thickened. The resulting reaction mixture was distilled. At 58°, 3.9 g (45% of theoretical) of trimethylchlorosilane was isolated; found Cl 33.2%; 33.1%; calculated Cl 32.6%; in the still residue was a polymer—a solid substance of dark color.

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## CITED LITERATURE

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

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