Chemistry

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Abstract

Full Text

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On the Reaction of Titanium Tetrachloride with Hexamethyldisiloxane

Various methods for cleaving siloxane bonds by the action of sulfuric acid ([1–3]), alkalis ([4,5]), and $AlCl_3$ ([6]) on hexamethyldisiloxane have been described in the literature. Our experiments showed that, when titanium tetrachloride acts on hexamethyldisiloxane at temperatures exceeding 100°, cleavage of the siloxane bond occurs with the formation of trimethylsiloxy chloro derivatives of titanium.

In investigating the cleavage reaction of the siloxane bond in hexamethyldisiloxane by titanium tetrachloride, it was found that, if the process is carried out at temperatures of 120–200°, the reaction proceeds according to the scheme

$$TiCl_4 + (CH_3)_3SiOSi(CH_3)_3 \rightarrow Cl_3Ti[OSi(CH_3)_3] + (CH_3)_3SiCl;$$

in this case only trimethylchlorosilane and trimethylsiloxytrichlorotitanium are obtained (yield 69.8%).

All attempts to obtain products of higher degrees of substitution, namely bis-(trimethylsiloxy)-dichlorotitanium, led to nothing. However, when the reaction temperature was raised to 280–350°, bis-(trimethylsiloxy)-dichlorotitanium was formed according to the reaction

$$TiCl_4 + 2(CH_3)_3SiOSi(CH_3)_3 \rightarrow Cl_2Ti[OSi(CH_3)_3]_2 + 2(CH_3)_3SiCl.$$

The yield of bis-(trimethylsiloxy)-dichlorotitanium was 34.7%. This indicates that replacement of the halide at titanium by a second siloxy group probably occurs as a result of the interaction of trimethylsiloxytrichlorotitanium with hexamethyldisiloxane. To confirm this proposition, experiments were carried out in which trimethylsiloxytrichlorotitanium was allowed to act on hexamethyldisiloxane at temperatures of 280–320°. In this case, bis-(trimethylsiloxy)-dichlorotitanium was formed (yield 43.0%) according to the reaction

$$Cl_3TiOSi(CH_3)_3 + (CH_3)_3SiOSi(CH_3)_3 \rightarrow Cl_2Ti[OSi(CH_3)_3]_2 + (CH_3)_3SiCl.$$

We believe that the reaction involving cleavage of siloxane bonds in hexamethyldisiloxane by titanium tetrachloride proceeds according to the following mechanism.

The titanium atom in titanium tetrachloride coordinates with the oxygen of hexamethyldisiloxane, with the formation of a transition complex:

$$\begin{array}{c} (CH_3)_3Si \\ \diagdown \\ O + TiCl_4 \rightarrow \end{array} \left[\begin{array}{ccc} (CH_3)_3Si & Cl & Cl \\ \diagdown & | & \diagup \\ O \cdots Ti & Cl & \diagdown \\ & & Cl \end{array} \right] . \qquad \text{(I)}$$

$$\begin{array}{c} (CH_3)_3Si \\ \diagup \end{array}$$

The further process, as a result of redistribution of electron density, is accompanied by cleavage of the siloxane bond with attachment of titanium to oxygen and the formation of trimethylchlorosilane and trimethylsiloxytrichlorotitanium:

$$\left[\begin{array}{ccc} (CH_3)_3Si & Cl & Cl \\ \diagdown & | & \diagup \\ O \cdots Ti & Cl & \diagdown \\ & & Cl \end{array} \right] \rightarrow (CH_3)_3SiCl + (CH_3)_3SiOTiCl_3. \qquad \text{(II)}$$

The addition of the second siloxy group to the titanium atom probably also occurs through coordination of the titanium atom of trimethylsiloxytrichlorotitanium with hexamethyldisiloxane:

$$\begin{array}{l} (CH_3)_3Si \\ \qquad \diagdown \\ \qquad\quad O + Cl_3TiOSi(CH_3)_3 \longrightarrow \\ \qquad \diagup \\ (CH_3)_3Si \end{array} \left[\begin{array}{ccc} (CH_3)_3Si & Cl & \\ \diagdown & & | \\ & O \cdots Ti & \diagdown Cl \\ \diagup & & | \\ (CH_3)_3Si & OSi(CH_3)_3 & \end{array} \right] \qquad \text{(III)}$$

with subsequent formation of trimethylchlorosilane and bis-(trimethylsiloxy)-dichlorotitanium:

$$\left[\begin{array}{ccc} (CH_3)_3Si & Cl & \\ \diagdown & & | \\ & O \cdots Ti & \diagdown Cl \\ \diagup & & | \\ (CH_3)_3Si & OSi(CH_3)_3 & \end{array} \right] \longrightarrow (CH_3)_3SiCl + Cl_2Ti[OSi(CH_3)_3]_2. \qquad \text{(IV)}$$

Experimental Part

Preparation of trimethylsiloxytrichlorotitanium. A mixture of 58.6 g (0.308 mole) of $TiCl_4$ and 50.0 g (0.308 mole) of hexamethyldisiloxane was charged into a Favorskii flask equipped with a high dephlegmator. The mixture was heated at 120° for one hour; then 29.6 g of trimethylchlorosilane (Cl — 32.4%) was distilled off at 58-60°, and the still residue was subjected to vacuum distillation at 62-63°/8 mm (literature data 67°/9 mm). A total of 52.52 g of trimethylsiloxytrichlorotitanium was isolated, yield 69.8%.

Found, %: Cl 43.56; 43.20

$C_3H_9OSiTiCl_3$. Calculated, %: Cl 43.71

Preparation of bis-(trimethylsiloxy)-dichlorotitanium. 1. A mixture of 29.0 g (0.153 mole) of $TiCl_4$ and 50.0 g (0.306 mole) of hexamethyldisiloxane was passed through a quartz tube filled with broken glass and placed in a furnace. The furnace temperature was 350°. The mixture collected in a receiver cooled with water was fractionated. At 87-88°/8 mm, 15.6 g of bis-(trimethylsiloxy)-dichlorotitanium was isolated. Yield 34.7%.

Found, %: C 24.49; H 6.36; Si 18.8; Ti 16.40; Cl 23.5

$C_6H_{18}O_2Si_2TiCl_2$. Calculated, %: C 24.15; H 6.04; Si 18.8; Ti 16.45; Cl 23.88

2. In an analogous manner, but at a furnace temperature of 320°, 20.5 g of bis-(trimethylsiloxy)-dichlorotitanium was isolated by fractionation (at 63°/3 mm) from 39.1 g (0.16 mole) of trimethylsiloxytrichlorotitanium and 25.9 g (0.16 mole) of hexamethyldisiloxane. Yield 43.0%.

Found, %: Si 18.2; Ti 15.95; Cl 24.6

$C_6H_{18}OSi_2TiCl_2$. Calculated, %: Si 18.8; Ti 16.45; Cl 23.88

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