NEW METHOD OF SYNTHESIZING TRIALKOXYTITANIUM CHLORIDES

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Until recently, the only known compound of the type \((\text{AlkO})_3\text{TiCl}\) has been triethoxytitanium chloride, prepared by the action of acetyl chloride on ethyl orthotitanate [1]. We have shown that triethoxytitanium chloride is obtained smoothly by the interaction of equimolecular quantities of pyridine hydrochloride and ethyl orthotitanate in a medium of benzene at 60-70°C [2]. This observation permitted us to develop a method of direct synthesis of triethoxytitanium chloride by the reaction of \(\text{TiCl}_4\) with ethanol in presence of pyridine in benzene medium. At the same time, ethyl orthotitanate and pyridine hydrochloride are formed, and in the subsequent heating of the reaction mixture these form triethoxytitanium chloride according to the equations:

\[
4\text{C}_2\text{H}_5\text{OH} + \text{TiCl}_4 + 4\text{C}_2\text{H}_5\text{N} \rightarrow (\text{C}_2\text{H}_5\text{O})_3\text{Ti} + 4\text{C}_2\text{H}_5\text{NHCl}
\]

\[
(\text{C}_2\text{H}_5\text{O})_4\text{Ti} + \text{C}_2\text{H}_5\text{N} \cdot \text{HCl} \rightarrow (\text{C}_2\text{H}_5\text{O})_3\text{TiCl} + \text{C}_2\text{H}_5\text{OH} + \text{C}_2\text{H}_5\text{N}
\]

In this way, triethoxytitanium chloride became a readily accessible substance [2]. However, this method does not appear to be a general one; attempts at preparing the triallyloxy- and tri-n-butoxytitanium chlorides and other such compounds were not successful [2]. Only the attempt to prepare tri-n-propoxytitanium chloride by treating n-propyl orthotitanate with pyridine hydrochloride was successful [3].

We considered that it might be possible to prepare trialkoxytitanium chlorides by transesterification (alcoholysis) of the accessible triethoxy compound by the action of alcohols according to the scheme:

\[
(\text{C}_2\text{H}_5\text{O})_3\text{TiCl} + 3\text{ROH} \rightleftharpoons (\text{RO})_3\text{TiCl} + 3\text{C}_2\text{H}_5\text{OH}
\]

The replacement of the last Cl in \((\text{C}_2\text{H}_5\text{O})_3\text{TiCl}\) by an alkoxy group by the action of an alcohol must be very difficult, for it is known that in dichlorodialkoxytitaniums the further replacement of chlorine by alkoxy groups by the action of alcohols does not take place even with prolonged heating [1]. The application of the transesterification reaction to triethoxytitanium chloride met with difficulties, for it was found that under the required conditions replacement of chlorine by alkoxy occurs. Since trialkoxytitanium chlorides and alkyl orthotitanates containing the same alkoxy groups boil at similar temperatures, it was not found possible to separate them by distillation. Nevertheless, it was established by special experiments that even in the case of the higher alcohols, which distill off at a higher temperature, the replacement of Cl in \((\text{AlkO})_3\text{TiCl}\) by an alkoxy group goes extremely slowly.

Thus, when 10 g of tri-n-hexyloxytitanium chloride is mixed with 50 ml of n-hexyl alcohol and the latter slowly distilled off, then HCl can be detected in the distillate, but even after repeating this procedure ten times, using 500 ml of n-hexyl alcohol, the reaction does not go to completion. If, however, in the above-described experiment triethoxytitanium chloride and ethyl alcohol are taken, then in the first 50 ml of the distillate no trace of HCl can be detected, and with further distillation only traces of chlorine can be detected in the distillate. In contrast with this extremely slow reaction, the transesterification reaction proceeds very rapidly. Hence, by observing definite conditions it was found possible to prepare various trialkoxytitanium
chlorides practically free from contamination with the corresponding alkyl ortho-
titanates. These conditions comprise the conducting of the transesterification
process at as low a temperature as possible and, in the case of the higher alco-
hol, also without continual addition of fresh portions of alcohol and, conse-
quently, without their subsequent distillation. According to our observations, a
two-fold excess of alcohol, taken at the beginning of the experiment, is suffi-
cient.

The process of transesterification must be watched by making tests on the
distillate for chlorine content or by introducing a solution of AgNO₃ in absolute
alcohol in the receiver prior to the experiment. If HCl makes its appearance in
the distillate, it is necessary to carry on distilling off the alcohol in a vacu-
um at a lower temperature. These precautions are particularly necessary when
conducting transesterification with high-boiling alcohols. By this method we
have succeeded in preparing the previously unknown tri-n-butoxy-, tri-isobutoxy-
tri-isooamyloxy-, tri-n-hexyloxy-, tri-β-chloroethoxy-, and tri-β-ethoxyethoxy-
titanium chlorides.

All the chlorides obtained, with the exception of tri-β-chloroethoxytitanium
chloride, are colorless, transparent, viscous, hygroscopic liquids that may be
distilled in a vacuum. The viscosity of the chlorides falls with increase in their
molecular weight. Tri-β-chloroethoxytitanium chloride, both crude and doubly re-
distilled, is an extremely viscous (at room temperature) black mass.

Thus, the proposed method is sufficiently general, and it is simple to carry
out. The transesterification reaction requires very little time and gives an al-
most quantitative yield.

EXPERIMENTAL

All the experiments described below were carried out with completely dry
starting substances and under conditions that prevented the admittance of moisture
from the atmosphere.

Preparation of Tri-isooamyloxytitanium Chloride (iso-C₅H₁₁O₃)₂TiCl

A mixture of triethoxytitanium chloride (10 g = 0.06 mole) and isoamy alcohol
(25 g = 0.28 mole) was introduced into a Claisen flask connected to condenser
and receiver. The apparatus was protected from the moisture of the air by a drying
system. The reaction mixture was heated on an oil bath. At a bath temperature of
140-150° a mixture of ethyl and isoamy alcohol distilled off (b.p. 78-122, 6.2 g).
When the temperature of the vapor reached 122°, the reaction mixture was cooled and
further isoamy alcohol (10 g) was added. Distillation of the alcohol mixture
then proceeded until the boiling point of isoamy alcohol was reached; this indi-
cated the end of the reaction. The excess of isoamy alcohol was driven off in a
vacuum. The product, which remained in the flask after driving off the alcohol,
was distilled over at 174-175° at 2 mm. Yield 13.4 g, corresponding to 85% of
theoretical.

On allowing the product to stand, a small number of crystals separated. On
the assumption that these crystals consisted of a double compound of tri-isooamy
oxytitanium chloride and isoamy alcohol, we heated the product in a vacuum (2 hr,
190-210°, 40 mm) in order to break up the double compound. During this time only
a few drops of liquid distilled over. The product was then distilled twice in
vacuo from a Favorsky flask. The tri-isooamyloxytitanium chloride obtained is a
colorless viscous hygroscopic liquid, boiling at 173.5-175° at 2 mm: nD²⁰ 1.5092;
D₂⁰ 1.0600.