[CONTRIBUTION FROM THE TEXAS RESEARCH FOUNDATION]

ORGANIC COMPOUNDS OF TITANIUM. I. TETRAALKYL ORTHOTITANATES

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Several previous investigators (1–9) have reported the preparation of certain aliphatic esters of orthotitanic acid having the general formula $Ti(OR)_4$. Unlike the corresponding esters of orthosilicic acid, the alkyl silicates, these compounds are not formed by the direct action of titanium tetrachloride on the appropriate alcohol (5, 10). To date, the most generally satisfactory procedure [by Bischoff and Adkins (2) as modified by MacCorquodale and Adkins (3)] entails the reaction between the metal chloride and sodium alcoholate in alcohol solution:

$$TiCl_4 + 4NaOR\ (+xs.ROH) = Ti(OR)_4 + 4NaCl\ (+ROH)$$

This method, however, suffers from certain disadvantages and limitations. It necessitates the dissolution of metallic sodium in a large excess of alcohol prior to the addition of titanium tetrachloride. In the case of the primary alcohols, up to and including *n*-amyl alcohol, the reaction with sodium is reasonably fast and satisfactory; however, with secondary, tertiary, or higher molecular weight alcohols, it is exceedingly slow even at elevated temperatures. Further, in those instances where the alcohol is expensive or available only in small amounts, the need for a large excess is undesirable.

In this laboratory, the above procedure has been successfully employed; however, our results have indicated that, through certain minor modifications, it can be simplified and made more generally useful. In accord with the results of Havill, Joffe, and Post (10) on polyethers from trichlorosilane, benzene has been employed as a mutual solvent in this work and found to be very beneficial. Further, the order of addition of reagents has been changed. According to this modification, the titanium tetrachloride is allowed to react with an alcohol in benzene solution, and the sodium added later to this reaction mixture. Thus, both time and reagents are conserved while the yield and purity of products appear to be improved.

It has also been reported (6) that tetraalkyl orthotitanates can be prepared in good yield by the action of titanium tetrachloride on alcohols in the presence of ammonia or organic nitrogen bases. Repeated efforts in this laboratory to employ this method or to duplicate the examples cited in this patent have been uniformly unsuccessful. Only one experiment, designed to yield tetra-*tert*-butyl orthotitanate from *tert*-butanol in the presence of N,N-dimethylaniline, gave analytical evidence that some of the desired product was obtained. This could not be confirmed by isolation of a pure sample of the material in question. In substantiation of our negative results with this preparative method, it was found that anhydrous ammonia, in absolute alcohol, is capable of reacting with tetraalkyl orthotitanates to form a white, insoluble, titanium-containing solid, from which the titanic ester cannot be regenerated. It should be noted, however, that several months after this experimental work was completed, information was received (11) which appeared to contradict these results. McTaggart and coworkers (12) have reported the preparation of butyl titanate from the condensation of *n*-butanol and titanium tetrachloride in the presence of gaseous ammonia. No analytical data or physical constants were reported. Work is now under way in this laboratory relative to the described process. While evidence is as yet incomplete, preliminary results would indicate that the butyl titanate described by these workers was probably a mixture consisting of tetra-*n*-butyl orthotitanate, chlorotri-*n*-butoxytitanium, and higher molecular weight condensed butyl titanate esters. None of the pure tetra-*n*-butyl orthotitanate has, so far, been obtained from this study. These results are in accord with our experience with *tert*-butanol referred to above.

Relatively few data are available with regard to the physical properties and constants of titanic esters. In our investigation the work of Bischoff and Adkins (2) has been extended to include additional physical characteristics as well as certain new compounds of this general class. It should be noted that the values reported for densities and refractive indices are merely the best approximations, since the tetraalkyl orthotitanates hydrolyze quite rapidly in moist air, and these values change slowly as the determinations are made.

Many experiments were conducted in an effort to prepare tetra-*tert*-butyl orthotitanate in the presence of condensing agents such as sodium, N,N-dimethylaniline, pyridine, ammonia, etc. None of the desired ester was obtained in this manner; *tert*-butyl chloride was usually the only volatile product which could be isolated. This new compound was finally secured through a transesterification between tetraethyl orthotitanate and an excess of *tert*-butanol.

A discussion of the preparation and properties of "tetramethyl orthotitanate" has been avoided since this material appears to warrant a detailed and separate report at a later date.

EXPERIMENTAL

Tetraalkyl orthotitanates which have been prepared in this investigation include the ethyl, *n*-propyl, *n*-butyl, isobutyl, *sec*-butyl, *tert*-butyl, and *n*-octyl esters. Of these, the ethyl and *n*-butyl compounds have been reported previously, but it appears that the *n*-propyl, isobutyl, *sec*-butyl, *tert*-butyl, and *n*-octyl derivatives have been prepared for the first time in this study. The first four examples could be made by the original method (2) discussed above, whereas the *sec*-butyl and *n*-octyl esters could be made successfully only by the new technique. As mentioned before, the *tert*-butyl analog could not be obtained by either method, and was secured only through an ester exchange reaction. With this exception, the general synthetic method was identical for all members of this series of compounds, hence a description of the experimental work with secondary butanol will suffice as an example:

Tetra-sec-butyl orthotitanate, $Ti(O\text{-}s\text{-}C_4H_9)_4$. A solution of 296.5 grams (4.0 moles) of freshly distilled *sec*-butanol in 300 ml. of anhydrous benzene was placed in a two-liter, 3-neck flask equipped with a dropping-funnel, reflux condenser with calcium chloride drying tube, thermometer, and a mercury-seal mechanical agitator. External cooling lowered the temperature of this mixture to 0–10°. Ninety-five grams (95.0 g., 0.5 mole) of Fisher C.P.

titanium tetrachloride was added dropwise over a period of about 80 minutes while the temperature was maintained below 10°. After 45 minutes further agitation at this temperature, the reaction mixture was allowed to warm slowly to room temperature (*ca.* 30°) and stirred for two hours longer. Then metallic sodium (46.0 grams, 2.0 moles) was added in small pieces at such a rate that the temperature rose slowly to 75°. After standing overnight at 30° the reaction mixture was heated to reflux for 3 hours. A further portion of benzene (100 ml.) was added during this period to reduce the gel-like consistency and facilitate agitation. The reaction product was cooled somewhat and centrifuged to remove sodium chloride. The solid residue was washed twice with hot benzene (100 ml.) and the centrifugate added to the initial benzene solution.

Atmospheric distillation of the solvent served to concentrate the product, which was isolated by vacuum fractionation, b.p. 90–110°/1–3 mm. The crude, water-white oil weighed 71.5 grams (0.2 mole); yield 40%. After careful fractionation through a 24-inch Widmer column, the product showed the following properties: b.p. 90–92°/0.5–1.0 mm.; n_D^{35} 1.4550 (Abbé); d_4^{35} 0.9196; viscous, water-white oil having an odor of freshly cut apples. The recovery of purified product amounted to approximately 90% of the crude material described above.

This titanic acid ester hydrolyzes quite readily when exposed to moist air with the deposition of hydrated orthotitanic acid. This fact was utilized to design a very simple analytical method, which is described below.

Anal. Calc'd for $Ti(OC_4H_9)_4$:TiO_2, 23.48. Found: TiO_2, 23.24.

The qualitative solubilities of this compound, tetra-*sec*-butyl orthotitanate, are exemplary of the general class of orthotitanic esters (See Table I).

Attempted preparation of tetraalkyl orthotitanates using basic nitrogen condensing agents. In an effort to employ ammonia and organic nitrogen bases as condensing agents as reported previously (6), a large number of experiments were conducted. Pyridine, N,N-dimethylaniline, and ammonia have been studied in connection with ethanol, *n*-propanol, isopropanol, *n*-butanol, *tert*-butanol, and *n*-octanol with and without solvents. With the exception of the single result mentioned above (with *tert*-butanol), the results were uniformly negative. A description of the use of N,N-dimethylaniline will serve as an example of these experiments. In an apparatus similar to that described above, 92.1 grams (2.0 moles) of absolute ethanol was dissolved in 250 ml. of anhydrous benzene and chilled to 0–10°. With vigorous agitation, 47.5 grams (0.25 mole) of titanium tetrachloride was dropped in during 45 minutes. After 30 minutes at the above temperature, the mixture was allowed to warm slowly to room temperature and stirred for an additional 30 minutes. External cooling served to reduce the temperature again to 0–10°, and a solution of 145.5 grams (1.2 mole) of anhydrous N,N-dimethylaniline in 150 ml. of dry benzene was added during 30 minutes. This mixture was stirred for ½ hour at 10°, warmed to room temperature for 4 hours, and finally heated to reflux for 1 hour.

Atmospheric distillation of solvent served to concentrate the reaction products which were subsequently isolated by fractionation at 3–4 mm. After a considerable fore-run of low-boiling material (below 100°), 21.7 grams of viscous yellow oil was collected, b.p. 100–160°/10 mm. Extensive decomposition occurred during this distillation, such that a lower operating pressure could not be obtained. This crude product, which partially solidified on cooling, was redistilled through a 24-inch Widmer column. The fore-run consisted of dimethylaniline, but a very small amount of water-white oil was collected at 75–78°/1 mm. On cooling, this material solidified, m.p. 75–6°. This purified product, however, contained no titanium and, obviously, was not the expected ester. None of the desired tetraethyl orthotitanate could be isolated from this reaction.

Tetra-tert-butyl orthotitanate, $Ti(O\text{-}t\text{-}C_4H_9)_4$. Seventy-four grams (74.0 g., 1.0 mole) of *tert*-butanol was mixed with 22.8 grams (0.1 mole) of crude tetraethyl orthotitanate and warmed to rapid reflux. Volatile material was allowed to distil slowly until the pot temperature reached 100°. A fresh portion of 37.0 grams (0.5 mole) of *tert*-butanol was added and the slow distillation repeated. Finally, yet a third portion of fresh *tert*-butanol (37.0 g., 0.5 mole) was added and the process repeated. Distillation of the final residue at reduced pressure yielded 15.2 grams (0.045 mole, 45%) of the desired product, tetra-*tert*-butyl orthotitanate, boiling at 62–3°/1 mm.; n_D^{20} 1.4436; d_4^{20} 0.8893.

Anal. Calc'd for $Ti(OC_4H_9)_4$:TiO_2, 23.48. Found: TiO_2, 23.36.

Analytical Method. A simple but effective analytical procedure was devised to determine the titanium content of these products. It involved weighing a sample (*ca.* 0.25 g.) of the ester directly into an ignited and weighed crucible. The sample was covered with 10 ml. of distilled water containing 2 drops of concentrated nitric acid. The crucible was then heated on a hot plate until almost all of the water had evaporated. It was then cooled, and a fresh portion of 10 ml. of water and 2 ml. of concentrated nitric acid added. Careful evaporation (considerably facilitated by an electric heat lamp suspended above the crucible) was followed by ignition for one hour at 600–650°. The residue was weighed as titanium dioxide. In this laboratory, duplicate analyses have usually agreed within 1 part in 300.

TABLE I

SOLUBILITIES OF TETRAALKYL ORTHOTITANATES

SOLVENT	COLD	HOT
Water	Insol. white ppt.	Insol. white ppt.
Ethanol	Soluble	Soluble
n-Butanol	Soluble	Soluble
Benzene	Soluble	Soluble
Chloroform	Soluble	Soluble
2,3-Dimethylbutane	Soluble	Soluble
Diethyl ether	Soluble	Soluble
Carbon disulfide	Soluble	Soluble
Acetone	Insol. white ppt.	Insol. white ppt.
Octanone-2	Sol., yellow color	Insol. yellow ppt.
Ethyl acetate	Insol. white ppt.	Soluble
Acetic acid	Insol. white ppt.	Insol. white ppt.
Pyridine	Soluble	White, gel-like solid
Turpentine	Soluble	Soluble, yellow color
Linseed Oil	Soluble	Soluble, red color, viscous
Soybean Oil	Soluble	Soluble, ruby red color, viscous
Glycerine	Soluble, viscous	Soluble, white opalescence, viscous

TABLE II

TETRAALKYL ORTHOTITANATES, $Ti(OR)_4$

R	YIELD, %	B.P., MM.	n^t_D	d^t_4
C_2H_5	66.0	104°/1	1.5051/35°	1.107/35°
n-C_3H_7	42.0	170°/3	1.4803/35°	0.9970/35°
n-C_4H_9	49.7	134–136°/0.5–1	1.4863/35°	.9927/35°
iso-C_4H_9	68.8	141°/1	1.4749/54°	.9750/55°
sec-C_4H_9	40.0	90–92°/0.5–1	1.4550/35°	.9196/35°
tert-C_4H_9	45.0	62–63°/1	1.4436/20°	.8893/20°
n-C_8H_{17}	63.3	219°/1	1.4762/35°	—

DISCUSSION

A summary of data relative to yields and physical constants appears in Table II. In general terms, the tetraalkyl orthotitanates may be described as high-boiling, clear, viscous oils; they vary in color from water-white to a light yellow depending upon the care with which purification is accomplished. They tend to become extremely viscous at room temperature, and in the case of the isobutyl ester, a low-melting solid is formed. These products have a mild, fruit-like odor.

It has been the general experience in this laboratory, that the yields of tetraalkyl orthotitanates claimed by Adkins and co-workers (2, 3) could not be achieved. Whereas their method usually yielded 25–35% of the desired product (claimed 67–81%), the modified method described above gave 45–65%. In addition, the latter method appeared to give a purer product (judging from color, analysis, and physical constants). Furthermore, the original method failed when applied to *n*-octanol and *sec*-butanol while the modified process worked reasonably satisfactorily.

SUMMARY

An improved method for the preparation of tetraalkyl orthotitanates is described together with the physical constants of several new examples of this type of ester. Those compounds which have been prepared for the first time are: tetra-*n*-propyl orthotitanate, tetraisobutyl orthotitanate, tetra-*sec*-butyl orthotitanate, tetra-*tert*-butyl orthotitanate, and tetra-*n*-octyl orthotitanate.

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