524. *Titanium Chloride Alkoxides.*

By D. C. BRADLEY, D. C. HANCOCK, and W. WARDLAW.

Various methods for the preparation of the new compounds, $TiCl_4,CH_3{\cdot}CO_2Et$, $TiCl_3{\cdot}OEt,CH_3{\cdot}CO_2Et$, and $TiCl_3{\cdot}OPr^i,CH_3{\cdot}CO_2Et$, are described. These compounds distilled under reduced pressure without change in composition and the possibility that titanium exhibits here a covalency of 5 is considered. The new alkoxides $TiCl_3{\cdot}OR$ where R = Me, Et, Pr^i, and Bu^n were readily obtained from the rapid radical-interchange reaction between the tetrachloride and the appropriate tetra-alkoxide. Certain of the titanium chloride alkoxides disproportionate when heated under reduced pressure.

TITANIUM CHLORIDE ETHOXIDES have been known since 1875 when Demarçay (*Compt. rend.*, 1875, **80**, 51) reported that the reaction between titanium tetrachloride and ethanol led to the formation of a crystalline solid to which he assigned the formula $TiCl(OEt)_3,HCl$. Sixty years elapsed before the error in this formulation was pointed out and the correct formula $TiCl_2(OEt)_2,EtOH$ deduced by Jennings, Wardlaw, and Way (*J.*, 1936, 637). In addition these authors demonstrated that in general the reaction between titanium tetrachloride and an alcohol took the course :

$$TiCl_4 + 3ROH \longrightarrow TiCl_2(OR)_2,ROH + 2HCl$$

Further it was shown that titanium monochloride triethoxide could be prepared from titanium tetraethoxide and acetyl chloride :

$$Ti(OEt)_4 + CH_3{\cdot}COCl \longrightarrow TiCl(OEt)_3 + CH_3{\cdot}CO_2Et$$

In view of the successful isolation of the monochloride triethoxide from titanium tetraethoxide (1 mol.) and acetyl chloride (1 mol.) it seemed possible that the hitherto unknown trichloride monoethoxide might be obtained from the tetraethoxide (1 mol.) and acetyl chloride (3 mols.) in accordance with the reaction :

$$Ti(OEt)_4 + 3CH_3{\cdot}COCl \longrightarrow TiCl_3{\cdot}OEt + 3CH_3{\cdot}CO_2Et$$

Actually, the very stable compound $TiCl_3(OEt),CH_3{\cdot}CO_2Et$ was isolated and could be distilled unchanged under reduced pressure. Further investigation disclosed that by using excess of acetyl chloride it was possible to prepare $TiCl_4,CH_3{\cdot}CO_2Et$:

$$Ti(OEt)_4 + 4CH_3{\cdot}COCl \longrightarrow TiCl_4,CH_3{\cdot}CO_2Et + 3CH_3{\cdot}CO_2Et$$

Like $TiCl_3{\cdot}OEt,CH_3{\cdot}CO_2Et$, this new complex can be distilled unchanged under reduced pressure. In a further endeavour to obtain the simple $TiCl_3{\cdot}OEt$ an excess of titanium tetrachloride was added to titanium tetraethoxide. A vigorous reaction ensued and a solid was deposited which could be recrystallised from the tetrachloride. The crystalline product proved to be the required $TiCl_3{\cdot}OEt$:

$$3TiCl_4 + Ti(OEt)_4 \longrightarrow 4TiCl_3{\cdot}OEt$$

The simplicity of this preparation encouraged us to examine the reaction between excess of titanium tetrachloride and other tetra-alkoxides of titanium. The isolation of the new trichloride monoalkoxides $TiCl_3{\cdot}OR$, where R = Me, Et, Pr^i, and Bu^n, demonstrates the scope of this useful radical-interchange reaction.

Further investigation of reactions involving titanium tetrachloride and titanium tetraethoxide in different proportions gave some interesting results. For example, when the tetrachloride (1 mol.) was added to the tetraethoxide (1 mol.) a crystalline solid (A) with the empirical formula $TiCl_2(OEt)_2$ was obtained. However, the action of heat showed that this substance was not pure titanium dichloride diethoxide. Substance (A) on distillation gave some titanium trichloride ethoxide whereas the authentic $TiCl_2(OEt)_2$ gave none. We formed the opinion that substance (A) consisted of titanium dichloride diethoxide mixed with the trichloride ethoxide and chloride triethoxide. Similarly, the product obtained from a mixture of the tetrachloride (1 mol.) and the tetra-*n*-butoxide (1 mol.) gave a distillate containing $TiCl_3{\cdot}OBu^n$ although authentic $TiCl_2(OBu^n)_2$ gave no $TiCl_3{\cdot}OBu^n$ on distillation.

It was not surprising to find that the product from the reaction between titanium tetrachloride (1·43 mols.) and titanium tetraethoxide (1 mol.) gave on distillation a considerable quantity of titanium trichloride ethoxide. It is suggested that in these radical-interchange reactions an equilibrium is attained involving the various chloride alkoxides of titanium and that only in certain cases (*e.g.*, excess of tetrachloride) will a single chloride alkoxide be formed.

A characteristic property of titanium chloride alkoxides is the tendency to disproportionation when they are heated under reduced pressure. Thus the trichloride methoxide furnished a mixture of $TiCl_3{\cdot}OMe$, $TiCl_2(OMe)_2$, and $TiCl_4$, probably in accordance with the scheme:

$$2TiCl_3{\cdot}OMe \longrightarrow TiCl_2(OMe)_2 + TiCl_4$$

The trichloride *n*-butoxide behaved similarly when heated under reduced pressure. In addition the trichloride methoxide disproportionated when crystallised from boiling carbon tetrachloride.

During these studies an interesting property of titanium tetra-*tert.*-amyloxide was observed. Thus even at a low temperature this compound readily reacted with excess of titanium tetrachloride and gave a product which was shown to be impure $TiCl_3{\cdot}O{\cdot}CMe_2Et$. In an attempt to prepare the latter in a higher state of purity the reaction between titanium tetra-*tert.*-amyloxide (1 mol.) and acetyl chloride (3 mols.) was investigated. However, the tetra-amyloxide proved resistant to attack and a mixture of $TiCl(O{\cdot}CMe_2Et)_3$ and unchanged tetra-alkoxide was obtained.

By the addition of ethyl acetate to $TiCl_3{\cdot}OEt$ it was possible to isolate the complex $TiCl_3{\cdot}OEt,CH_3{\cdot}CO_2Et$ identical with that obtained from the reaction between the tetraethoxide and acetyl chloride. Similarly, $TiCl_3{\cdot}OPr^i,CH_3{\cdot}CO_2Et$ was prepared by the addition of ethyl acetate to $TiCl_3{\cdot}OPr^i$ and could be distilled unchanged under reduced pressure. The thermal stability of $TiCl_4,CH_3{\cdot}CO_2Et$, $TiCl_3{\cdot}OEt,CH_3{\cdot}CO_2Et$, and $TiCl_3{\cdot}OPr^i,CH_3{\cdot}CO_2Et$ demonstrates the strength of the co-ordinate link between titanium and oxygen, while the volatility of these compounds raises the question of whether titanium is exhibiting here a covalency of 5 or 6.

EXPERIMENTAL

Apparatus.—All-glass apparatus fitted with standard interchangeable joints was used and special precautions were taken to exclude moisture.

Chemicals.—Titanium tetrachloride (B.D.H. product) was redistilled immediately before use. Ethyl and methyl alcohols were dried over the appropriate magnesium alkoxide and distilled.

Ethyldimethylcarbinol (B.D.H. purified *tert.*-amyl alcohol) was azeotropically dried and carefully fractionated. *n*-Butyl and *iso*propyl alcohols (" AnalaR " grade) were dried over the appropriate aluminium alkoxide and distilled.

Ethyl acetate was washed with calcium chloride solution, then water, and after being dried (K_2CO_3) was distilled.

Acetyl chloride was treated with phosphorus pentachloride and then carefully fractionated.

Carbon tetrachloride was dried over phosphoric oxide and distilled.

Hydrocarbons were dried over sodium wire and distilled.

Analytical Methods.—Samples were dissolved in dilute nitric acid and gravimetric methods used for determining titanium (as TiO_2) and chloride (as AgCl). Alkoxide determinations were carried out volumetrically by the methods of Bradley and Wardlaw (*J.*, 1951, 280). Carbon and hydrogen determinations were carried out by Drs. Weiler and Strauss (Oxford).

Molecular-weight Determinations.—(i) *Ebullioscopic method.* A modified Menzies–Wright apparatus was used, as described by Bradley, Mehrotra, and Wardlaw (*J.*, in the press).

(ii) *Cryoscopic method.* Apparatus of the conventional type was used and atmospheric moisture excluded by a slow stream of nitrogen.

Preparation of Titanium Tetra-alkoxides.—The alkoxides $Ti(OR)_4$ where R = Et, Pr^i, and Bu^n were prepared by the method developed in these laboratories (Bradley, Mehrotra, and Wardlaw, *loc. cit.*). The solution of titanium tetrachloride in the appropriate alcohol was diluted with benzene and treated with ammonia. After the removal of ammonium chloride and solvent the titanium tetra-alkoxide was distilled under reduced pressure. Other alkoxides were prepared by the alcohol-interchange method.

Titanium tetraethoxide. From the reaction involving titanium tetrachloride (75 g.) and ethanol (145 g.), the titanium tetraethoxide (72 g.) was obtained as a colourless viscous liquid (b. p. 124°/1·6 mm.) which slowly solidified [Found : Ti, 21·0; EtO, 78·0. Calc. for $Ti(OC_2H_5)_4$: Ti, 21·0; C_2H_5O, 79·0%]. Speer (*J. Org. Chem.*, 1949, **14**, 655) and Cullinane *et al.* (*J. Appl. Chem.*, 1951, **1**, 400) found b. p. 104°/1 mm. and 146°/8·0 mm. respectively.

*Titanium tetra*iso*propoxide.* Titanium tetrachloride (78 g.) and *iso*propyl alcohol (197 g.) were likewise converted into titanium tetra*iso*propoxide (93 g.), a colourless mobile liquid, b. p. 97°/7·5 mm. [Found : Ti, 16·9; C_3H_7O, 83·0. Calc. for $Ti(OC_3H_7)_4$: Ti, 16·9; C_3H_7O, 83·1%].

*Titanium tetra-*n*-butoxide.* Titanium tetrachloride (110 g.) and *n*-butanol (205 g.) were converted into titanium tetra-*n*-butoxide (115 g.) which was distilled at 160°/0·8 mm. (cf. Speer, b. p. 134—136°/0·5—1·0 mm.) [Found : Ti, 14·1. Calc. for $Ti(OC_4H_9)_4$: Ti, 14·1%].

*Titanium tetra-*1 : 1*-dimethylpropoxide.* Titanium *iso*propoxide (23·4 g.) was treated with *tert.*-amyl alcohol (54 g.), and the solution fractionated until no more *iso*propyl alcohol was liberated. The excess of *tert.*-alcohol was recovered by distillation under reduced pressure and the final *tetra-alkoxide*, a colourless mobile liquid (27 g.), was distilled at 106°/0·3 mm. [Found : Ti, 12·0. $Ti(OC_5H_{11})_4$ requires Ti, 12·1%].

Titanium tetramethoxide. Titanium *iso*propoxide (79 g.) was heated for 1½ hours with boiling methanol and gave a solid product. To complete the interchange it was necessary to repeat the treatment. The final solid product (45 g.) was dried at 40°/0·1 mm. [Found : Ti, 27·9; MeO, 71·7. Calc. for $Ti(OMe)_4$: Ti, 27·9; MeO, 72·1%]. A portion of this product was sublimed (170°/0·01 mm.) and gave silky white needles (Found : Ti, 27·9; MeO, 71·2%).

Preparation of $TiCl_4,CH_3{\cdot}CO_2Et$.—(i) *From titanium tetraethoxide.* Acetyl chloride (50 c.c.) reacted vigorously with the tetraethoxide (11·8 g.) at 0°. The solution was refluxed for 1½ hours and the excess of solvent removed by distillation. The solid product was distilled (*ca.* 80°/2 mm.) and gave the *complex* as a pale yellow crystalline mass (10 g.) (Found : Ti, 16·8; Cl, 49·2. $TiCl_4,CH_3{\cdot}CO_2Et$ requires Ti, 17·2; Cl, 51·0%). The compound dissolved instantly in water and gave a clear acidic solution which smelled of ethyl acetate.

(ii) *From titanium tetrachloride.* The tetrachloride (11·3 g.) reacted vigorously with ethyl acetate (50 c.c.) at 0° and gave a yellow solid which dissolved on warming. After removal of excess of ethyl acetate the solid product (*ca.* 10 g.) was purified by distillation (*ca.* 85°/1 mm.). This product appeared to be identical in crystalline form and properties with that prepared in the previous experiment (Found : Ti, 17·1; Cl, 50·3%).

Preparation of $TiCl_3(OEt),CH_3{\cdot}CO_2Et$.—(i) Acetyl chloride (12·3 g., 3 mols.) was added to titanium tetraethoxide (11·9 g., 1 mol.), and the products were refluxed for 2 hours. After removal of ethyl acetate by distillation the remaining solid was distilled (*ca.* 90°/0·5 mm.) and afforded a pale yellow crystalline *complex* (12 g.) (Found : Ti, 17·1; Cl, 38·2; C, 23·4; H, 4·75. $TiCl_3{\cdot}OC_2H_5,CH_3{\cdot}CO_2C_2H_5$ requires Ti, 16·7; Cl, 37·0; C, 25·1; H, 4·56%).

(ii) Ethanol (1·1 g.) in benzene (30 c.c.) was added to a solution of $TiCl_4,CH_3{\cdot}CO_2Et$ (6·8 g.)

in benzene (40 c.c.). The solution evolved hydrogen chloride during $1\frac{1}{2}$ hours' refluxing. After removal of solvent a pale yellow crystalline solid was obtained which was distilled as in (i) (Found: Ti, 16·9; Cl, 39·4%).

(iii) Ethyl acetate (40 c.c.) was added to titanium trichloride ethoxide (4 g.), and a clear solution resulted. Removal of excess of ethyl acetate left a solid which was distilled (*ca.* 80—90°/2 mm.) and gave a crystalline product (5 g.) (Found: Ti, 17·1; Cl, 37·0%).

Molecular-weight determinations. (*a*) Four b. p. elevations (ΔT) between $m =$ 0·426 and $m =$ 1·204 g. in benzene (35·9 c.c.) gave slope $\Delta T/m = 0{\cdot}214°$ (Found: *M*, 410. $TiCl_3{\cdot}OEt,CH_3{\cdot}CO_2Et$ requires *M*, 287).

(*b*) With 0·324, 0·552, 0·7505, and 1·144 g. of solute dissolved in benzene (25·7 g.) the following cryoscopic results were obtained: *M*, 384, 428, 445, and 446 (average, 426). The agreement between the two method is probably fortuitous.

Radical-interchange reactions

Preparation of $TiCl_3{\cdot}OEt$.—Titanium tetrachloride (46 g.) reacted vigorously and exothermally with titanium tetraethoxide (8 g.) and gave a yellow solid which was recrystallised from the excess of tetrachloride. The crystals were separated, washed with carbon tetrachloride, and when purified by distillation (b. p. 60—85°/2 mm.) gave the pale yellow *trichloride ethoxide* (27 g.) (Found: Ti, 24·0; Cl, 52·5; EtO, 22·1. $TiCl_3{\cdot}OEt$ requires Ti, 24·0; Cl, 53·4; EtO, 22·6%). Four b. p. elevations [0·324—0·965 g. of solute in benzene (36·6 c.c.)] gave $\Delta T/m$ 0·311° (Found: *M*, 277. $TiCl_3{\cdot}OEt$ requires *M*, 199·3). 0·266 and 0·614 g. of solute in benzene (21·2 g.) gave cryoscopically *M*, 304, 249.

Preparation of $TiCl_3{\cdot}OBu^n$.—Titanium tetrachloride (57 g.) was added dropwise to the tetra-*n*-butoxide (10 g.) at 0°. The solid *trichloride* n-*butoxide* (20 g.) obtained after separation and washing with light petroleum was dried at 20°/0·1 mm. (Found: Ti, 20·8; Cl, 46·4. $TiCl_3{\cdot}OBu^n$ requires Ti, 21·1; Cl, 46·8%). The product was dissolved in boiling light petroleum and the solution separated from a small insoluble residue. Cooling to 0° brought about deposition of a white solid which was dried at 20°/0·1 mm. (Found: Ti, 20·7; Cl, 45·7%). When the foregoing solid (3·0 g.) was heated at 65—80°/0·5 mm. a crystalline distillate of unchanged material (1·3 g.) (Found: Ti, 21·4; Cl, 45·7%) was obtained and a viscous brown residue (1·2 g.) remained. A more volatile fraction (0·5 g.) (Found: Ti, 27·0; Cl, 60·6. Calc. for $TiCl_3{\cdot}OH$: Ti, 28·5; Cl, 62·0%), presumably partly hydrolysed $TiCl_4$, was collected in the cold trap (−78°). The residue when further heated gave two more fractions, at 100°/0·5 mm. and 100—160°/0·5 mm. (1·0 g.) [Found: Ti, 19·9; Cl, 40·0%; Cl/Ti, 2·72. A mixture of $TiCl_3{\cdot}OBu^n$ (2 mols.) and $TiCl_2(OBu^n)_2$ (1 mol.) requires Ti, 20·0; Cl, 39·4%].

Preparation of $TiCl_3{\cdot}OMe$.—Titanium tetrachloride (40 g.) was added dropwise to the tetramethoxide (3·6 g.) and the mixture heated at 120° for 10 minutes. In view of the insolubility of the tetramethoxide in organic solvents the ready dissolution in titanium tetrachloride is of some interest. The clear solution deposited a mass of crystals on cooling. After separation and washing with light petroleum, the *trichloride methoxide* (14·1 g.) was dried at 40°/1 mm. (Found: Ti, 25·8; Cl, 55·9; MeO, 18·0. $TiCl_3{\cdot}OMe$ requires Ti, 25·8; Cl, 57·4; MeO, 16·8%). A sample (2·5 g.) of this product was heated at 0·1 mm. At 90—100° a crystalline distillate (1·2 g.) (Found: Ti, 26·0; Cl, 45·0; MeO, 26·8%; Cl/Ti, 2·34. MeO/Ti, 1·60), evidently a mixture of $TiCl_3(OMe)$ and $TiCl_2(OMe)_2$, was collected, in addition to some more volatile material (probably titanium tetrachloride) condensed in the trap (−78°). A white residue (0·6 g.) (Found: Ti, 28·3; Cl, 34·8; MeO, 34·0%; Cl/Ti, 1·66; MeO/Ti, 1·85) remained.

Another portion (7·0 g.) of the original product was refluxed with carbon tetrachloride (150 c.c.) for $\frac{1}{2}$ hour. Some insoluble residue remained while the vapour contained a titanium compound having an acid reaction (probably the tetrachloride). The hot filtrate deposited needle-like crystals (2·5 g.) which were uniform in appearance (Found: Ti, 25·8; Cl, 45·7; MeO, 27·9%; Cl/Ti, 2·4; MeO/Ti, 1·6). Evidently $TiCl_3{\cdot}OMe$ disproportionates when heated in solution or under reduced pressure.

Preparation of $TiCl_3{\cdot}OPr^i$.—When mixed at room temperature, the tetrachloride and tetra-*iso*propoxide gave an insoluble product (Found: Cl/Ti, 1·46) and hydrogen chloride was evolved. To obtain $TiCl_3{\cdot}OPr^i$ the addition of the tetrachloride (37 g.) to the tetra-alkoxide (5·6 g.) was carried out very slowly at 0°. The solid product was immediately separated and washed with carbon tetrachloride. Pale yellow *titanium trichloride* iso*propoxide* (4·5 g.) remained after drying (25°/0·1 mm.) (Found: Ti, 22·5; Cl, 49·3. $TiCl_3{\cdot}OPr^i$ requires Ti, 22·5; Cl, 49·9%). A portion of this product was distilled at *ca.* 65°/1 mm. and gave needle-like crystals (Found: Ti, 22·4; Cl, 49·5%).

Preparation of $TiCl_3{\cdot}OPr^i,CH_3{\cdot}CO_2Et$.—Titanium trichloride *iso*propoxide (2 g.) was dissolved in ethyl acetate (30 c.c.), the clear solution evaporated to dryness under reduced pressure, and the solid *complex* dried at room temperature (0·1 mm.) (Found: Ti, 15·8; Cl, 33·8. $TiCl_3{\cdot}OPr^i,CH_3{\cdot}CO_2Et$ requires Ti, 15·9; Cl, 35·3%). The foregoing product was distilled at *ca.* 70°/0·1 mm. and gave a crystalline distillate (Found: Ti, 16·1; Cl, 35·2%).

Preparation of $TiCl_2(OEt)_2,EtOH$ *and* $TiCl_2(OEt)_2$.—Titanium tetrachloride (33 g.) was added to ethanol (33 g.) in light petroleum (250 c.c.). The mixture was refluxed until hydrogen chloride evolution ceased (66 hours). The crystalline mass (29·7 g.) which was deposited on cooling was dried at room temperature (0·1 mm.) [Found: Ti, 18·6; Cl, 27·8. Calc. for $TiCl_2(OEt)_2,EtOH$: Ti, 18·8; Cl, 27·8%].

A portion (6·7 g.) of the compound was heated and gave a distillate (3 g.; b. p. 118°/8 mm.) which solidified on cooling [Found: Ti, 22·6; Cl, 30·2. Calc. for $TiCl_{1\cdot8}(OEt)_{2\cdot2}$: Ti, 22·7; Cl, 30·3%].

A portion (5 g.) was submitted to azeotropic distillation (light petroleum) to remove the solvate alcohol. Some needle-like crystals were deposited on cooling [Found: Ti, 22·9; Cl, 33·1. Calc. for $TiCl_2(OEt)_2$: Ti, 22·9; Cl, 33·9%]. Four b. p. elevations (m = 0·168 – 0·922 g.) in benzene (34·2 c.c.) gave $\Delta T/m$ = 0·306° [Found: M, 300. Calc. for $TiCl_2(OEt)_2$: M, 208].

A portion (0·5 g.) of the foregoing product was heated under reduced pressure and gave a distillate, b. p. 80—85°/0·1 mm. (Found: Cl/Ti, 1·79), and a residue (Found: Cl/Ti, 1·33).

Preparation of Substance (*A*).—Titanium tetrachloride (17·8 g., 1 mol.) was added dropwise to a solution of the tetraethoxide (21·4 g., 1 mol.) in light petroleum (200 c.c.) at 0°. The mixture was refluxed for 5 hours and gave a clear solution which crystallised on cooling. The solid product (A) was separated, washed with light petroleum, and dried at 50°/0·2 mm. [Found: Ti, 22·9; Cl, 33·8; EtO, 43·0. Calc. for $TiCl_2(OEt)_2$: Ti, 22·9; Cl, 33·9; EtO, 43·2%]. A portion was recrystallised from light petroleum (Found: Ti, 22·9; Cl, 33·9%). A further portion was distilled at 0·2 mm. and gave three fractions between 100° and 120°: the most volatile (Found: Ti, 24·0; Cl, 48·9%; Cl/Ti, 2·76) readily solidified and was evidently mainly the trichloride ethoxide. The middle fraction (Found: Ti, 23·3; Cl, 37·8; EtO, 38·6%; Cl/Ti, 2·20; EtO/Ti, 1·76), clearly a mixture of dichloride diethoxide with some trichloride ethoxide, slowly solidified, as did the third fraction (Found: Ti, 23·0; Cl, 35·6%) which was chiefly $TiCl_2(OEt)_2$. Similar behaviour occurred when (A) (6·0 g.) was heated at 18 mm. The more volatile fraction (1 g.; b. p. 100°) was mainly the trichloride ethoxide, whilst the other fraction (3·1 g.; b. p. 100—154°) (Found: Ti, 23·2; Cl, 37·2%; Cl/Ti, 2·16) consisted of the dichloride diethoxide with some trichloride ethoxide.

Treatment of (A) with ethanol gave a clear solution on warming. The solution was evaporated to dryness under reduced pressure and the solid product dried at room temperature (0·1 mm.) [Found: Ti, 18·5; Cl, 26·7. Calc. for $TiCl_2(OEt)_2,EtOH$: Ti, 18·8; Cl, 27·8%]. This product was distilled at 1 mm. and gave no trichloride ethoxide but, instead, two fractions [b. p. 118—122° (Found: Ti, 22·3; Cl, 30·4%; Cl/Ti, 1·84) and b. p. 123° (Found: Ti, 22·0; Cl, 26·0%; Cl/Ti, 1·6)], which were evidently mixtures of dichloride diethoxide and chloride triethoxide.

Preparation of $TiCl_2(OBu^n)_2$.—(*a*) Titanium tetrachloride (25 g.) was added slowly to *n*-butanol (50 g.), and the mixture refluxed for 52 hours. Excess of butanol was removed by distillation and the remaining product distilled at 4 mm. The main fraction (10 g.; b. p. 130—140°) [Found: Ti, 18·0; Cl, 26·1. Calc. for $TiCl_2(OBu^n)_2$: Ti, 18·1; Cl, 26·8%] was the dichloride di-*n*-butoxide, but the less volatile fraction (b. p. 140—200°) (Found: Ti, 15·7; Cl, 18·6%; Cl/Ti, 1·6) was a mixture thereof with the chloride tri-*n*-butoxide.

(*b*) Titanium tetrachloride (9·5 g., 1 mol.) was added dropwise to a solution of the tetra-*n*-butoxide (17·2 g., 1 mol.) in light petroleum (50 c.c.) at 0°. The clear solution was refluxed for 2 hours and the solvent then removed by distillation. The final product was heated at 1 mm. and gave a distillate (7 g.; b. p. 104°) (Found: Ti, 20·3; Cl, 31·3%; Cl/Ti, 2·08) which evidently contained some trichloride *n*-butoxide. The residue (Found: Ti, 17·7; Cl, 18·0%; Cl/Ti, 1·38) did not distil below 200° and appeared to be a partly decomposed mixture of dichloride di-*n*-butoxide and chloride tri-*n*-butoxide.

Reaction between Titanium Tetrachloride (1·43 *Mols.*) *and Titanium Tetraethoxide* (1 *Mol.*).—Titanium tetrachloride (18·1 g.) was slowly added to titanium tetraethoxide (15·1 g.) at 0°. The mixture was heated at 100° for 15 minutes and a viscous liquid remained on cooling. This substance was distilled at 2 mm. and with the heating-bath at 80° gave a solid distillate (9 g.) [Found: Ti, 23·75; Cl, 48·4%; Cl/Ti, 2·75. Calc. for a mixture of $TiCl_3{\cdot}OEt$

(3 mols.) + $TiCl_2(OEt)_2$ (1 mol.): Ti, 23·7; Cl, 48·4%]. A viscous liquid residue (21·9 g.) remained [Found: Ti, 23·7; Cl, 31·2. Calc. for $TiCl_2(OEt)_2$: Ti, 22·9; Cl, 33·9%]. Further heating of this residue at 100°/3 mm. gave more crystalline distillate (5 g.), followed at 200° by a liquid which was contaminated by the aforementioned solid.

*Reaction between Titanium Tetrachloride and Titanium Tetra-*tert.*-amyloxide.*—Titanium tetrachloride (24 g.) in light petroleum (50 c.c.) was added dropwise to a solution of the tetra-alkoxide (4·7 g.) in light petroleum (30 c.c.) at −78°. The solid *trichloride* tert.*-amyloxide* produced was separated and washed three times with carbon tetrachloride, then dried at room temperature (0·1 mm.) (Found: Ti, 19·7; Cl, 38·7%; Cl/Ti, 2·65. $TiCl_3{\cdot}OC_5H_{11}$ requires Ti, 19·8; Cl, 44·1%). This (11 g.) gave dense white fumes when exposed to moist air and acquired a violet colour. It was soluble in ethyl acetate but decomposed when heated under reduced pressure.

*Reaction between Titanium Tetra-*tert.*-amyloxide and Acetyl Chloride.*—Acetyl chloride (1·18 g., 3 mols.) was added to the alkoxide (2 g., 1 mol.), and the mixture heated at 50° for ½ hour, and then for ½ hour at 80°. Excess of acetyl chloride was removed by distillation and the final product distilled at 115—120°/0·3 mm. (Found: Ti, 13·27; Cl, 6·65%; Cl/Ti, 0·68). This was evidently a mixture of tetra-*tert.*-amyloxide and chloride tri-*tert.*-amyloxide.

BIRKBECK COLLEGE, LONDON, W.C.1.

[*Received, March* 19*th*, 1952.]