598. *Reactions of Ortho-esters of Titanium. Part IV.* Alcoholysis Reactions of Alkyl Orthotitanates.*

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Reactions of $Ti(OMe)_4$, $Ti(OEt)_4$, $Ti(OPr^i)_4$, and $Ti(OBu^t)_4$ with alcohols (MeOH, EtOH, Pr^iOH, and Bu^tOH) have revealed the following order of reactivity in replacement reactions: $OMe \gg OEt > OPr^i > OBu^t$. It has therefore been possible to synthesise the following pure mixed orthotitanates: $MeO{\cdot}Ti(OR)_3$, $(MeO)_2Ti(OR)_2$ (OR = OEt, OPr^i, OBu^t), and $(MeO)_3Ti{\cdot}OR$ (OR = OEt, OPr^i). The mixed ethyl methyl orthotitanates crystallise from benzene and distil unchanged under reduced pressure. Isopropyl methyl and methyl t-butyl titanates are liquids and undergo disproportionation, mainly into monomethyl tri-isopropyl or tri-t-butyl and tetramethyl titanates. Fresh light has been thrown on the nature of tetramethyl titanate.

A FEW mixed ortho-esters of titanium [1] and of zirconium [2] have been reported. Higher ortho-esters of titanium have been prepared by alcohol-interchange reactions,[3,4] which have now been shown to be reversible. Data presented in Tables 1 and 2 exhibit

TABLE 1. *Reaction:* $Ti(OR)_4 + MeOH$ (*molar ratio* 1 : 3).

Ester	$Ti(OBu^t)_4$	$Ti(OPr^i)_4$	$Ti(OEt)_4$
MeO : Ti (in product)	2·3	2·1	2·0

TABLE 2. *Reaction:* $Ti(OR)_4 + R'OH$ (*molar ratio* 1 : 4).

	OR′ : Ti (in product)					OR′ : Ti (in product)			
Ester	MeOH	EtOH	Pr^iOH	Bu^tOH	Ester	MeOH	EtOH	Pr^iOH	Bu^tOH
$Ti(OMe)_4$	—	1·5	1·5	—	$Ti(OPr^i)_4$	—	—	—	2·3
$Ti(OEt)_4$	—	—	—	1·6	$Ti(OBu^t)_4$	2·7	2·4	1·8	—

the following comparative reactivity of the alkoxy-groups in alcoholysis reactions: $MeO \gg EtO > Pr^iO > Bu^tO$.

* Part III, *J. prakt. Chem.*, in the press.

[1] Ghosh, Ghosh Mazumdar, Bose, and Sen Gupta, *J. Indian Chem. Soc.*, 1954, **34**, 683; Nesmeyanov and Nogina, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1954, 41 (*Chem. Abs.*, 1955, **49**, 6084).
[2] Mehrotra, *J. Indian Chem. Soc.*, 1954, **31**, 905.
[3] Bradley, Mehrotra, and Wardlaw, *J.*, 1952, 2027, 4204, 5020.
[4] Bradley, Mehrotra, Swanwick, and Wardlaw, *J.*, 1953, 2025.

The foregoing and also reactions for the molar ratios 1 : 1 and 1 : 2 are represented in Tables 4—8. By carrying out the reactions in benzene the compounds of types (I) and (II) have been isolated (R = Et, Pr^i, or Bu^t).

$$Ti(OR)_4 + MeOH \longrightarrow MeO{\cdot}Ti(OR)_3 \text{ (I)} + ROH$$
$$Ti(OR)_4 + 2MeOH \longrightarrow (MeO)_2Ti(OR)_2 \text{ (II)} + 2ROH$$

The identity of some of these orthotitanates (particularly the ethyl methyl orthotitanates) has been established by distilling them unchanged (Table 3). In other cases the mixed orthotitanates have been found to disproportionate when distilled under reduced pressure. The isopropyl (or t-butyl) methyl titanates, in general, yield mainly a monomethyl derivative and tetramethyl titanate.

TABLE 3.

Alkyl orthotitanate	B. p./mm.	*M* (obs.)	Mol. complexity	Alkyl orthotitanate	B. p./mm.	*M* (obs.)	Mol. complexity
$Ti(OEt)_4$	121°/0·8	556	2·4	$Ti(OEt)(OMe)_3$...	142°/0·3	657	3·5
$Ti(OEt)_3(OMe)$ ...	143°/1·5	553	2·6	$Ti(OMe)_4$	190°/1·5 (Sublimn. temp.)	—	4·0 (extrap.)
$Ti(OEt)_2(OMe)_2$	130°/0·2	604	3·0				

Tetramethyl titanate is unique among the orthotitanates, in being an infusible white solid, insoluble in most organic solvents. The mixed methyl titanates are all soluble in benzene. Of these the ethyl methyl titanates crystallise as white solids from benzene, and their individual identity was further established by the unchanged analyses of the products after repeated crystallisation. Attempts have been made to explain the insoluble nature of tetramethyl titanate by its highly polymerised nature or by strong inductive effects of the methyl group. The molecular weights of ethyl methyl orthotitanates (Table 3) have been measured ebullioscopically by a method already described,[3] and appear to indicate that the main controlling factor in the unique properties of tetramethyl titanate is not its highly polymerised character but the inductive effects of methyl group.

EXPERIMENTAL

Apparatus.—Moisture was excluded in all the experiments.[5]

Materials.—Alcohols [6] and benzene [5] were purified as described elsewhere. $Ti(OEt)_4$ and $Ti(OPr^i)_4$ (Peter Spence products) were purified by distillation.[5] $Ti(OBu^t)_4$ [7] and $Ti(OMe)_4$ [8] were prepared and purified by distillation and sublimation respectively.

Analytical Methods.—Titanium was estimated as TiO_2. Ethoxy- and isopropoxy-contents of esters were determined by oxidation with dichromate.[9]

Reaction between Methanol and Tetraethyl Titanate.—Methanol (0·74 g., 23 mmoles) was added with constant stirring to $Ti(OEt)_4$ (5·15 g., 23 mmoles); heat was evolved and a white precipitate settled. Benzene (15·0 g.) was distilled into the reaction mixture. After refluxing gently at 90° for 3 hr., the clear solution was allowed to crystallise overnight at room temperature. After the supernatant liquor had been decanted, the white crystals were dried at 30°/1 mm. (1·6 g.) (Found: Ti, 22·3%). The supernatant liquor was evaporated to dryness at 30°/1 mm. A white solid (2·9 g.) was obtained (Found: Ti, 22·55%). The two solids were mixed and recrystallised from benzene (Found: Ti, 22·3. Calc. for $C_7H_{18}O_4Ti$: Ti, 22·4%). The above compound (2·2 g.) distilled at 143°/1·5 mm. and a wax-like solid (1·8 g.) was obtained (Found: Ti, 22·25%). It was recrystallised from benzene (Found: Ti, 22·3%). Other reactions are condensed in Tables 4—9.

[5] Varma and Mehrotra, *J. prakt. Chem.*, 1959, **8**, 235.
[6] Vogel, " A Text-book of Practical Organic Chemistry," Longmans, Green and Co., London, 1956, pp. 169, 170.
[7] Speer, *J. Org. Chem.*, 1949, **14**, 655.
[8] Bischoff and Adkins, *J. Amer. Chem. Soc.*, 1924, **46**, 256.
[9] Mehrotra, *J. Indian Chem. Soc.*, 1953, **30**, 585; 1954, **31**, 904; *J. Amer. Chem. Soc.*, 1954, **76**, 2266.

TABLE 4. *Reaction of methanol with tetraethyl or diethyl dimethyl titanate.*

Reactants (g.)			Product		Action of heat on product			
					Distillate			
$Ti(OEt)_4$	MeOH	C_6H_6 (g.)	Yield (g.)	Ti (%) *	B. p./mm.	g.	Found * Ti (%)	Solid (g.)
5·15	0·74 (1 mol.)	15·0	4·5 [a]	22·3	143°/1·5	1·8 [b]	22·25	2·2
5·65	1·59 (2 mol.)	5·0	5·1 [a]	23·0	130°/0·2	4·0 [b]	23·8	4·4
7·82	3·29 (3 mol.)	8·2	6·9 [a]	23·8	130°/0·2	5·6 [b]	23·9	6·0
$Ti(OEt)_2(OMe)_2$								
3·61	2·52 (>4 mol.)	6·0	3·1 [a]	25·5	142°/0·3	2·4 [b]	25·55	2·6
6·63	18·7 (†)	—	5·4 [c]	27·6	Subl. 190°/1·5		27·6 [d]	—

* Ti (%) calc. for: $Ti(OEt)_3(OMe)$, 22·4; for $Ti(OEt)_2(OMe)_2$ 23·95; for $Ti(OEt)(OMe)_3$, 25·75; for $Ti(OMe)_4$, 27·85.

Key for Tables 4—9.

[a] White powder sol. in C_6H_6.
[b] Wax-like solid sol. in C_6H_6.
[c] White solid insol. in C_6H_6.
[d] Found in sublimate.
[e] Reaction mixture became clear on refluxing.
[f] Colourless liquid miscible with C_6H_6.
[g] Thick colourless liquid sol. in C_6H_6.
[h] Cooling occurs when reagents are mixed.
[i] Heat evolved when reagents are mixed.
† Large excess.

TABLE 5. *Reaction of methanol with tetraisopropyl titanate.*

Reactants (g.)			Product		Product taken	Action of heat on product				
						Distillate			Sublimate	
$Ti(OPr^i)_4$	MeOH	C_6H_6 (g.)	Yield (%)	Ti (%) *	(g.)	B. p./mm.	g.	Ti (%) *	g.	Ti (%) *
6·34	0·71 (1 mol.)	—	5·7 [f]	18·7	5·1	101°/1·5	4·3 [f]	17·8	0·5 [c]	27·0
5·5	1·22 (2 mol.)	—	4·6 [g]	20·3	3·8	120°/1·5	2·7 [f]	18·3	0·5 [c]	27·5
6·19	2·10 (3 mol.)	50	4·9 [g]	21·25	4·17	126°/2	2·83 [f]	18·8	0·9 [c]	28·0
3·56	1·87 (>4 mol.)	10	2·8 [g]	24·3	2·2	145°/2·5	1·1 [f]	18·9	0·8 [c]	27·8
4·50	10·30 (†) [e]	—	2·2 [c]	27·55		Subl. 190°/1·5		—	—	27·7

* Ti (%) calc. for: $Ti(OMe)(OPr^i)_3$, 18·7; for $Ti(OMe)_2(OPr^i)_2$, 21·0; for $Ti(OMe)_3(OPr^i)$, 23·95.

TABLE 6. *Reaction of methanol with tetra-t-butyl or dimethyl di-t-butyl titanate.*

Reactants (g.)			Product		Product taken	Action of heat on product				
						Distillate			Sublimate	
$Ti(OBu^t)_4$	MeOH	C_6H_6 (g.)	Yield (g.)	Ti (%) *	(g.)	B. p./mm.	g.	Ti (%) *	g.	Ti (%) *
6·25	0·59 (1 mol.)	—	5·6 [f]	16·0	4·9	99°/1·2	4·1 [f]	15·0	0·3 [c]	26·7
5·57	1·05 (2 mol.)	20	4·5 [f]	18·5	4·1	84°/0·7	2·95 [f]	14·7	0·7 [c]	27·2
5·88	1·73 (3 mol.)	15	3·9 [f]	19·6	2·7	105°/1·5	1·5 [f]	16·0	0·8 [c]	27·6
1·63	0·70 (4 mol.)	6·0	1·1 [g]	21·0	—	—	—	—	—	—
$Ti(OMe)_2(OBu^t)_2$										
2·75	15·0 (†) [e]	—	1·9 [c]	28·3	—	Subl. 190°/1·5			—	27·5

* Ti (%) calc. for: $Ti(OMe)(OBu^t)_3$, 16·1; $Ti(OMe)_2(OBu^t)_2$, 18·7; $Ti(OMe)_3(OBu^t)$, 22·4; $Ti(OMe)_4$, 27·85.

TABLE 7. *Reaction of t-butanol with tetraethyl or tetraisopropyl titanate* [$Ti(OR)_4$].

Reactants (g.)			Product				Product taken	Action of heat on product				
								Distillate		Found in distillate		
$Ti(OEt)_4$	Bu^tOH	C_6H_6 (g.)	Yield (g.)	Ti (%)	OR (%)	OR : Ti	(g.)	B. p./mm.	g.	Ti (%)	OR (%)	OR : Ti
5·61	1·87 (1 mol.)	14	6·1 [f]	19·3	60·15	3·3	—	—	—	—	—	—
7·90	5·19 (2 mol.)	19	9·0 [f]	18·5	51·9	3·0	5·9	97—140°/9—10	3·6	17·3	38·6	2·4
5·24	6·80 (4 mol.)	19·5	6·4 [f]	17·1	38·2	2·4	—	—	—	—	—	—
$Ti(OPr^i)_4$												
7·30	1·98 (1 mol.)	15	7·6 [f]	16·2	63·4	3·1	4·3	103·5°/8·5	4·0 [f]	16·2	62·5	3·1
7·52	3·93 (2 mol.)	11	8·0	15·7	50·2	2·6	—	—	—	—	—	—
4·60	4·80 (4 mol.)	18	5·9	14·9	32·6	1·7	—	—	—	—	—	—

TABLE 8. *Reaction of alcohols* (R·OH) *with tetra-t-butyl titanate.*

Reactants (g.)			Product				Action of heat on product					
							Product taken	Distillate		Found in distillate		
$Ti(OBu^t)_4$	Pr^iOH	C_6H_6 (g.)	Yield (%)	Ti (%)	OR (%)	OR : Ti	(g.)	B. p./mm.	g.	Ti (%)	OR (%)	OR : Ti
5·50	1·05 (1 mol.)	10 [h]	5·3 [f]	14·8	18·8	1·0	2·0	103°/3·5	1·8 [f]	14·6	16·1	0·9
5·34	1·87 (2 mol.)	10	5·1	14·9	26·1	1·4	—	—	—	—	—	—
5·96	4·18 (4 mol.)	19	5·7 [f]	15·2	34·4	1·8	—	—	—	—	—	—
2·58	7·30 (†)	—	2·2 [f]	16·3	61·0	3·0	—	—	—	—	—	—
	EtOH											
6·42	3·53 (4 mol.)	20	5·2 [f]	17·6	40·2	2·4	—	—	—	—	—	—
3·97	8·56 (†)	—	2·9	19·9	63·6	3·4	2·1	120°/0·8	1·8 [f]	19·9	65·7	3·5

TABLE 9. *Reaction of alcohols* (R·OH) *with tetramethyl titanate.*

Reactants (g.)			Product		Action of heat on product			
					Product	Distillate		
$Ti(OMe)_4$	EtOH	C_6H_6 (g.)	Yield (g.)	Ti (%)	taken (g.)	B. p./mm.	g.	Ti (%)
1·33	1·43 (4 mol.)	25	1·55 [a]	24·9	—	—	—	—
1·70	6·70 (†)	—	1·0 [a]	23·85	0·8	130°/0·2	0·6 [b]	23·9
	Pr^iOH							
1·32	1·92 (4 mol.)	25	1·7 [g]	22·2	—	—	—	—
1·65	16·5 (†)	—	2·0 [f]	18·2	1·5	61°/0·3	1·1 [f]	17·2

Ti (%) calc. for: $Ti(OMe)_2(OEt)_2$, 23·95; for $Ti(OPr^i)_4$, 16·85.

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