ORGANIC COMPOUNDS OF NIOBIUM

I. REACTIONS OF NIOBIUM PENTA-ETHOXIDE WITH ORGANIC ESTERS

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SUMMARY

The reactions between niobium penta-ethoxide and organic esters (*n*-propyl, isopropyl, *n*-butyl, *sec.*-butyl, *tert.*-butyl, *n*-amyl and phenyl acetate) have been studied using the organic esters also as solvent, except in the cases of *n*-amyl and phenyl acetates, where cyclohexane was used as a solvent. This technique provides a suitable method for the synthesis of niobium penta-*tert.*-butoxide.

INTRODUCTION

A survey of the literature reveals that a considerable amount of work has already been carried out on the reactions of the alkoxides of aluminium[1,2], titanium[3], zirconium, hafnium and vanadium[4] with organic esters.

It has been shown[3] that when zirconium tetra-isopropoxide is treated with an excess of *tert.*-butyl acetate, zirconium tetra-*tert.*-butoxide is obtained. This method was of particular interest because all the other methods reported for the synthesis of tetra-*tert.*-butoxide had failed to give the pure product in good yield. It may be mentioned that in the case of niobium also BRADLEY *et al.*[5] were unable to synthesize the penta-*tert.*-butoxide even after repeated attempts. The only successful synthesis of niobium penta-*tert.*-butoxide which has been described is by the reaction of niobium dialkylamide with *tert.*-butyl alcohol[6]. The reaction between niobium penta-ethoxide and an excess of *tert.*-butyl acetate has now been found to give niobium penta-*tert.*-butoxide in fairly high yield, a reaction which can be extended to other organic esters. The various reactions may be represented in general as follows:

$$\mathrm{Nb(OEt)_5 + 5\ R'OOCMe \rightarrow Nb(OR')_5 + 5\ CH_3COOEt}$$

The alkoxy group of esters and niobium penta-ethoxide react readily and the resulting equilibrium is shifted to completion by distilling off the lower boiling organic ester, (CH_3COOEt), which is formed.

In the reactions using normal amyl acetate and phenyl acetate, cyclohexane was used as solvent; this forms an azeotrope with the liberated ethyl acetate. All these products are soluble in benzene and distil or sublime under reduced pressure.

EXPERIMENTAL

Materials

Niobium penta-ethoxide was prepared by the ammonia method[7]. The organic esters were prepared by the usual methods[8] and were dried carefully over anhydrous sodium sulphate and purified by careful fractionation. Phenyl acetate was distilled before use. Cyclohexane was refluxed over metallic sodium and fractionated before use (b.p. 80.7°C).

Apparatus

All-glass apparatus with interchangeable standard joints was used throughout and special precautions were taken to exclude moisture from the system.

Analytical

Niobium was estimated as niobium pentoxide, by direct ignition of the compound in a platinum crucible after digestion with ammonia and nitric acid. Isopropoxy group[9] was estimated by oxidation with N-dichromate in 12.5% sulphuric acid. The phenoxy group was estimated by adding a known amount of bromate-bromide solution to the test solution, acidifying and titrating the excess of bromide iodometrically.

The method of ester-interchange employed was similar in all the cases. The following are typical examples.

REACTIONS

Reaction of niobium penta-ethoxide with tert.*-butyl acetate*

Tert.-butyl acetate (42.2 g) was added to niobium penta-ethoxide (2.17 g). The reaction mixture was refluxed under a fractionating column at a bath temperature of 130°–150°C. About 3 ml of the distillate (ethyl acetate) was collected from 77°–79°C after about one hour. Then the temperature of distillation rose to 83°C and refluxing was continued whilst a further 15 ml of distillate was collected from 83°C to 96°C. The remaining *tert.*-butyl acetate was then distilled at a high reflux-ratio to bring the reaction to completion. The refluxing was carried out for a total of about 8 h. Finally, the product was allowed to cool and the remaining *tert.*-butyl acetate was removed under reduced pressure at room temperature. A white crystalline solid was obtained which sublimed at 110°–120°C/0.3 mm.

Found: Nb = 20.5; ethoxy = 1.07. $Nb(OBu^t)_5$ requires: Nb = 20.27%.

Reaction of niobium penta-ethoxide with phenyl acetate

Phenyl acetate (10.6 g) was added to a solution of niobium penta-ethoxide (1.69 g) in cyclohexane (60 g). A dark yellow solution was obtained. The contents were refluxed under a fractionating column. After one hour the azeotrope of ethyl acetate and cyclohexane was collected at 71°–73°C. The excess of cyclohexane was fractionated out at 80°–81°C. A clear yellow solution was thus obtained which was dried at 100°C/0.05 mm. A yellow crystalline solid, m.p. 204°C, was obtained which was distilled at 320°C/0.2 mm as a yellow liquid, which solidified immediately to a yellow solid.

Found: Nb = 16.39; Phenoxy = 80.92%. $Nb(OPh)_5$ requires: Nb = 16.63; Phenoxy = 83.37%.

TABLE I

REACTIONS OF NIOBIUM PENTA-ETHOXIDE WITH ORGANIC ESTERS

Sample number	*Reactants*	*Sol-vent*	*Hours of refl.*	*Product and state*	*b.p. (°C)/mm*	*Analysis*			
						Niobium		*Alkoxy or phenoxy*	
						Found(%)	*Calc.(%)*	*Found(%)*	*Calc.(%)*
1	$Nb(OEt)_5$ + *n*-propyl acetate	—	7	$Nb(OPr^n)_5$ Orange yellow liquid	182–183/0.8	24.1	23.92	—	—
2	$Nb(OEt)_5$ + isopropyl acetate	—	10	$Nb(OPr^i)_5$ White crystalline solid	*60–80/0.1	24.3	23.92	79.3	76.08
3	$Nb(OEt)_5$ + *n*-butyl acetate	—	10	$Nb(OBu^n)_5$ Yellow mobile liquid	189–190/0.1	20.5	20.27	—	—
4	$Nb(OEt)_5$ + *Sec.*-butyl acetate	—	10	$Nb(OBu^s)_5$ Yellow liquid	105–115/0.15	20.5	20.27	—	—
5	$Nb(OEt)_5$ + *tert.*-butyl acetate	—	8	$Nb(OBu^t)_5$ White crystalline solid	*110–120/0.3	20.5	20.27	1.07	—
6	$Nb(OEt)_5$ + *n*-amyl acetate	Cyclo-hexane	10	$Nb(OAm^n)_5$ Yellow liquid	233/0.7–0.8	17.78	17.57	—	—
7	$Nb(OEt)_5$ + phenyl acetate	Cyclo-hexane	6	$Nb(OPh)_5$ Yellow solid	320/0.2	16.39	16.63	80.92	83.37

* Sublimes

Similar reactions were carried out with isopropyl, *n*-propyl, *n*-butyl, *sec.*-butyl, *n*-amyl acetate, and the results obtained are described in Table I.

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