

ORGANIC COMPOUNDS OF NIOBIUM AND TANTALUM. REACTIONS OF NIOBIUM AND TANTALUM PENTAETHOXIDES WITH ETHYL BENZOYLACETATE

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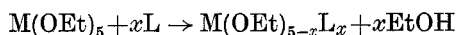
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Summary

The following two types of new compounds have been isolated: $M(\text{OEt})_4(\text{etbzac})$ and $M(\text{OEt})_3(\text{etbzac})_2$ (where M is niobium or tantalum) by the reactions of niobium and tantalum pentaethoxides with ethyl benzoylacetate. Further replacement of the ethoxide group by the ligand is very slow. These derivatives interchange their ethoxide groups with tertiary butanol, yielding the corresponding tertiary butoxide derivatives. All these derivatives can be purified by distillation under reduced pressure. Molecular weight determinations show them to be monomeric in boiling benzene.

The reactions of niobium and tantalum pentaalkoxides with β -diketones¹⁻³ and β -keto esters⁴ have been studied and interesting results have been observed regarding their volatility and coordination number. In view of the above, it was considered of interest to study the reactions of pentaethoxides of these two elements with ethyl benzoylacetate.

For the preparation of such derivatives, the technique of alcohol interchange was adopted and the reactions of niobium and tantalum pentaethoxides with dry ethyl benzoylacetate were carried out in different stoichiometric ratios in benzene. The ethanol produced in these reactions was removed azeotropically with benzene and estimated by an oxidimetric method.⁵ These reactions can be represented by the following equation:



where M is Nb or Ta, $x = 1$ or 2 , and L = ethyl benzoylacetate.

The experimental technique was the same as already described.^{1,4} A plausible mechanism for these reactions would be one similar to alcoholysis S_N2 reactions.

All the products are yellow viscous liquids, susceptible to moisture and soluble in benzene (Table 1). The replacement of the first ethoxide group by the

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¹ Kapoor, P. N., and Mehrotra, R. C., *J. less-common Metals*, 1965, **8**, 339.

² Whitley, A., Ph.D. Thesis, London University, 1955.

³ Gut, R., Buser, H., and Schmid, E., *Helv. chim. Acta*, 1965, **48**, 878.

⁴ Mehrotra, R. C., and Kapoor, P. N., *J. less-common Metals*, 1964, **7**, 176, 453.

⁵ Bradley, D. C., Halim, F. M. A., and Wardlaw, W., *J. chem. Soc.*, 1950, 3450.

TABLE 1
REACTIONS OF NIOBIUM AND TANTALUM PENTATHOXIDES WITH ETHYL BENZOYLACETATE
Each product was a yellow viscous liquid

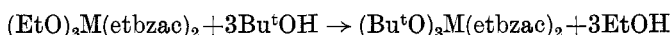
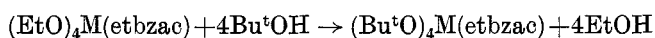
Ethoxide (g)	H- etbzac (g)	Molar Ratio	EtOH in Azeotrope (g)		Product Formed and Yield (g)	B.P. (°C/mm)	Found (%)		Calc. (%)		Mol. Wt.		n_D^{20}
			Found	Calc.			Metal	Alkoxy	Metal	Alkoxy	Found	Calc.	
Nb(OEt) ₅ 3.56 3.14 2.45	2.10	1:1	0.49	0.51	Nb(OEt) ₄ (etbzac) (5.1)	178°/0.5	20.2	39.8	20.0	38.8	436	464.4	1.5710
	3.80	1:2	0.88	0.91	Nb(OEt) ₃ (etbzac) ₂ (5.8)	180°/0.4	15.8	22.9	15.2	22.1	563	610.5	1.5925
	4.45	1:3	0.68	0.71	Nb(OEt) ₃ (etbzac) ₂ (4.83)	181°/0.5	15.5	—	15.2	—	—	—	—
Ta(OEt) ₅ 2.85 3.90 2.98	1.35	1:1	0.30	0.32	Ta(OEt) ₄ (etbzac) (3.9)	156°/0.2	32.6	33.5	32.7	32.6	522	552.4	1.5500
	3.70	1:2	0.78	0.88	Ta(OEt) ₃ (etbzac) ₂ (6.7)	185°/1.0	25.7	22.0	25.9	19.3	650	698.6	1.5630
	4.20	1:3	0.68	0.68	Ta(OEt) ₃ (etbzac) ₂ (4.8)	188°/1.5	26.1	—	25.9	—	—	—	—

TABLE 2
INTERCHANGE WITH TERTIARY BUTANOL
Each product was a yellow solid

Compound (g)	Bu ^t OH (g)	EtOH in Azeotrope (g)		Product Formed and Yield (g)	B.P. (°C/mm)	Metal (%)		Mol. Wt.	
		Found	Calc.			Found	Calc.	Found	Calc.
Nb(OEt) ₄ (etbzac) (2.53)	9.60	1.01	1.0	Nb(OBu ^t) ₄ (etbzac) (3.4)	180–182°/1.0	15.8	16.1	569	576.6
Nb(OEt) ₃ (etbzac) ₂ (1.48)	7.6	0.34	0.33	Nb(OBu ^t) ₃ (etbzac) ₂ (1.86)	178°/0.5	13.1	13.4	670	694.7
Ta(OEt) ₄ (etbzac) (1.79)	8.2	0.60	0.59	Ta(OBu ^t) ₄ (etbzac) (2.20)	180°/0.8	27.6	27.2	639	664.6
Ta(OEt) ₃ (etbzac) ₂ (1.27)	6.8	0.28	0.25	Ta(OBu ^t) ₃ (etbzac) ₂ (1.42)	165–168°/0.8	22.9	23.1	738	782.7

ethyl benzoylacetate molecule occurs readily, but further reaction is very slow and requires several hours of refluxing. The reactions of pentaethoxides of niobium and tantalum and ethyl benzoylacetate in molar ratio of 1:5 yielded disubstituted products, whereas further reaction appeared to be very slow and only 2.3 moles of ethanol could be distilled out during 40 hr of refluxing. The slowness of these reactions could be ascribed to greater steric hindrance encountered in these reactions compared to those with methyl and ethyl acetoacetate.

Further alcoholysis reactions of mono- and di-substituted derivatives with tertiary butanol in the presence of benzene provided a good method for the preparation of the corresponding tertiary butoxide derivatives. Estimation of ethanol liberated gave not only a check on the completeness of the reaction but also provided a means of analysis of ethoxide content in the original derivative. These reactions proceeded comparatively more readily in the case of tantalum:



These derivatives are yellow solids (Table 2) soluble in benzene. All these ethoxide derivatives as well as tertiary butoxide derivatives can be purified by distillation or sublimation under reduced pressure. Their molecular weights were determined ebullioscopically in benzene and found to be monomeric. The niobium and tantalum have achieved the coordination number six and seven in mono- and di-substituted derivatives, which is now well established.⁶ The boiling points of these derivatives indicate that the tantalum derivatives are more volatile than the corresponding niobium derivatives.

EXPERIMENTAL

Experimental techniques, reagents, and analytical methods were similar to those described previously.^{1,4} The ethyl benzoylacetate was distilled under reduced pressure before use.

(i) Reaction of Niobium Pentaethoxide with Ethyl Benzoylacetate in the Molar Ratio of 1:1

Ethyl benzoylacetate (2.1 g) was added to a benzene (50 g) solution of niobium pentaethoxide (3.56 g). The colour of the solution became light yellow. The solution was refluxed under a fractionating column and the binary azeotrope of ethanol-benzene was collected at 68–80°. After about 12 hr, the excess of the solvent was distilled off at a high reflux ratio. A yellow solution was obtained which was evaporated under reduced pressure at room temperature. A yellow viscous liquid (5.1 g) remained which was distilled under reduced pressure, b.p. 178°/0.5 mm (Ethanol in the azeotrope 0.49 g; replacement of 1 equiv. requires 0.51 g. Found: Nb, 20.2; EtO, 39.8; mol. wt., 436. Nb(OEt)₄(etbzac) requires Nb, 20.0; EtO, 38.8%; mol. wt., 464.4).

(ii) Reaction of Tantalum Tetraethoxide Monoethylbenzoylacetate with *t*-Butanol

t-Butanol (8.2 g) was added to a solution of the above compound (1.79 g) in benzene (40 g). The reaction mixture was refluxed under the column as above with slow fractionation of the azeotrope. Excess of the solvent was distilled out under reduced pressure. A yellow solid (2.20 g) (b.p. 180°/0.8 mm) was obtained (Ethanol in the azeotrope 0.60 g; replacement of 4 equiv. requires 0.59 g. Found: Ta, 27.6; mol. wt. 639. Ta(OBu^t)₄(etbzac) requires Ta, 27.2%; mol. wt. 664.6).

⁶ Clark, R. J. H., Kepert, D. L., and Nyholm, R. S., *J. chem. Soc.*, 1965, 2877.