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N-Aryl Alkyl Carbamate Derivatives of Ta(V)

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In continuation to our studies [1, 2], on the insertion reactions across M–O bonds (where M = As(III), Sb(III) and Nb(V)), we report in the present communication the synthesis of N-aryl alkyl carbamate derivatives of tantalum by the insertion of arylisocyanate across Ta–O bonds:

$$Ta(OR)_5 + nR'{-}N{=}C{=}O \xrightarrow{\text{benzene}} (OR)_{5-n}Ta(-NR'{-}Co{-}OR)_n$$

(where R = Et, Pr^i; R′ = phenyl or naphthyl, and n = 1–5)

The formation of these derivatives was indicated by the disappearance of a characteristic i.r. band due to multiply bonded group accompanied by the appearance of a new band in their i.r. spectra.

Experimental

Reactions were carried out under strictly anhydrous conditions. Tantalum pentaethoxide and isopropoxide were prepared by the ammonia method [3]. Benzene (B.D.H.) was dried over sodium followed by azeotropic fractionation in the presence of ethanol. Ethanol, isopropanol, phenylisocyanate, and α-naphthylisocyanate were also dried and distilled before use.

Tantalum was estimated as tantalum oxide. Nitrogen was estimated by the Kjeldahl procedure. Infrared spectra of the derivatives were recorded as neat or in nujol using KBr optics (Perkin-Elmer 337) in the range 4000–400 cm^{-1}.

Discussion

Tantalum alkoxides have been found to add phenyl or α-naphthylisocyanates yielding mono- to penta-insertion products, $(RO)_{5-n}Ta(-NR'{-}Co{-}OR)_n$, with the cleavage of Ta–O bonds (Table I). Completion of the insertion reaction was indicated by the absence of a band at ~2250–2275 cm^{-1} (due to $\nu N{=}C{=}O$). The appearance of an intense band at ~1710 cm^{-1} (due to $\nu C{=}O$) in the product suggests that insertion has occurred at the C=N site with the formation of N-aryl alkyl carbamate derivatives of tantalum(V).

The reactions were carried out in the presence of a small amount of benzene to maintain homogenity. Insertion reactions with phenylisocyanate shown by the above equation have been found to be instantaneous and exothermic up to the formation of tris-products; the tetra and penta insertions could be completed only under refluxing conditions (~5 hours). It was observed that the rate of the reaction decreases with increasing mass of isocyanates. Thus, insertion reactions with α-naphthylisocyanates are comparatively slow and only mono-insertion products could be obtained in cold. However, the reaction could be forced to completion in this case also under refluxing conditions (~6 hours).

All these products are soluble in benzene but they are immediately hydrolysed by moisture to yield metal free urethanes (R–NH–Co–OR) and hydrated metal oxides.

During these investigations, trimerization of phenylisocyanate was slowly brought about by tantalum isopropoxide at room temperature. For example, when phenylisocyanate (~2 g) was mixed with tantalum alkoxide (0.1 g), a white crystalline solid begins to settle out after about ten days. The analysis of this crystalline solid as well as its m.p. (294 °C) corresponds to $(PhNCO)_3$ [4, 5]. The i.r. spectrum of the trimer displayed a strong amide carbonyl absorption around 1690 cm^{-1} but it did not show any NH band. Crystals of the trimer (triphenylcyanurate) were also formed when the insertion products of tantalum were stored for a few weeks. This behaviour is similar to that observed in case of other metal alkoxides and can be explained on similar lines [4, 5]:

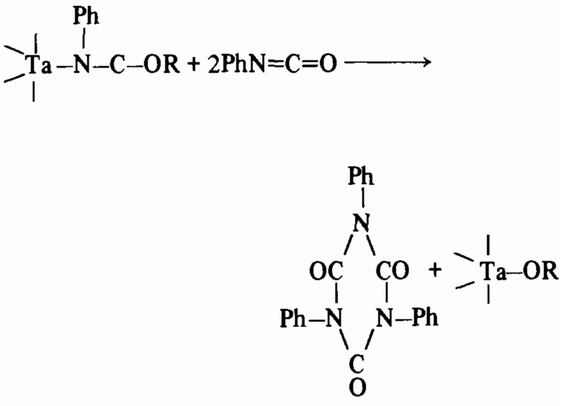

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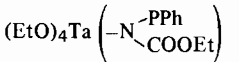
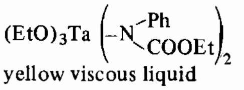
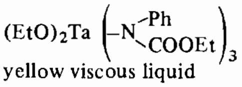
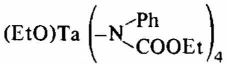
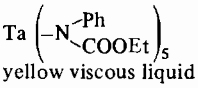
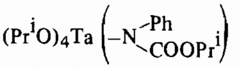
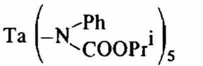
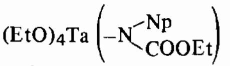
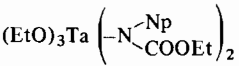
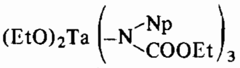
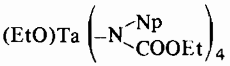
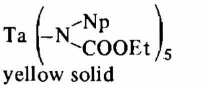
TABLE I. Reactions of Tantalum Alkoxides with Isocyanates.

S.No. I	Reactants II	(g) III	Molar Ratio IV	Yield (g) Found (Calc.) V	Products and Nature VI	B.P. °C/mm (% yield) VII	% Analysis VIII		I.r. Assignments $\nu C{=}O$, cm^{-1} IX
							Ta Found (Calc.)	N Found (Calc.)	
1.	$Ta(EOt)_5$	1.42	1:1	1.82	 $(EtO)_4Ta\left(-N{<}^{PPh}_{COOEt}\right)$	142/.1	33.8	2.4	1715 vs[a]
	PhNCO	0.41		(1.83)	yellow viscous liquid	(50)	(34.4)	(2.7)	
2.	$Ta(OEt)_5$	2.04	1:2	3.20	 $(EtO)_3Ta\left(-N{<}^{Ph}_{COOEt}\right)_2$	decomp.	27.8	4.3	1725 vs
	PhNCO	1.19		(3.23)	yellow viscous liquid		(28.1)	(4.3)	
3.	$Ta(OEt)_5$	1.73	1:3	(3.24)	 $(EtO)_2Ta\left(-N{<}^{Ph}_{COOEt}\right)_3$	decomp.	23.5	5.3	1710 vs[a]
	PhNCO	1.52		(3.25)	yellow viscous liquid		(23.7)	(5.5)	
4.	$Ta(OEt)_5$	1.61	1:4	3.52	 $(EtO)Ta\left(-N{<}^{Ph}_{COOEt}\right)_4$	decomp.	20.5	6.2	1710 vs[a]
	PhNCO	1.93		(3.54)	yellow viscous liquid		(20.5)	(6.3)	
5.	$Ta(OEt)_5$	1.86	1:5	4.56	 $Ta\left(-N{<}^{Ph}_{COOEt}\right)_5$	decomp.	17.6	6.8	1710 vs
	PhNCO	2.72		(4.58)	yellow viscous liquid		(18.0)	(7.0)	
6.	$Ta(OPr^i)_5$	1.03	1:1	1.28	 $(Pr^iO)_4Ta\left(-N{<}^{Ph}_{COOPr^i}\right)$	135/0.4	30.6	2.2	1685 s
	PhNCO	0.26		(1.29)	yellow liquid	(40)	(30.4)	(2.35)	
7.	$Ta(OPr^i)_5$	0.73	1:5	1.62	 $Ta\left(-N{<}^{Ph}_{COOPr^i}\right)_5$	decomp.	16.7	6.2	1710 vs
	PhNCO	0.91		(1.64)	yellow sticky solid		(16.9)	(6.5)	
8.	$Ta(OEt)_5$	4.05	1:1	5.70	 $(EtO)_4Ta\left(-N{<}^{Np}_{COOEt}\right)$	142/0.3	31.0	2.0	1700 vs
	NpNCO	1.68		(5.73)	yellow viscous liquid	(83)	(31.4)	(2.4)	
9.	$Ta(OEt)_5$	2.47	1:2	4.49	 $(EtO)_3Ta\left(-N{<}^{Np}_{COOEt}\right)_2$	decomp.	23.9	3.7	1720 m[a]
	NpNCO	2.06		(4.53)	yellow sticky solid		(24.3)	(3.8)	
10.	$Ta(OEt)_5$	1.23	1:3	2.71	 $(EtO)_2Ta\left(-N{<}^{Np}_{COOEt}\right)_3$	decomp.	19.6	4.5	1730 vs
	NpNCO	1.53		(2.76)	yellow solid		(19.8)	(4.6)	
11.	$Ta(OEt)_5$	0.98	1:4	2.58	 $(EtO)Ta\left(-N{<}^{Np}_{COOEt}\right)_4$	decomp.	16.8	5.0	1725 vs
	NpNCO	1.63		(2.61)	yellow solid		(16.7)	(5.2)	
12.	$Ta(OEt)_5$	0.56	1:5	1.70	 $Ta\left(-N{<}^{Np}_{COOEt}\right)_5$	decomp.	14.2	5.3	1710 s[a]
	NpNCO	1.18		(1.74)	yellow solid		(14.4)	(5.6)	

[a] In nujol, otherwise neat. m = medium, s = strong, vs = very strong.

References

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