## NOTES

### THE PREPARATION OF ALKOXIDES AND TRIETHYLSILANOLATES OF Ti, Zr, V, Nb, Ta, AND Sn FROM THE DIALKYLAMIDES

# I. M. Thomas\*

The chemical properties of the dialkylamides of titanium, zirconium, vanadium, niobium, tantalum, and tin have recently been studied in this laboratory (1), and it has been found that they are very reactive to reagents containing replaceable hydrogen atoms. Besides being extremely sensitive to moisture, they react smoothly and completely with alcohols and triethylsilanol at room temperature in benzene to give the corresponding alkoxides and triethylsilanolates with the liberation of the dialkylamine:

$$\begin{split} \mathrm{M}(\mathrm{NR}_2)_x &+ x\mathrm{R}^1\mathrm{OH} \to \mathrm{M}(\mathrm{OR}^1)_x + x\mathrm{R}_2\mathrm{NH},\\ \mathrm{M}(\mathrm{NR}_2)_x &+ x\mathrm{Et}_3\mathrm{SiOH} \to \mathrm{M}(\mathrm{OSiEt}_3)_x + x\mathrm{R}_2\mathrm{NH}. \end{split}$$

This method has been used by Gilman *et al.* (2) to prepare uranium<sup>IV</sup> tetraalkoxides from tetrakis-diethylamido-uranium<sup>IV</sup>.

Previous methods of preparation of transition metal alkoxides have utilized the metal chloride as starting material, and subsequent side reactions have reduced the yields in many cases. No niobium penta-*t*-alkoxides (3) or vanadium<sup>IV</sup> tetraalkoxides have been reported.

The preparation of trialkylsilanolates from trialkylsilanols is also hindered by the ease with which the trialkylsilanols condense to a disiloxane and water under the influence of acidic or 'Lewis acidic' reagents (4), with subsequent hydrolysis of the product.

The absence of side reactions in this method enables near quantitative yields to be obtained in all cases, and it is particularly suitable for the preparation of all alkoxides of vanadium<sup>IV</sup> and tin, and the tertiary alkoxides of zirconium and niobium.

It should be noted that niobium<sup>IV</sup> tetra-dialkylamides on reaction with alcohols and triethylsilanol give pentavalent derivatives. Repeated attempts to prepare tetraalkoxides were unsuccessful, and it is evident that reduction of the alcohol by Nb<sup>IV</sup> readily takes place even at 0° with subsequent formation of a pentavalent product. However, the comparative stability of vanadium in the tetravalent state enabled substantially pure tetra derivatives to be prepared, from vanadium<sup>IV</sup> tetra-dialkylamides.

#### EXPERIMENTAL

Special precautions, e.g. carefully dried all-glass apparatus, were adapted to avoid hydrolysis, and all experiments were conducted under an atmosphere of dry, oxygen-free nitrogen.

#### Analysis

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Metals, except vanadium, were determined gravimetrically as the ignited oxides (4), and silicon as silica (4). An oxidation method (5) was used for the determination of ethoxy and isopropoxy groups, and basic nitrogen was estimated in a modified Kjeldahl apparatus (1). Estimation of vanadium and valency determination were carried out using a Jones reductor and ceric sulphate solution (6).

The alcohols and benzene were dried azeotropically prior to use.

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The preparations of dialkylamido compounds of titanium, zirconium, and tantalum have been described (1, 7). Those of vanadium and niobium will be reported in another communication. Tetrakis-diethylamido-tin was prepared as described below.

# Preparation of Tetrakis-diethylamido-tin

Stannic chloride (19.0 g) in benzene (50 ml) was added, over 20 minutes, to a stirred solution of lithium diethylamide in ether (300 ml of 1.18 N solution). The mixture was refluxed for 3 hours after the addition and then stirred overnight at room temperature. Evaporation of the solvent under reduced pressure, and distillation of the residue under high vacuum gave tetrakis-diethylamido-tin (8.90 g: 30% yield) as a pale yellow liquid, b.p. 90°/0.1 mm. Found: Sn, 29.1%; N, 13.4%; Cl, zero. Calc. for Sn(NEt<sub>2</sub>)<sub>4</sub>: Sn, 29.1%; N, 13.8%.

Since the technique used in the alcoholysis and silanolysis reactions was essentially the same in each experiment, the details are given for the preparation of zirconium tetrat-butoxide and the other results summarized in Tables I and II.

# TABLE I Preparation of alkoxides

	Dialkylamide		Product			Found (%)		Calc. (%)	
Alkoxide	Туре	Wt. (g)	Wt. (g)	% yield	B.p./mm	М	OR	М	OR
$Ti(OBu^n)_4$	$Ti(NPr_{2}^{n})_{4}$	5.30	3.85	95	140°/0.1	13.9		14.1	
V(OBu <sup>t</sup> ) <sub>4</sub>	$V(NMe_2)_4$	3.10	4.07	87	$55^{\circ}/0.05$	$15.0^{*}$		14.8	
V(OPr <sup>i</sup> ) <sub>4</sub>	$V(NMe_2)_4$	6.65	8.10	98	$55^{\circ}/0.1$ §	17.91	82.6	17.7	82.3
Nb(OBu <sup>‡</sup> ) <sub>5</sub>	$Nb(NEt_2)_4$	1.98	1.76	74	90°/0.1‡	20.4		20.3	
Nb(OPr <sup>i</sup> ) <sub>5</sub>	$Nb(NEt_2)_4$	5.44	3.90	72	80°/0.1‡	24.0	76.6	24.0	-76.0
Ta(OBu <sup>n</sup> ) <sub>5</sub>	$Ta(NPr_2^n)_3NPr^n$	6.44	6.15	98	$210^{\circ}/0.05$	33.0		33.1	—
Ta(OEt) <sub>5</sub>	Ta(NPr2n)3NPrn	4.75	3.16	92	$145^{\circ}/0.05$	44.2	54.6	44.6	55.4
Sn(OPr <sup>4</sup> ) <sub>4</sub>	$Sn(NEt_2)_4$	7.00	4.60	75	$120^{\circ}/0.05$	33.3	66.6	33.4	66.6

\*Valency 4.10, royal blue liquid. †Valency 4.08, dark green solid. ‡Sublimation temperature.

M.p. 40°. Note: All products were analyzed for basic nitrogen content and this was found to be zero in every case. All products, except ose of vanadium, were colorless solids or liquids.

TABLE II Preparation of triethylsilanolates

Trainabart	Dialkylamide		Product			Found (%)		Calc. (%)	
silanolate	Type	Wt. (g)	Wt. (g)	yield	B.p./mm	M	Si	M	Si
Ti(OSiEt <sub>3</sub> ) <sub>4</sub> Zr(OSiEt <sub>3</sub> ) <sub>4</sub> V(OSiEt <sub>3</sub> ) <sub>4</sub> Nb(OSiEt <sub>3</sub> ) <sub>5</sub> Ta(OSiEt <sub>3</sub> ) <sub>5</sub>	$\begin{array}{c} Ti(NEt_2)_4\\ Zr(NEt_2)_4\\ V(NEt_2)_4\\ Nb(NPr_2^n)_4\\ Ta(NEt_2)_3NEt \end{array}$	$\begin{array}{r} 4.95 \\ 4.07 \\ 3.54 \\ 3.78 \\ 4.93 \end{array}$	$7.60 \\ 6.17 \\ 5.53 \\ 5.79 \\ 8.67$	90 93 92 100 95	150°/0.1* 150°/0.1 150°/0.1 	$\begin{array}{r} 8.41 \\ 14.9 \\ 9.10 \\ 12.5 \\ 21.7 \end{array}$	$19.5 \\ 18.1 \\ 19.2 \\ 18.6 \\ 16.9$	$\begin{array}{r} 8.36 \\ 14.8 \\ 8.84 \\ 12.4 \\ 21.6 \end{array}$	$19.6 \\ 18.2 \\ 19.5 \\ 18.7 \\ 16.8$

\*M.p. 110°. †Valency 4.15, blue-green liquid. ‡This product decomposes on sublimation at 210°/0.1 mm.

\$Sublimation temperature. Note: All products, except those of vanadium, were colorless liquids or solids. All products were analyzed for basic nitrogen content, which was found to be zero in every case.

# Preparation of Zirconium Tetra-t-butoxide

t-Butanol (12 ml: ca. 100% excess) was added dropwise to tetrakis-diethylamidozirconium (5.63 g) in benzene (30 ml). An exothermic reaction took place and the solution

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was left at room temperature for 20 minutes after the addition. Evaporation of the solvent under reduced pressure and distillation of the residue under high vacuum gave zirconium tetra-t-butoxide (5.00 g: 88% yield) as a colorless liquid, b.p. 60°/0.1 mm. Found: Zr, 23.7%; N, zero. Calc. for Zr(OBu<sup>1</sup>)<sub>4</sub>: Zr, 23.8%.

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#### THE ACIDITY OF 9-MONOALKYL- (OR ARYL-) FLUORENES

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In a previous publication (1) it was shown that the reaction between equivalent amounts of alkyl halide and 9-fluorenyl-potassium (or -sodium) in ether solvents gave not only the expected 9-monoalkyl fluorene but as much as 35% yield of 9,9-dialkylfluorene. This latter product was considered to occur as result of cross metalation between unreacted 9-fluorenyl-potassium (or -sodium) and the 9-alkylfluorene initially produced. For the 9-alkylfluorene to compete with the alkyl halide for the remaining 9-fluorenylpotassium as successfully as it apparently did, the postulation was made that the C<sub>2</sub>monoalkylated fluorene was at least as acidic as, and probably more acidic than, the parent unsubstituted fluorene. It is known that 9-phenylfluorene is more acidic than is fluorene (2, 3), but that an *alkyl* substituent at C<sub>9</sub> of fluorene should also lead to enhanced acidity of the remaining hydrogen at carbon 9 is unexpected. The explanation given (1) was that of a tendency of the  $C_9$  substituent to become coplanar with the planar fluorene moiety, hence assisting the tendency to rehybridization of carbon 9 from  $sp^3$  to  $sp^2$ , in agreement with the known capability of fluorene for carbanion formation (4). Such coplanarity is quite possible if the carbon atom attached to  $C_9$  of fluorene is methyl or methylene.

Some evidence has now been obtained that certain 9-alkylfluorenes do in fact possess somewhat greater acidity than that of the parent fluorene. Several reports concerning nuclear magnetic resonance studies show that the chemical shift observed for the proton signal is related to the electronic environment and hence the acidity of the proton (5, 6). Accordingly an examination was made of the N.M.R. spectra of fluorene, 9-benzylfluorene, 9-methylfluorene, and 9-phenylfluorene in chloroform solution. The position of the  $C_9$  proton signal, referred to the proton signal of the solvent, is shown for each of these compounds.

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