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ATRANES

VII. 1-Oxovanadatranes*

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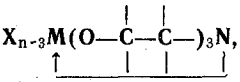
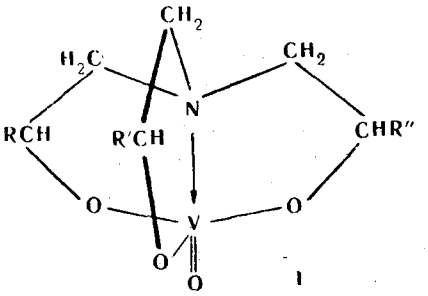
Methods of synthesizing hitherto unknown 1-oxovanadatranes (intracomplex orthovanadic esters of triethanolamine and its derivatives) are worked out. They are based on the reaction trialkanolamines with vanadium pentoxide, metavanadic acid, ammonium vanadate, or trialkylorthovanadates. Five such compounds are prepared, their molecular weights determined, and some of their physical properties described.

Intracomplex cyclic inorganic esters and alkoxides of the trialkanolamine type



where M is an atom of an element of valence 3 or over, with an incomplete p or d electron shell, and X is a univalent substituent, have been named atranes [1-5]. At present, atranes are known with M = B [6-9], Al [10], Si [1-5], Ti [11-13], Zr [14-15], Bi, Fe.**



The present paper describes methods for synthesizing new members of the atranes class, namely tri-N-alkanolaminoorthovanadates or 1-oxovanadatranes (I), where R, R', and R" = H, a hydrocarbon group, or other substituent. We have developed four methods for synthesizing I [16], based on reaction of trialkanolamines II with vanadium pentoxide (1), metavanadic acid (2), ammonium metavanadate (3), and trialkyl or orthovanadates (4):

$$2\ \mathrm{II} + \mathrm{V_2O_5} \rightarrow 2\ \mathrm{I} + 3\mathrm{H_2O} \quad (1)$$

$$\mathrm{II} + \mathrm{HVO_3} \rightarrow \mathrm{I} + 2\mathrm{H_2O} \quad (2)$$

$$\mathrm{II} + \mathrm{NH_4VO_3} \rightarrow \mathrm{I} + 2\mathrm{H_2O} + \mathrm{NH_3} \quad (3)$$

$$\mathrm{II} + \mathrm{OV(OR'''')_3} \rightarrow \mathrm{I} + 3\mathrm{R''''OH}\ (\mathrm{R''''} = \text{alkyl}) \quad (4)$$

In the first three cases, synthesis is effected by heating the mixed reactants together in a suitable inert solvent (benzene). The water formed in the reaction is removed by continuous azeotropic distillation with the same solvent, and the reaction can be followed by the volume of water evolved. Reaction of trialkanolamines with trialkylorthovanadates (4) takes place readily even at room temperature (preferably in a suitable solvent), being completed almost as soon as the components are mixed. It is then precipitated in almost quantitative yield*** in a crystalline state.

*For Part VI see [1].

**References given only to papers not mentioned in [2, 4].

***The reaction between trialkylorthovanadates and ethanolamine proceeds similarly.

Compound no.	R	R′	R″	Mp, ° C (decomp)	Recrystallization solvent	M Found	M Calculated	Formula	Found, % C	Found, % H	Found, % N	Found, % V	Calculated, % C	Calculated, % H	Calculated, % N	Calculated, % V	Yield, % (1)	Yield, % (2)	Yield, % (3)	Yield, % (4)
III	H	H	H	255—260*	p-C_4H_9OH	—	213	$C_6H_{12}NO_4V$	33.84	5.85	6.54	23.50	33.80	5.63	6.57	23.94	30	96	68	100
IV	CH_3	H	H	235	CH_3OH	209; 213	227	$C_7H_{14}NO_4V$	36.82	5.84	5.88	22.18	37.00	6.16	6.16	22.45	33	85	64	99
V	CH_3	CH_3	H	239	C_6H_6	231; 235	241	$C_8H_{16}NO_4V$	40.40	6.71	5.65	20.70	39.83	6.63	5.81	21.66	45	70	70	98
VI	CH_3	CH_3	CH_3	247—248	C_6H_6, C_2H_5OH	249; 246	255	$C_9H_{18}NO_4V$	41.64	6.84	6.08	20.01	42.35	7.05	5.49	20.00	27	94	65	95
VII	$ClCH_2$	H	H	179—180	CH_3OH	—	261.5	$C_7H_{13}NO_4Cl$**, V	31.88	5.03	5.78	19.65	32.12	4.97	5.35	19.54	—	—	—	98

* Decomposition temperature

** Found: Cl 13.37%. Calculated: Cl 13.57%.

There are considerable advantages of this latter method over the others, i.e., the very high reaction rate, the absence of side products and of any need to heat the reaction mixture, and the possibility of using thermally unstable trialkanolamines, or of synthesizing thermolabile I compounds. Instead of trialkanolamines, it is possible to use directly the products of reaction of organic α-oxides with mono- or dialkanolamines, or ammonia, without separation from the corresponding trialkanolamines. The starting trialkylorthovanadates are easily obtained by treating the appropriate alcohols with vanadium pentoxide [17–18], metavanadic acid, ammonium metavanadate [19], or $VOCl_3$ [20].

The table gives yields of I, obtained by the above methods, melting points, solubilities, analytical data, and molecular weights found. All the compounds synthesized were greenish white or white solids, forming beautiful crystals of different forms, and with rather sharp melting points. The exception was the 1-oxovanadatrane III sparingly soluble in all organic solvents, and decomposing without melting at 260° C. All the compounds I were readily soluble in water, did not undergo change on keeping [with the exception of 1-oxo-3-(chloromethyl) vanadatrane], and were quite thermostable.

Some of the compounds I (e.g., 1-oxo-3,7-dimethylvanadatrane, 1-oxo-3,7-10-trimethylvanadatrane) can be mixtures of stereoisomers, but it was not possible to separate the individual components.

Cryoscopic determination of the molecular weight of I in nitrobenzene or benzene shows them to be monomolecular (see table). This, equally with the physical and chemical properties of these compounds synthesized, affords a basis for giving them the formula I. The presence of an intramolecular coordination link in I, between nitrogen and vanadium, is indicated by their relatively high stability in comparison with trialkylorthovanadates, the similarity to the corresponding silicon and boron compounds, the high dipole moments (7–8D), and the lack of appreciably manifest donor properties in the case of the nitrogen atom (I, for example, does not form ammonium derivatives with MeI).

The results of study of reactivity, data obtained by investigating I using molecular spectroscopy and radio spectroscopy, as well as by use of other physical methods (determination of dipole moment, magnetic susceptibility, etc), will be given in later papers.

Experimental

Vanadium pentoxide, ammonium metavanadate, and triethanolamine. These were commercially available CP products.

Methyl-substituted triethanolamines. Prepared by reacting propylene oxide with ammonia, ethanolamine, or diethanolamine, and were purified by vacuum-distillation.

Metavanadic acid. 20 g (0.17 mole) ammonium metavanadate was dissolved in a hot solution of 8 g (0.5 mole) NaOH in 240 ml water. After filtering, concentrated HCl was added to the hot solution until it became acid. The precipitate was then filtered off with suction, and vacuum-dried, yield 8 g (47%).

Tri-n-amylorthovanadate. A flask was fitted with a trap for separating off water and a reflux condenser, then charged with 70.2 g (0.6 mole) ammonium metavanadate and 600 ml n-

AmOH. The reaction mixture was boiled until water ceased to separate, then filtered.* Excess AmOH was distilled off under reduced pressure. Yield of tri-n-amylorthovanadate 135 g (68%), 176° C (7 mm), d_4^{20} 1.005; n_D^{20} 1.4867.

1-Oxovanadatrane (III). A round bottom flask was fitted with a water-separating trap and reflux condenser, then charged with 7.5 g (0.05 mole) triethanolamine, 4.5 g (0.025 mole) V_2O_5, 0.1 g powdered KOH as catalyst, and 200 ml benzene. The whole was boiled till separation of water ceased, time required 6–8 hr.

The solid precipitate (a mixture of III, unreacted V_2O_5 and its partial reduction products) was filtered off, and extracted with 500 ml boiling n-BuOH (other higher alcohols or dioxane could be used as the solvent). On cooling, the solution deposited 3.4 g (32%) III, as greenish white crystals, which decomposed without melting at 255°–260° C.

1-Oxo-3-methylvanadatrane (IV). A mixture of 8.1 g (0.05 mole) diethanolisopropanolamine, 5.85 g (0.05 mole) ammonium metavanadate, and 200 ml benzene were heated together as described above, for 6–8 hr. After water had ceased to separate out in the trap, 200 ml benzene was added, and unreacted ammonium metavanadate filtered off. The IV formed on cooling, the solution was filtered off, and recrystallized from MeOH, yield 7.2 g (64.2%), white crystals mp 235° C (decomp).

1-Oxo-3,7-10-trimethylvanadatrane (VI). A mixture of 9.5 g (0.05 mole) triisopropanolamine, 5.0 g (0.05 mole) metavanadic acid, and 200 ml benzene was refluxed together until water ceased to separate out in the water-separating trap. Then 300 ml benzene was added, the whole filtered after heating to boiling, and the crystals of VI filtered off using suction, and washed with MeOH, yield 10.1 g (85%), mp 246°–248° C.

1-Oxo-3-(chloromethyl) vanadatrane (VII). 10.5 g (0.1 mole) diethanolamine was dissolved in 300 ml $CHCl_3$, and with cooling a solution of 9.3 g (0.1 mole) epichlorohydrin in 50 ml $CHCl_3$ added. The mixture was left at room temperature for 24 hr, then 32.8 g (0.1 mole) tri-n-amylorthovanadate added with stirring. After a few minutes, crystals of VII separated, and these were filtered off with suction, washed with EtOH, and vacuum-dried, yield 24.0 g (92.5%, based on the epichlorohydrin taken), mp 179°–180° C (decomp).

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*The resultant solution of tri-n-amylorthovanadate could successfully be used as it was for synthesizing I.