ATRANES

XII. 1-Hydroxy-1-Oxomolybdatranes*

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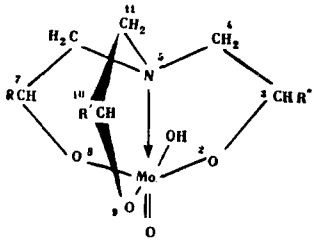
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 3, No. 3, pp. 561–563, 1967

UDC 547.89+546.776

Methods of synthesizing hitherto unknown 1-hydroxy-1-oxomolybdatranes, are developed. They are based on the reactions of trialkanolamines with molybdenum trioxide, meta- or orthomolybdic acids, or ammonium molybdate. Four compounds of this kind are characterized, $HO(O=)\overset{\downarrow}{Mo}(OCH_2CH_2)_3N$, and its 3-methyl, 3,7-dimethyl, and 3,7,10-trimethyl derivatives.

This communication describes methods of synthesizing new representatives of the metalloatranes class, 1-hydroxy-1-oxomolybdatranes I, of the following structure:



(R,R′,R″=H, alkyl)

They are based on reacting molybdenum trioxide, meta- or orthomolybdic acid, or ammonium molybdate, with the appropriate trialkanolamines $HOCH_2CHRN(CHR'CH_2OH)CHR''CH_2OH$ (II), the equations being:

$$MoO_3 + II \rightleftarrows I + H_2O \quad (1)$$

$$(HO)_2MoO_2 + II \rightleftarrows I + 2H_2O \quad (2)$$

$$(HO)_4MoO + II \rightleftarrows I + 3H_2O \quad (3)$$

$$(NH_4)_2MoO_4 + II \rightleftarrows I + 2H_2O + 2NH_3 \quad (4)$$

In all cases synthesis was effected by continuous azeotropic distillation, the water formed by reaction of the reagents being distilled off with the solvent. The yield of I is a maximum when ammonium molybdate is used, i. e. when using reaction 4. The I compounds synthesized by these routes are stable white crystalline compounds, only slightly soluble in organic solvents, readily soluble in water. The table gives yields, melting points, solubilities and analytical data.

From the results of investigations of IR and PMR spectra, and other physical properties, to be published separately, as well as analytical results, the compounds have the structure I.

The poor solubilities of I in the usual organic solvents made it impossible to determine the molecular weights and dipole moments.

IR spectra confirm that I contains OH. These spectra generally resemble those of 1-oxovanadatranes [2, 3], but differ from them by an absorption in the 3560 cm^{-1} region. However, it did not prove possible to prove the presence of active hydrogen in I by reaction with MeMgI (Chugaev-Zerewitinoff), obviously because of the basic nature of the hydroxyl.

The toxicities of the I compounds were low, and were about 300 mg/kg (for white mice).

EXPERIMENTAL

Starting reagents:

Molybdenum trioxide, ammonium molybdate, and triethanolamine. These were commercial C. P. reagents.

Orthomolybdic acid (metamolybdic acid hydrate) was prepared as described in [4].

Methyl-substituted triethanolamines were synthesized by the action of propene oxide on ammonia, ethanolamine, and diethylanolamine, and purified by vacuum-distillation.

1-Hydroxy-1-oxomolybdatrane (III). An r.b. flask, fitted with a Dean and Stark apparatus and a reflux condenser, was charged with 7.45 g (0.05 mole) triethanolamine, 9.8 g (0.05 mole) ammonium molybdate, and 200 ml benzene. The mixture was boiled vigorously, until water ceased to appear in the trap, which required 6–8 hr. The precipitate (a mixture of III, unreacted ammonium molybdate, and its decomposition products) was filtered off, dried, and recrystallized from dimethylformamide. Yield of recrystallized III 10.9 g (81%).

1-Hydroxy-1-oxo-3-methylmolybdatrane (IV). A mixture of 8.1 g (0.05 mole) diethanolisopropanolamine, 7.2 g (0.05 mole) molybdic anhydride, and 200 ml benzene was boiled as described above, for 6–8 hr. The solid was filtered off with suction, dried, and recrystallized from EtOH. Yield of recrystallized IV 4.3 g (30%).

1-Hydroxy-1-oxo-3,7-dimethylmolybdatrane (V). A mixture of 8.7 g (0.05 mole) ethanoldiisopropanolamine, 9.0 g (0.05 mole) orthomolybdic acid and 200 ml benzene was boiled as described above for 6 hr. The solid was filtered off with suction, dried, and recrystallized from a large volume of EtOH. Yield of V, mp 226° C (decomp), 6.1 g (40.7%).

*For Part XI see [1].

1-Hydroxy-1-oxomolybdatranes (I)

Compound	R	R′	R″	Mp, ° C (decomp)	Solvent for recrystallization	Formula	Found, %				Calculated, %				Yield, %*		
							C	H	N	Mo	C	H	N	Mo	(1)	(3)	(4)
III	H	H	H	—	Dimethyl-formamide	$C_6H_{13}NMoO_5$	26.11	4.96	5.15	34.30	26.18	4.87	5.09	34.90	25	38	81
IV	CH_3	H	H	223—224	$CHCl_3$, C_2H_5OH	$C_7H_{15}NMoO_5$	28.97	5.22	4.94	33.05	29.06	5.19	4.86	33.22	30	37	85
V	CH_3	CH_3	H	226—227	$CHCl_3$, C_2H_5OH	$C_8H_{17}NMoO_5$	31.88	5.73	4.52	31.96	31.68	5.61	4.62	31.68	31	40.7	84
VI	CH_3	CH_3	CH_3	235	$CHCl_3$, C_2H_5OH	$C_9H_{19}NMoO_5$	34.11	6.08	4.40	30.22	34.07	6.01	4.41	30.28	29	42.5	83

*The figures in parentheses represent the equation of the method of preparation used.

REFERENCES

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26 October 1965

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