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Glycollates of Samarium
Reactions of Samarium Isopropoxide with Glycols

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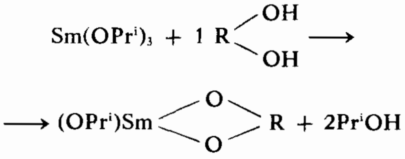
The reactions of samarium isopropoxide with glycols e.g., ethylene glycol (ethane 1,2-diol) propylene glycol (propane 1,3-diol), 1 methyl trimethylene glycol (butane 1,3-diol), 1,2 dimethyl ethylene glycol (butane 2,3-diol), hexylene glycol (2 methyl pentane 2,4-diol), neopentyl glycol, and pinacol 2,3 dimethyl butane 2,3-diol) in equimolecular ratios have been carried out in benzene. All these glycollates are either faint yellow or light brown non volatile solids, sparingly or insoluble in benzene. The reactions are spontaneous and the products are separated from the reaction mixture even on shaking. The only appreciably soluble derivatives being those of hexylene glycol and pinacol.

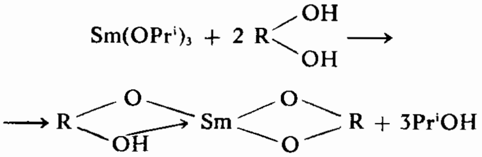
Introduction

A considerable amount of work has been published on the preparation and properties of the glycol derivatives of aluminium,[1] boron,[2] silicon,[3] germanium,[4] niobium[5] and tantalum.[6,7] A survey of the literature reveals that no work on the glycol derivatives of samarium has been carried out. It was, therefore, considered of interest to synthesise the glycol derivatives of samarium.

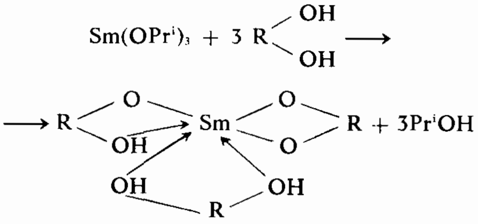
The reactions of samarium isopropoxide with different glycols (e.g., ethane diol, 1,3 propone diol, 1,3 and 2,3 butane diols, hexylene glycol, pinacol, and neopentyl glycol) in different molar ratios have been carried out in benzene medium. On the basis of the analytical results of the products obtained, these reactions can be represented by the following equations:



(1)



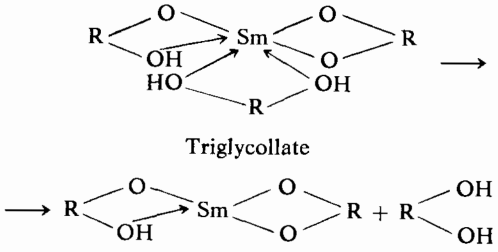
(2)



(3)

All these derivatives are yellow, faint yellow or light brown non volatile powdered solids, insoluble in benzene.

It has been observed that the hexylene glycol and pinacol derivatives exhibit the tendency to form soluble products. Moreover, the solubility of these derivatives also decrease as the concentration of these glycols increase. The fact that the third glycol molecule has entered in some sort of loose combination, as represented in the equation 3 above, is demonstrated by the fact that when these derivatives were washed with benzene and again dried, they lose their addition molecule of glycol forming the corresponding diglycollates:



Triglycollate

Diglycollate Glycol

The insoluble nature of most of these glycol derivatives suggest that samarium has achieved high coordination number in these compounds and that these derivatives are polymeric. It is due to their insoluble nature that the studies regarding the determination of their molecular weight could not be carried out.

The typical behaviour of pinacol and hexylene glycol derivatives of samarium finds parallelism with aluminium and titanium but nothing definitive can be concluded except the presence of two methyl group on one of the £-carbon atom, which can bring about this difference.

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(2) R. C. Mehrotra and G. Srivastava, *J. Chem. Soc.*, *1032*, 3819 (1962).
(3) R. C. Mehrotra and B. C. Pant., *J. Ind. Chem. Soc.*, *41*, 563 (1964).
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(6) R. C. Mehrotra and P. N. Kapoor, *J. Less Common Metals*, *10*, 237 (1966).
(7) R. N. Kapoor, S. Prakash and P. N. Kapoor, *Z. für Anorg. Allgem. Chemie* (In press).

Table I. Monoglycollates of samarium. Reactions of samarium isopropoxide with glycols in benzene (molar ratio 1 : 1)

Samarium iso-propoxide (g)	Glycols (g)	Products and state (g)	Amount of alcohol in the azeotrope (g) Found	Calc.	Analysis Found Sm %	Found Glycoxy %	Found Alkoxy %	Calculated Sm %	Calculated Glycoxy %	Calculated Alkoxy %
1.749 g	Ethane diol	$(OPr^i)Sm(C_2H_4O_2)$								
	(0.332 g)	faint yellow powder (1.72 g)	0.627	0.641	56.11	22.88	—	55.75	22.35	—
1.591 g	Propane 1,3-diol	$(OPr^i)Sm(C_3H_6O_2)$								
	(0.582 g)	faint yellow powder (1.65 g)	0.589	0.584	54.01	—	20.70	53.06	—	20.82
1.478 g	Butane 1,3-diol	$(OPr^i)Sm(C_4H_8O_2)$								
	(0.411 g)	light brown powder (1.69 g)	0.552	0.546	50.70	—	19.22	50.55	—	19.84
1.353 g	Butane 2,3-diol	$(OPr^i)Sm(C_4H_8O_2)$								
	(0.381 g)	faint yellow powder (1.42 g)	0.490	0.496	49.61	29.26	—	50.55	29.59	—
1.608 g	Neopentyl glycol	$(OPr^i)Sm(C_5H_{10}O_2)$								
	(0.511 g)	faint yellow powder (1.73 g)	0.599	0.590	48.90	—	17.69	48.29	—	18.94
1.661 g	Pinacol	$(OPr^i)Sm(C_6H_{12}O_2)$								
	(0.612 g)	light brown powder (1.79 g)	0.682	0.690	46.97	35.07	—	46.18	35.65	—
1.610 g	Hexylene glycol	$(OPr^i)Sm(C_6H_{12}O_2)$								
	(0.599 g)	light brown powder (1.80 g)	0.611	0.590	46.11	—	17.98	46.18	—	18.13

Table II. Diglycollates of samarium. Reactions of samarium isopropoxide with glycols in benzene (molar ratio 1 : 2)

Samarium iso-propoxide (g)	Glycols (g)	Products and state (g)	Amount of alcohol in the azeotrope (g) Found	Calc.	Analysis Found Sm %	Found Glycoxy %	Calculated Sm %	Calculated Glycoxy %
1.983 g	Ethane diol	$(C_2H_5O_2)Sm(C_2H_4O_2)$						
	(0.736 g)	faint yellow powder (1.98 g)	1.012	1.091	55.04	44.12	55.40	44.60
1.643 g	Propane 1,3-diol	$(C_3H_7C_2)Sm(C_3H_6O_2)$						
	(1.199 g)	light brown powder (1.77 g)	0.892	0.903	49.98	—	50.19	—
1.640 g	Butane 1,3-diol	$(C_4H_9O_2)Sm(C_4H_8O_2)$						
	(0.999 g)	light brown powder (1.79 g)	0.874	0.902	46.30	—	45.91	—
1.212 g	Butane 2,3-diol	$(C_4H_9O_2)Sm(C_4H_8O_2)$						
	(0.677 g)	faint yellow powder (1.28 g)	0.654	0.666	44.53	54.62	45.91	54.09
1.262 g	Neopentyl glycol	$(C_5H_{11}O_2)Sm(C_5H_{10}O_2)$						
	(0.802 g)	faint yellow powder (1.29 g)	0.708	0.694	42.90	—	42.32	—
1.722 g	Pinacol	$(C_6H_{13}O_2)Sm(C_6H_{12}O_2)$						
	(1.252 g)	light brown powder (1.84 g)	0.906	0.947	38.11	59.47	39.23	60.77
1.441 g	Hexylene glycol	$(C_6H_{13}O_2)Sm(C_6H_{12}O_2)$						
	(1.082 g)	brown powder (1.60 g)	0.782	0.792	40.80	—	39.23	—

Table III. Reactions of samarium isopropoxide with glycols in benzene (molar ratio 1 : 3)

Samarium iso-propoxide (g)	Glycols (g)	Products and state (g)	Amount of alcohol in the azeotrope (g) Found	Calc.	Analysis Found Sm %	Found Glycoxy %	Calculated Sm %	Calculated Glycoxy %
1.534 g	Ethane diol	$(C_4H_{11}C_4)Sm(C_2H_4O_2)$						
	(0.882 g)	faint yellow powder (1.61 g)	0.856	0.843	45.07	55.16	45.10	54.90
1.630 g	Propane 1,3-diol	$(C_6H_{15}O_4)Sm(C_3H_6O_2)$						
	(1.826 g)	light brown powder (1.70 g)	0.854	0.896	39.92	—	40.03	—
1.625 g	Butane 2,3-diol	$(C_8H_{19}O_4)Sm(C_4H_8O_2)$						
	(1.356 g)	faint yellow powder (1.75 g)	0.890	0.894	35.26	63.02	36.01	66.99
1.080 g	Neopentyl glycol	$(C_{10}H_{23}O_4)Sm(C_5H_{10}O_2)$						
	(1.026 g)	faint yellow powder (1.15 g)	0.590	0.592	32.00	—	32.74	—
1.553 g	Pinacol	$(C_{12}H_{27}O_4)Sm(C_6H_{12}O_2)$						
	(1.684 g)	light brown powder (1.73 g)	0.822	0.854	28.25	69.84	29.96	70.04
1.439 g	Hexylene glycol	$(C_{12}H_{27}O_4)Sm(C_6H_{12}O_2)$						
	(1.278 g)	light brown powder (1.59 g)	0.801	0.792	29.21	—	29.96	—

Experimental Section

Samarium isopropoxide used in these reactions was prepared fro samarium chloride by sodium alkoxide method.[8] Rest of the experimental procedure was same as described in the previous published work.[9] Glycols were purified by careful fractionation and the middle fraction boiling within ±0.5°C was used. Propane 1,3 diol was distilled under reduced pressure (109°C / 0.2 mm). Glycoxy groups in some of the products

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(9) B. S. Sankhla and R. N. Kapoor, *J. Less Common Metals*, *10*, 116 (1965).

were estimated with sodium periodate by Malaprade method.[10] Isopropoxy groups were estimated by estimating isopropyl alcohol in the ternary azeotrope (benzene-water-isopropanol) by oxidation with Normal chromic acid in 12.5% H_2SO_4.[11] Glycoxy groups in the pinacol derivatives were also estimated by the same method.[11]

Reactions

Reactions of samarium isopropoxide with butane 2,3-diol in benzene (molar ratio 1:1). Butane 2,3-diol (0.381 g) was admitted to a benzene solution of samarium isopropoxide (1.353 g). On shaking the reaction mixture for some time the precipitation of the products took place slowly. After refluxing the reaction mixture for about 5 hours, the binary azeotrope of benzene isopropyl alcohol was fractionated out carefully. On removing the excess solvent by distillation and drying the compound under reduced pressure (50°C/0,3 mm) a faint yellow powder was obtained. Yield (1.42 g). Found : Amount of alcohol in azeotrope 0.490 g; replacement of two moles require 0.496 g, Sm: 49.61% and glycoxy: 29.3%. Calc. for $Sm(OPr^i)(C_4H_8O_2)$; Sm: 50.55% and glycoxy: 29.59%.

Other reactions with different glycols forming mono-, di-, and tri- glycollates are given in Table No. I, II and III respectively.

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(11) D. C. Bradley, F. M. El-Halim and W. Wardlaw, *J. Chem. Soc.,* 3450 (1950).