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Zirconium Glycoxides

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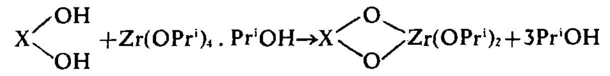
Reactions between zirconium isopropoxide and various glycols in different stoichiometric ratios have led to the synthesis of a series of alkylenedioxy diisopropoxide, bis-alkylene-dioxy as well as tris derivatives of zirconium. The molecular complexities of some soluble glycoxides have been determined in boiling benzene and infra-red studeis have also been made.

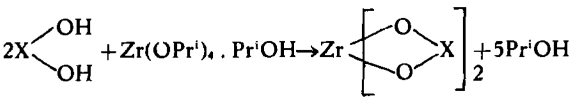
Introduction

A considerable amount of work has been carried out on alkoxides and allied derivatives of zirconium.[1] However, except for some work on catecholates[2,3] of zirconium in the aqueous medium and reported synthesis of hexylene glycoxide by Puri,[4] no systematic study appears to have been made of the derivatives of zirconium with glycols.

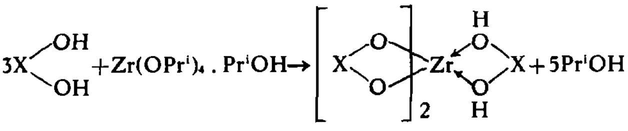
In view of above, it was considered of interest to study in detail the reactions of zirconium isopropoxide, $Zr(OPr^i)_4 . Pr^iOH$, with various glycols. The reactions are carried out in molar ratios 1:1, 1:2, and 1:3 and can be represented by the following equations:



I

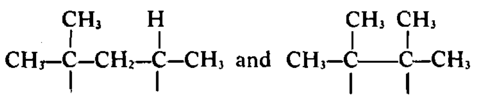


II



III

where X = $-CH_2-CH_2-$, $-CH_2-(CH_2)_3-CH_2-$, $-CH_2(CH_2)_6-CH_2-$, $CH_3-CH-CH-CH_3$,



$CH_3-C(CH_3)(-)-CH_2-C(H)(-)-CH_3$ and $CH_3-C(CH_3)(-)-C(CH_3)(-)-CH_3$

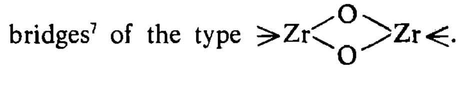
The isopropanol liberated during the reactions was fractionated out azeotropically with benzene and the progress of the reaction was followed by estimating the quantity of isopropanol in the azeotrope.

Results and Discussion

The mono-glycoxide derivatives (I) of ethane 1,2 diol, butane 2,3 diol, 2-methyl pentane 2,4 diol (hexylene glycol) and 2,3 dimethyl butane 2,3 diol (pinacol) are found to be soluble in benzene where as similar other derivatives found to be sparingly soluble. Ethane 1,2 diol and butane 2,3 diol derivatives show the molecular complexities of about nine whereas similar derivative of hexylene glycol show the value of seven only in boiling benzene. The pinacol derivative show little tendency of polymerisation. It is difficult to say about the arrangement of isopropoxide and glycoxide groups in polymeric derivatives even from infra-red studies. The bridged and terminal isopropoxide groups show absorption bands in the region of 960-1050 cm^{-1} and 1070-1150 cm^{-1} respectively. The absorption bands due to $\nu(C-H)$, $\nu(C-O)$, $\delta(CH_3)$, and ρCH_3 are also present in the same region.

The diglycoxide derivatives (II) of all the above glycols are insoluble in common organic solvents and are generally white solids.

The triglycoxide derivatives (III) of butane 2,3 diol, hexylene glycol and pinacol are white solids and readily soluble in benzene except that of ethane 1,2 diol which is sparingly soluble. The derivatives are confirmed on the basis of elemental analysis, nature of the product, thermal stability and molecular weight measurements. These derivatives are found to be monomeric in boiling benzene and are quite stable upto about 120° under reduced pressure and lose the attached glycol molecule when heated above this temperature. The end product, so obtained correspond in analysis and behaviour to diglycoxide derivatives (II). Similar triglycoxide derivatives of titanium[5] and aluminium[6] have also been reported by Mehrotra and coworkers.

Zirconium alkoxides have been shown to be associated through bridges[7] of the type .

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[1] R.C. Mehrotra, *Inorg. Chim. Acta Reviews, 1,* 99(1967).
[2] A. Rosenheim, R. Schnabel and R. Bilecki, *Ber. 48,* 447(1915).
[3] A. Rosenheim, B. Raibmann and G. Schendel, *Z. Anorg. Allgem. Chem., 196,* 160 (1931).
[4] D.M. Puri, *J. Ind. Chem. Soc., 47,* 535 (1970).
[5] R.C. Mehrotra and D.M. Puri, *Ind. J. Chem., 5,* 448 (1967).
[6] R.C. Mehrotra and R.K. Mehrotra, *J. Ind. Chem. Soc., 39,* 635 (1962).
[7] S.A. Imam, *Nature, 206,* 1146 (1965).

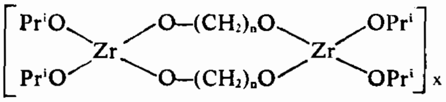
Table .I Reactions of Zr $(OPr^i)_4 . Pr^iOH$ with glycols in benzene.

S.N.	Reactions (g)	Molar ratio	Product, Yield (g) and state	Amount of Pr^iOH(g) in azeotrope. Found.	Calc.	Zirconium Found.	Calc.	Molecular weight Found.	Calc.
1.	$Zr(OPr^i)_4 . Pr^iOH$, 4.73 Ethane 1,2 diol, 0.75	1:1	$Zr(OPr^i)_2(O_2C_2H_4)$* 2.40, white foamy solid soluble	2.06	2.19	33.13	33.84	2601	269
2.	$Zr(OPr^i)_4 . Pr^iOH$, 5.13 Butane 1,4 diol, 1.19	1:1	$Zr(OPr^i)_2(O_2C_4H_8)$ 3,1, soluble, white powder: insoluble portion, found: Zr=33.0%	2.35	2.38	31.06	30.66	—	—
3.	$Zr(OPr^i)_4 . Pr^iOH$, 5.13 pentane 1,5 diol, 1.37	1:1	$Zr(OPr^i)_2(O_2C_5H_{10})$ 3.3, white powder, soluble; insoluble portion 0.7, found: Zr=29.74%	2.38	2.38	28.81	29.28	—	—
4.	$Zr(OPr^i)_4 . Pr^iOH$, 4.76 Decane, 1,10 diol, 2.14	1:1	$Zr(OPr^i)_2(O_2C_{10}H_{20})$ 4.2. white powder, insoluble	2.18	2.20	23.72	23.91	—	—
5.	$Zr(OPr^i)_4 . Pr^iOH$, 2.29 Butane 2,3 diol, 0.53	1:1	$Zr(OPr^i)_2(O_2C_4H_8)$ 1.60, white foamy solid, soluble	1.07	1.07	31.41	30.65	23.62	207
6.	$Zr(OPr^i)_4 . Pr^iOH$, 2.79 2,Methyl pentane 2,4 diol, 0.86	1:1	$Zr(OPr^i)_2(O_2C_6H_{12})$ 2.46, white pasty, soluble	1.29	1.29	28.76	28.01	2329	325
7.	$Zr(OPr^i)_4 . Pr^iOH$, 2.69 2,3 Dimethyl butane 2,3 diol, 0.8	1:1	$Zr(OPr^i)_2(O_2C_6H_{12})$ 2.0, white foamy powder, soluble	1.17	1.23	28.74	28.01	437	325
8.	$Zr(OPr^i)_4 . Pr^iOH$, 3.01 Ethane 1,2 diol, 0.97	1:2	$Zr(O_2C_2H_4)_2$, 1.6 white powder, insoluble	2.18	2.23	41.77	43.15	—	—
9.	$Zr(OPr^i)_4 . Pr^iOH$, 2.64 Butane 2,3 diol, 1.22	1:2	$Zr(O_2C_4H_8)_2$, 1.89 Light Brown powder insoluble	1.99	2.04	33.60	34.07	—	—
10.	$Zr(OPr^i)_4 . Pr^iOH$, 2.89 2-Methyl pentane, 2,4 diol, 1.76	1:2	$Zr(O_2C_6H_{12})_2$, 2.53 white powder, insoluble sublimes at 270-280°/0.3-1.5 mm in about 20% yield	2.12	2.24	28.20	28.18	—	—
11.	$Zr(OPr^i)_4 . Pr^iOH$, 2.56 2,3 Dimethyl butane 2,3 diol, 1.57	1:2	$Zr(O_2C_6H_{12})^*{}_2$, 2.36 white powder, insoluble sublimes at 200-220°C/0.6-1.0 mm in about 20% yield.	1.98	1.98	26.73	28.18	—	—
12.	$Zr(OPr^i)_4 . Pr^iOH$, 2.94 Ethane 1,2 diol, 1.41	1:3	$Zr(O_2C_2H_4)_2(H_2O_2C_2H_4)$ 2.2, white powder, insoluble	2.17	2.27	32.30	33.30	—	—
13.	$Zr(OPr^i)_4 . Pr^iOH$, 3.03 Butane 2,3 diol, 2.11	1:3	$Zr(O_2C_4H_8)_2(H_2O_2C_4H_8)$ 2.99, white powder, soluble	2.20	2.34	25.31	25.50	485	357
14.	$Zr(OPr^i)_4 . Pr^iOH$, 3.85 2-Methyl pentane 2,4 diol 3.53	1:3	$Zr(O_2C_6H_{12})_2(H_2O_2C_6H_{12})$ 4.39, white powder soluble	2.90	2.98	20.27	20.64	432	441
15.	$Zr(OPr^i)_4 . Pr^iOH$, 3.02 2,3 Dimethyl butane 2,3 diol, 2.76	1:3	$Zr(O_2C_6H_{12})(H_2O_2C_6H_{12})$* 3.3 white powder soluble	2.20	2.20	20.01	20.64	420	441

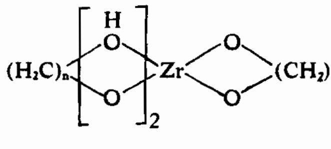
* *Glycoxy content;* Found (Calc.): 1-22.24 (22.29%); 11-73.61 (71.82%); 15-79.86 (79.36%).

The degree of association appears, to be decrease with the nature of alkoxide group,[8-9] being about 4 (when ROH is a primary alcohol), 2-3 when ROH is a secondary alcohol) and 1 (when ROH is a tertiary alcohol).

Glycoxide derivatives of a number of metals[5,6] (Ti, Al, etc.) have been found to show much higher degrees of association and lower solubility compared to alkoxides. The lower solubility could be understood on the basis of chelating tendency of these ligands. However, chelation would not occur with facility in derivatives of long chain glycols like, 1,10 decane diol. It, therefore appears that higher polymerisation in these derivatives occurs through intermolecular bonds of the type also:



Replacement of terminal isopropoxides by glycoxide groups would lead to greater polymerisation and hence lower solubility. 1:3 products are soluble and essentially monomeric indicating simple structures of the type:



As this is the only plausible structure for these 1:3 products, the assumption that lower solubility of 1:1 and 1:2 products is not due to chelation appears to be justified.

Infra-red spectra of some compounds were recorded in nujol mulls on Perkin Elmer Infracord, model 337, using KBr optics and attempt has been made to assign some characteristic absorption bands. It can be seen that the glycols themselves show absorption bands in the region 3300-3700 cm^{-1} indicating hydrogen bonded -OH stretching. However, some weak bands

(8) D.C. Bradley, R.C. Mehrotra and W. Wardla, *J. Chem. Soc.*, 2027, 4204, 5020 (1952).

(9) D.C. Bradley, R.C. Mehrotra, J.D. Swanwick and W. Wardlaw, *J. Chem. Soc.*, 2025 (1953).

do appear in few derivatives which could be due to a little unavoidable hydrolysis of the derivatives during mulling and recording. All the spectra show characteristic skeltal vibrations and the C-O stretches in the usual region[10-11]. A number of peaks appearing below ~ 600 cm^{-1} in the metal derivatives but absent in the corresponding glycol spectra, have been tentatively assigned to Zr-O stretching. The observed absorption bands with tentative assignments are given below.

Hexylene glycol (*neat liquid*): 3350sb(A), 2964vs (B), 2931s(C), 2919sh, 1639w, 1559s(D), 1379s(E), 1330s(D), 1293vw, 1258w, 1198vw(F), 1155vs(G), 1120w(H), 1074m(H), 1047s(I), 993vw, 968m, 943m, 903vs, 870m, 833s(I), 763s.

Zr(*hexyl. gly.*)$_2$: 3300-3365wb(A), 2930-2950sb(K), 2725w, 1590w, 1440s(K), 1390s(K), 1340s(D), 1335s (D), 1290m(F), 1270s(F), 1226s(D), 1190s(D), 1165s (F), 1140s(H), 1080m(H), 1060m, 1040s(I), 1000s (H), 975s, 925s, 880w, 845m, 830m(J), 800m, 765m, 720m, 670w, 600m(L), 520-560sb(M), 480s, 430m.

Zr(*hexyl. gly.*)$_3$: 3350-3400vbw(A), 2875-2930s(K), 1460s(K), 1375m(K), 1325m(D), 1290w, 1260m(F), 1218m, 1186m(D), 1158m(F), 1130w(H), 1080m(H), 1060w, 1040m(I), 995m(H), 970m, 935m, 910w, 900w, 875w, 860w, 835m(J), 790w, 760m, 730m, 720w, 670w, 610w(L), 590w, 550m(M), 520w(M).

Pinacol: 3425sb(A), 2975s(K), 2950s(K), 2875m (K), 1470m(K), 1380s(K), 1160s, 1145s, 1110s, 955s, 890m, 835m, 825m, 675mb, 550wb, 520wb, 500wb.

Zr(*OPr^i*)$_2$(*Pinacol*): 3331mb(A), 2831-2981sb(K), 2711sh, 1586vw, 1401s(K), 1361s(K), 1258w, 1153s (S), 1003s(H), 963s, 890s, 852mb, 718vw, 688mb, 613s, 585s(M), 551sb(M).

Zr(*pinacol*)$_2$: 3331b(A), 2851-2981sb(K), 2711sh, 1631wb, 1451s(K), 1371s(K), 1253w, 1153sb(I), 1128 s(H), 1017m(H), 1003m(H), 973s, 948m, 913vw, 888 s, 846m, 713m, 688m, 668m, 583s(M), 549s(M), 488 m, 456sh.

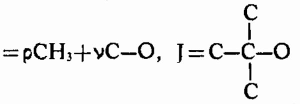
Zr(*pinacol*)$_3$: 3331b(A), 2910-2958sb(K), 2806s(K), 1451s(K), 1366s(K), 1194m, 1154s(I), 1128s(H), 1019 s(H), 1003m(H), 974s, 947m, 887s, 855m, 846m, 713 m, 689s, 665m, 597m, 582s(M), 551s(M), 492m, 456 m.

Butane 2,3 diol (*neat liquid*): 3366vbs(A), 2971 vs(Q), 2931sh, 2871s(C), 1631vw, 1451m(D), 1371s (D), 1280bw, 1160m(D), 1115s(S), 1055s(H), 1007m, 990sh, 963w, 927s, 887s, 813vw, 640bw, 545w, 445 bw.

Zr(*OPr^i*)$_2$ (*Butane 2,3 diol*): 3726w(A), 3176vw(A), 2976sb(K), 2901sb(K), 2726vw, 2626w, 1455s(K), 1371s(K), 1331m(D), 1302vw, 1278vw, 1258vw, 1165s, 1081s(H), 1011s(I), 968vw, 928s, 907s, 843 m(O), 818w, 784vwb, 718s(P), 688s, 552s(M), 445 sb.

Zr(*butane 2,3 diol*)$_2$: 3651w(A), 3336vwb(A), 3176 vwb(A), 2916sb(K), 2766vw, 2666vw, 1701vw, 1551 vw, 1451s(K), 1321vw, 1300vw, 1265w, 1165s, 1128 s(H), 1082s(H), 1015s(I), 995s, 970vw, 928s, 895s, 840vw, 818m, 785m, 715w, 670s, 628w, 580s(M), 465sb.

Zr(*butane 2,3 diol*)$_3$: 3352w(A), 2837-2977sb(K), 2717sh, 1557w, 1452s(K), 1372s(K), 1303sh, 1168s, 1148sb, 1128s(H), 1085sb(H), 1018s(I), 998w, 941s, 898s, 818m, 786w, 715w, 683m, 673m, 628m, 578s (M), 473mb.

(where A=νOH, B=νCH, C=νCH_2, D=δCH, E=δCH-+$(CH_3)_2$C–, F=$(CH_3)_2$C. G=δOH+(CH_3)2C, H=νC–O, I=ρCH_3+νC–O, J=  $\mathrm{C{-}\overset{\displaystyle C}{\underset{\displaystyle C}{C}}{-}O}$ group, K=Nujol, L=δC–CH_3 +νZr–O, M=νZr–O, N=νC–O+OPr^i, O=OPr^i group, P=πOH, Q=νCH_3, R=δOH, S=OPr^i+$(CH_3)_2$C+δOH, T=$(CH_3)_2$C+δOH).

Experimental Section

Apparatus and Chemicals. All glass apparatus fitted with interchangeable joints were used and precautions were taken to exclude moisture.

Molecular weights were determined ebullioscopically in benzene by a Gallenkamp ebulliometer fitted with highly sensitive thermistor sensing. Zirconium isopropoxide was prepared as described earlier. The glycols were purified by distillation before use. Benzene was dried as usual.

Analytical Methods. Zirconium was estimated in all derivatives by direct ignition of the compound after digestion with analytical grade ammonia and nitric acid in a platinum cruicible. Isopropanol was estimated by oxidation with $NK_2Cr_2O_7$ solution in 12.5 percent sulphuric acid. Ethane 1,2 diol and butane 2,3 diol are estimated with sodium periodate by Malaprade method,[12] pinacol was estimated by oxidation with normal chromic acid solution.

Reactions. Similar synthetic procedure was used in all the cases. Details are given only for the reaction of zirconium isopropoxide with ethane 1,2 diol in molar ratio 1: 1 and the rest of the reactions being summarised in the table.

Reaction between zirconium isopropoxide and ethane 1,2 diol in molar ratio 1 : 1 in benzene. Small amount of white precipitate was formed when ethane 1,2 diol (0.75 g) was added to a solution of $Zr(OPr^i)_4$. Pr^{i}OH (4.73 g) in benzene (80.0 g). The reaction mixture was refluxed under a column for about two hours at a bath temperature of about 120-125° and isopropanol liberated during the course of reaction was slowly fractionated out azeotropically till the distillate recorded a temperature of 80°C. The gelatinous white precipitate was filtered off and on drying gave a white solid (0.90 g). The filterate was dried under reduced pressure and a white foamy solid (2.40

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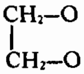
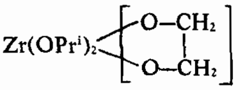
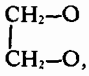
[10] L.J. Bellamy, Infra-red Spectra of complex Molecules, John Willey and Sons, Inc. N.Y. (1959).
[11] C.G. Barraclough, D.C. Bradley, J. Lewis and I.M. Thamas, *J. Chem. Soc.*, 2601 (1961)
[12] L. Malaprade ,*Bull. Soc. Chim.* (*France*), *43*, 683, (1928).

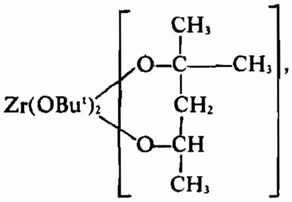
g), soluble in benzene was obtained. *Found*: Isopropanol in the azeotrope, 2.06 g; three moles require, 2.19 g. Analysis of the insoluble product: found Zr, 36.16%. Analysis of the soluble product. Found:

Zr, 33.13;

$\begin{matrix}\mathrm{CH_2{-}O}\\ |\\ \mathrm{CH_2{-}O}\end{matrix}$
22.24%; Calc. for

$\mathrm{Zr(OPr^i)_2}\left[\begin{matrix}\mathrm{O{-}CH_2}\\ |\\ \mathrm{O{-}CH_2}\end{matrix}\right]$

Zr, 33.86;

$\begin{matrix}\mathrm{CH_2{-}O}\\ |\\ \mathrm{CH_2{-}O,}\end{matrix}$
22.29%

Reaction between zirconium tertiary butoxide and 2-methyl pentane 2,4 diol in molar ratio 1 : 1. 1.37 g glycol was added to a benzene solution of zirconium tertiary butoxide (4.46 g) and the reaction mixture was refluxed and the liberated alcohol was fractionated out continuously. The excess solvent was distilled out and a white product crystallised out from benzene. The product was filtered out and dried.

Found: Zr, 25.94%, Mol. wt., 887; Calcd for



, Zr, 25.79%, mol wt. 353.