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Reactions of Zirconium(IV) Isopropoxide with Aliphatic and Aromatic Hydroxy Esters.
Part I, Five-, Six-, Seven- and Eight-coordinated Zirconium(IV) Complexes

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The reactions of zirconium(IV) isopropoxide with ethyl-α-(1-hydroxycyclohexyl) acetate ($HOC_6H_{10}R$)*, ethyl-β-hydroxy-β-phenyl propionate* (HOCHPhR) *and ethyl-β-hydroxy-β-phenyl butyrate* (HOCMePhR)*, where* ($R = CH_2CO_2Et$)*, have been carried out in refluxing benzene in different molar ratios under strictly anhydrous conditions. The dark brown products of the general composition,* $Zr(OPr^i)_{4-n}\cdot L_n$*, (where L = hydroxy ester anion; n = 1–4) have been isolated and characterized on the basis of elemental analyses, molecular weight, infrared and proton magnetic resonance spectral studies.*

Introduction

There has been considerable interest in the β-diketonate derivatives of zirconium(IV) during the last two decades [1–7]. The reactions of zirconium(IV) alkoxides with β-diketones and β-ketoesters [8, 9] have been well reported in the literature. In view of the interesting results obtained regarding the coordination number of zirconium(IV) in β-diketonates and β-ketoester derivatives, it was considered worthwhile to study the reactions of zirconium(IV) isopropoxide with some hydroxy esters. Such hydroxy esters are potentially bidentate ligands having complexing sites at hydroxyl and carbonyl groups and can give rise to complexes of varied coordination number depending upon the amount of esters used.

Results and Discussion

A systematic study of the reactions of zirconium(IV) isopropoxide isopropanolate [$Zr(OPr^i)_4\cdot Pr^iOH$], with hydroxy esters in the molar ratios of 1:1, 1:2, 1:3 and 1:4 has been carried out in refluxing benzene. The isopropanol produced in these reactions has been fractionated out azeotropically with benzene and estimated by an oxidation method [10]. These reactions can be represented by the following equations:

$$Zr(OPr^i)_4\cdot Pr^iOH + n\text{-}HOC_6H_{10}R \rightarrow$$
$$Zr(OPr^i)_{4-n}(OC_6H_{10}R)_n + (n+1)Pr^iOH$$

$$Zr(OPr^i)_4\cdot Pr^iOH + n\text{-}HOCHPhR \rightarrow$$
$$Zr(OPr^i)_{4-n}(OCHPhR)_n + (n+1)Pr^iOH$$

$$Zr(OPr^i)_4\cdot Pr^iOH + n\text{-}HOCMePhR \rightarrow$$
$$Zr(OPr^i)_{4-n}(OCMePhR)_n + (n+1)Pr^iOH$$

where $R = CH_2CO_2Et$ and n = 1–4

The reactions between zirconium(IV) isopropoxide and hydroxy esters in the molar ratios 1:1 and 1:2 are quite facile. The 1:3 and 1:4 ratio reactions were slow probably due to steric hindrance. The compounds, thus isolated are light yellow to brown viscous liquids soluble in ethanol, methanol, benzene, carbon tetrachloride, chloroform, acetone and ether. The mono-, bis- and tris-substituted ester derivatives of zirconium(IV) were purified by distillation under reduced pressure while the tetrakis-substituted derivatives decomposed during distillation under the reduced pressure. The molecular weight, of some of the compounds was determined ebullioscopically in refluxing benzene which corresponded to monomeric species indicating five-, six-, seven- and eight-coordination for zirconium(IV), in mono-, bis-, tris- and tetrakis-substituted derivatives, respectively. The five- and six-coordinate geometries are well established for zirconium(IV) complexes [11–13]. The seven- and eight-coordination numbers for zirconium(IV) complexes have also been reported [14–18] and confirmed by X-ray crystallography [1, 4, 5]. The tetrakis-(ester) derivatives of zirconium(IV) are of sixteen electron system, which is well estab-

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TABLE I. IR Frequencies (cm^{-1}) of Hydroxy Esters and Zirconium(IV) Complexes.

Compounds	ν(OH)	ν(C=O)	ν(C–O)	ν(C–H)	δ (C–H)	ν(OEt)	ν(M–O)
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
$HOC_6H_{10}R$	3500s	1710s 1755s[a]	1240s	2950s	1445s 1450m	1000s	–
$Zr(OPr^i)_3(OC_6H_{10}R)$	–	1710s	1255s	2900s	1450mb 1465sh	1000w	520m
$Zr(OPr^i)_2(OC_6H_{10}R)_2$	–	1710s	1260m	2850s 2930s	1450s 1475m	1015m	550m
$Zr(OPr^i)(OC_6H_{10}R)_3$	–	1710s	1260m	2850s 2920s	1450s 1460m	1010s	550w 520w 480w
$Zr(OC_6H_{10}R)_4$	–	1700s	1255m	2860s 2930s	1455s 1465m	1015s	550w 480m
HOCHPhR	3460s	1700s 1760s[a]	1270s	2980s 3015m	1445s 1450m	1030m	–
$Zr(OPr^i)_3(OCHPhR)$	–	1710s	1310m	2970s 3030m 3080m	1450s 1465sh	1010w	550w
$Zr(OPr^i)_2(OCHPhR)_2$	–	1710s	1310m	2970s 3030m 3070m	1455m 1465m	1020w	550m
$Zr(OPr^i)(OCHPhR)_3$	–	1720s	1315m	2980s 3035m 3065m	1450m 1465m	1000w	550w
$Zr(OCHPhR)_4$	–	1715s	1320m	2990s 3030m 3070m	1455m 1460m	1000w	540w
HOCMePhR	3500s	1710s 1760s[a]	1270m	2990s 3010sh	1450s 1455m	1025m	–
$Zr(OPr^i)_3(OCMePhR)$	–	1700s	1325m	2950s 3030sh 3060m	1455m 1465sh	1010w	550w
$Zr(OPr^i)_2(OCMePhR)_2$	–	1720s	1340m	2960s 3030m 3060m	1450s	1015m	550m 410m
$Zr(OPr^i)(OCMePhR)_3$	–	1720s	1340m	2960s 3030m 3060m	1450m 1465m	1000m	550m 420m
$Zr(OCMePhR)_4$	–	1715s	1335m	2960s 3040m 3080m	1445m 1460m	1000m	530m 480w

[a] ν(C=O) of dehydrated esters.

lished for several other zirconium(IV) complexes [4, 5].

The alcoholysis of mono-, bis- and tris-substituted ester derivatives of zirconium(IV) with tertiary butanol in refluxing benzene provided a good method for the synthesis of the corresponding tertiary butoxide derivatives. The estimation of isopropanol liberated gave not only a check on the completeness of the reactions but also provided a mean of analysis of isopropoxy contents in the parent derivatives. These tertiary butoxide derivatives of zirconium(IV) are yellow to dark brown liquids, soluble in benzene, ethanol, chloroform, carbon tetrachloride, ether and acetone. All these products can be purified by distillation under reduced pressure.

$$Zr(OPr^i)_3 \cdot L + \underset{\text{(excess)}}{Bu^tOH} \rightarrow Zr(OBu^t)_3 \cdot L + 3Pr^iOH$$

$$Zr(OPr^i)_2 \cdot L_2 + \underset{\text{(excess)}}{Bu^tOH} \rightarrow Zr(OBu^t)_2 \cdot L_2 + 2Pr^iOH$$

$$Zr(OPr^i) \cdot L_3 + \underset{\text{(excess)}}{Bu^tOH} \rightarrow Zr(OBu^t) \cdot L_3 + Pr^iOH$$

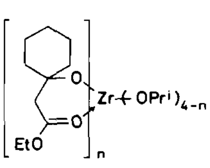
TABLE II. Reactions of Zirconium(IV) Isopropoxide with Hydroxy Esters.

Reaction mixture in benzene	Molar Ratio	Refluxing time (h)	Viscous liquid products	Amount of isopropanol in the azeotrope (g)	Metal %	Molecular weight, Found (Calcd)
				Found (Calcd.)	Found (Calcd.)	
(1)	(2)	(3)	(4)	(5)	(6)	(7)
$Zr(OPr^i)_4\cdot Pr^iOH + HOC_6H_{10}R$	1:1	6	$Zr(OPr^i)_3(OC_6H_{10}R)$	0.36	20.1	483
(1.25 g) (0.59 g)			Light brown	(0.39)	(20.1)	(453)
$Zr(OPr^i)_4\cdot Pr^iOH + HOC_6H_{10}R$	1:2	10	$Zr(OPr^i)_2\cdot(OC_6H_{10}R)_2$	0.44	15.7	–
(0.99 g) (0.96 g)			Light brown	(0.46)	(15.7)	
$Zr(OPr^i)_4\cdot Pr^iOH + HOC_6H_{10}R$	1:3	20	$Zr(OPr^i)(OC_6H_{10}R)_3$	0.56	13.3	690
(0.97 g) (1.39 g)			Brown	(0.60)	(12.9)	(705)
$Zr(OPr^i)_4\cdot Pr^iOH + HOC_6H_{10}R$	1:4	30	$Zr(OC_6H_{10}R)_4$	1.31	11.0	–
(1.76 g) (3.34 g)			Dark brown	(1.36)	(10.9)	
$Zr(OPr^i)_4\cdot Pr^iOH + HOCHPhR$	1:1	8	$Zr(OPr^i)_3(OCHPhR)$	0.35	10.8	–
(1.23 g) (0.62 g)			Light yellowish brown	(0.38)	(10.7)	
$Zr(OPr^i)_4\cdot Pr^iOH + HOCHPhR$	1:2	10	$Zr(OPr^i)_2(OCHPhR)_2$	0.44	15.3	600
(0.96 g) (0.97 g)			Light brown	(0.45)	(15.2)	(595)
$Zr(OPr^i)_4\cdot Pr^iOH + HOCHPhR$	1:3	18	$Zr(OPr^i)(OCHPhR)_3$	0.68	12.5	730
(1.12 g) (1.68 g)			Brown	(0.69)	(12.4)	(729)
$Zr(OPr^i)_4\cdot Pr^iOH + HOCHPhR$	1:4	25	$Zr(OCHPhR)_4$	1.00	10.5	–
(1.36 g) (2.72 g)			Dark brown	(1.05)	(10.5)	
$Zr(OPr^i)_4\cdot Pr^iOH + HOCMePhR$	1:1	10	$Zr(OPr^i)_3(OCMePhR)$	0.21	19.1	471
(0.79 g) (0.41 g)			Yellowish brown	(0.24)	(19.1)	(475)
$Zr(OPr^i)_4\cdot Pr^iOH + HOCMePhR$	1:2	15	$Zr(OPr^i)_2(OCMePhR)_2$	0.43	14.6	–
(0.92 g) (0.99 g)			Yellowish brown	(0.43)	(14.6)	
$Zr(OPr^i)_4\cdot Pr^iOH + HOCMePhR$	1:3	20	$Zr(OPr^i)(OCMePhR)_3$	0.60	11.9	–
(1.01 g) (1.62 g)			Yellowish brown	(0.62)	(11.8)	
$Zr(OPr^i)_4\cdot Pr^iOH + HOCMePhR$	1:4	30	$Zr(OCMePhR)_4$	0.81	9.9	1000
(1.07 g) (2.24 g)			Dark brown	(0.83)	(9.9)	(919)

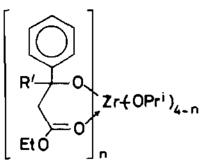
$OC_6H_{10}R$ = ethyl-α-(1-oxycyclohexyl)acetate, OCHPhR = ethyl-β-oxy-β-phenylpropionate and OCMePhR = ethyl-β-oxy-β-phenylbutyrate.

where L = hydroxy ester anion.

On the basis of elemental analysis, i.r., ^{1}H n.m.r. and molecular weight studies, the following plausible structures can be suggested to the various monomeric aliphatic [1, 4] and aromatic [5, 12] derivatives of zirconium(IV):



(1-4)



(5-12)

where R' = H: 5,6,7,8; Me: 9,10,11,12 and n = 1–4.

Infrared Spectra

In the i.r. spectra of the zirconium(IV) complexes, no absorption bands were observed in the 3500–3450 cm^{-1} region, indicating the absence of ν(OH) vibrations of the hydroxy esters. The coordination of the ester carbonyl group to the metal in these complexes can be clearly explained on the basis of the shift observed in ν(C=O), *ca.* 40–50 cm^{-1}. The coordination of ester carbonyl to metal has also been observed by Lappert [19] and Mehrotra [20]. The *ca.* 40–50 cm^{-1} decrease in ν(C=O) and 20–40 cm^{-1} increase in ν(C–O) are contiguous to the carbonyl group and 5–20 cm^{-1} change in δ(C–H) is consistent with carbonyl oxygen coordination of the esters. The ν(Zr–O) absorptions due to carbonyl oxygen [21, 22] appear at 550–400 cm^{-1}. The other important i.r. frequencies and their tentative assignments are listed in Table I.

^{1}H N.m.r. Spectra

The ^{1}H n.m.r. spectra of zirconium(IV) isopropoxide [23] and hydroxy esters [24] have been discussed in detail. In mono-, bis- and tris-substituted ester derivatives of zirconium(IV), the absence of hydroxyl proton in the δ (3.6–4.8) ppm region and presence of a septet centered at δ (5.2) ppm as well as doublet at δ (1.3) ppm due to -CH and -CH$_3$ protons of OPr^i group, respectively have been observed while in the tetrakis-substituted ester derivatives of zirconium(IV), no signals due to hydroxyl as well as OPr^i groups have been appeared. The other proton signals of the ester have retained their position in the complexes. The integrated intensities agreed with the number of the different kinds of protons present in the ligands as well as in zirconium(IV) complexes.

Experimental

Experimental techniques, reagents and analytical methods were similar to those described previously [24]. Zirconium(IV)isopropoxide was prepared by the ammonia method [25]. Zirconium was determined gravimetrically at ZrO$_2$. The isopropanol was estimated by an oxidation method [10].

The hydroxy esters were prepared by the reactions of ethyl bromoacetate and corresponding aldehyde or ketone using zinc dust [26–28].

Molecular weight was determined in benzene by a Gallenkamp Ebulliometer fitted with thermistor sensing. Infrared spectra were recorded as thin film and in nujol mull in the range (4000–200 cm^{-1}) on a Perkin Elmer-621 grating spectrophotometer and ^{1}H n.m.r. spectra in CDCl$_3$ on A-60 Varian and R32 Perkin Elmer instruments.

Reaction of Zirconium(IV) Isopropoxide with Ethyl α-(1-hydroxycyclohexyl)acetate

A clear colourless solution of zirconium(IV) isopropoxide isopropanolate (1.25 g) and ethyl α-(1-hydroxycyclohexyl)acetate (0.59 g) (molar ratio 1:1) in dry benzene (50 g) was refluxed in an oil bath under a fractionating column at 110 °C for *ca.* 6 h. The isopropanol–benzene azeotrope was collected at 72–80 °C. The clear brown solution, thus obtained, was cooled to room temperature. The solvent was removed under reduced pressure and the final product was distilled at 150–155 °C/0.05 mm in 70% yield. Found: Zr, 20.1%, -OPr^i 0.36 g, mol. wt. 483.22; calcd. for Zr(OPr^i)$_3$OC$_6$H$_{10}$R: Zr, 20.1% -OPr^i, 0.39 g, mol. wt. 453.22.

As the synthetic procedure used in all the reactions was the same, the other compounds were synthesized similarly and the results are summarized in Table II.

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