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Synthesis of novel monomeric zinc–oxygen compounds containing diethylzinc and pyrocatechol or saligenin moieties

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Abstract

Reactions of diethylzinc with dihydric phenols such as pyrocatechol and saligenin in a molar ratio of 1/1 yield zinc pyrocatecholate and ethylzinc 2-hydroxymethylphenoxide, whereas a molar ratio of 3/2 gives zinc bis(2-ethylzincoxyphenoxide) and zinc bis(2-ethylzincoxyphenylmethoxide), respectively. The latter ethylzinc-oxygen compounds, containing zinc diphenoxide – or zinc dimethoxide – units complexed internally by ethylzinc groups, form monomeric species in 1,4-dioxane.

Introduction

Ethylzinc-oxygen compounds such as those derived from reactions of diethylzinc with polyhydric phenols are receiving more attention owing to their use as catalysts for copolymerizations of carbon dioxide with heterocyclic monomers [1]. As far as we know, heterogeneous catalysts derived from diethylzinc and resorcinol have been developed from those based on dihydric phenols [2,3]. Here we describe a study of the reactions of diethylzinc with pyrocatechol and saligenin in a 1,4-dioxane solution. These reactions, involving dihydric phenols posessing functional substituents at the *ortho* position in the benzene ring, are thought to afford homogeneous catalysts, particularly in view of the behaviour of some polyfunctional ethylzinc and phenoxyzinc phenolates in 1,4-dioxane, described recently [4].

Experimental

Materials

Diethylzinc was synthesized from zinc powder and ethyl halides and distilled under nitrogen before use. Pyrocatechol and saligenin (commercial grade) were purified by sublimation under reduced pressure and stored under nitrogen. 1,4-Dioxane was dried by heating over calcium hydride and lithium aluminium hydride and distilled under nitrogen before use.

Procedure

1,4-Dioxane solutions of the relevant reactants, saturated with ethane before each reaction, were mixed by dropwise addition of one to the other (the appropriate phenol solution was added to diethylzinc) under vigorous stirring. Reactions were carried out at room temperature and were followed by a volumetric determination of the ethane evolved during their progress. When ethane evolution was complete, the post-reaction solution was diluted with 1,4-dioxane (to $[Zn] = 0.24 \times 10^{-3}$ g-atom cm^{-3}) and portions withdrawn for ^1H NMR studies. The spectra were recorded at 25 ° C on a Tesla BS 487C 80 MHz spectrometer. An equivalent amount of the post-reaction solution was then transferred to a cooled standard freezing point depression apparatus under nitrogen for measurement. Actual product concentrations were calculated from the mass of ethane evolved. The molecular weights were calculated after correction for the content of ethane (determined from the ^1H NMR spectra) present in the solution.

Results and discussion

In the reaction of diethylzinc ($ZnEt_2$) with pyrocatechol (PCL) in a molar ratio of 1/1, ethane evolution rapidly achieved nearly 100%, based on the amount of initial $ZnEt_2$, which is consistent with the course formulated previously [2] (eq. 1).

$$ZnEt_2 + PCL \longrightarrow \underset{(I)}{C_6H_4O_2Zn} + 2\ EtH \qquad (1)$$

However, eq. 1 depicts the ideal reaction in the system $ZnEt_2$/PCL (1/1); the actual system becomes turbid even if a small excess of PCL, relative to $ZnEt_2$, is present. The addition of $ZnEt_2$ to such a system results in a clear solution. In light of the above and the results of the cryoscopy, showing the molecular weight of the products to be in the range 1109–1331 (Table 1), the expected products of the reaction should be a mixture of the soluble zinc pyrocatecholate (coordination polymers) and the zinc pyrocatecholate condensation polymers with chains terminated by moieties originating from $ZnEt_2$ (soluble) or PCL (insoluble). The structure of zinc pyrocatecholate must involve four-coordinated zinc atoms, in view of the data published on organozinc-oxygen compounds [5]. Those zinc atoms which cannot attain coordination saturation with oxygen atoms of zinc pyrocatecholate

Table 1

Molecular weights and ^1H NMR spectra of the products of reactions of $ZnEt_2$ with pyrocatechol (PCL) and saligenin (SGN) in 1,4-dioxane solutions [a]

Entry	Reactants			Product				
			Molar ratio		Molecular weight		Chemical shift (δ ppm)	
					Found	Calcd. [b]	CH_2	CH_3
1	$ZnEt_2$	PCL	1/1	I	1220	173		
2	$ZnEt_2$	I	1/1	II	309	297	0.35	1.35
3	$ZnEt_2$	PCL	3/2	III	480	470	0.43	1.39
4	II	I	1/1	III	486	470	0.43	1.39
5	$ZnEt_2$	SGN	3/2	VII	508	498		

[a] For conditions see Experimental. [b] For the monomer.

can undergo complexation with 1,4-dioxane, which in turn should prevent this compound from forming larger associates. It has been reported elsewhere [6] that zinc pyrocatecholate obtained from the $ZnEt_2/PCL$ (1/1) reaction in n-hexane is a highly aggregated insoluble product.

The zinc–oxygen bonds in I are weak and readily undergo cleavage by $ZnEt_2$ added to the solution which results in the monomeric bis(ethylzinc) pyrocatecholate (II) according to eq. 2 (Table 1). The zinc atoms in II probably form internal coordinative bonds with oxygen atoms of the neighbouring groups [4] and attain coordination saturation by complexation with 1,4-dioxane.

$$ZnEt_2 + I \longrightarrow C_6H_4(OZnEt)_2 \qquad (2)$$

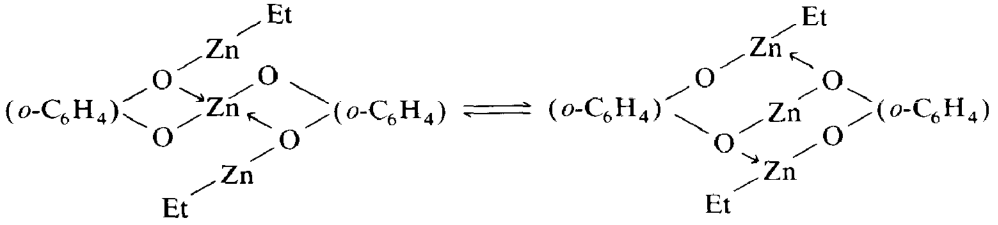
(II)

The reaction of $ZnEt_2$ with PCL in a molar ratio of 3/2 results in rapid evolution of ethane and formation of zinc bis(2-ethylzincoxyphenoxide) (III) according to eq. 3. The same product can also be obtained from the reaction of I with II in a molar ratio of 1/1 (Table 1).

$$3\ ZnEt_2 + 2\ PCL \longrightarrow Zn(OC_6H_4OZnEt)_2 + 4\ EtH \qquad (3)$$

(III)

The ethylzinc-oxygen compound, III, exists as a monomer in 1,4-dioxane solution (Table 1), probably because of: (i) the occurrence of internal zinc–oxygen coordinative bonds, such as those in IIIa and IIIb which are in equilibrium, and (ii) the coordination saturation of zinc atoms by 1,4-dioxane.



(IIIa) (IIIb)

The intramolecular complexation of both the ethylzincoxy groups with the OZnO unit prevents III from undergoing the association characteristic for zinc diphenoxide. Interestingly, a similar ethylzinc-oxygen compound having only one ethylzincoxy group per one OZnO unit in the molecule, such as ethylzinc phenoxyzinc pyrocatecholate, forms a trimeric associate in 1,4-dioxane [4].

In the reaction of $ZnEt_2$ with saligenin (SGN) in a molar ratio of 1/1, ethane evolution rapidly reaches almost 50%, based on the initial amount of $ZnEt_2$ present. The formation of a white precipitate was observed during the reaction. In view of the more acidic character of the phenolic group compared with that of the hydroxymethyl group in SGN, the reaction may be represented by eq. 4.

$$ZnEt_2 + SGN \longrightarrow EtZnOC_6H_4CH_2OH + EtH \qquad (4)$$

(IV)

Ethylzinc 2-hydroxymethylphenoxide (IV), formed as a white solid in the reaction, scarcely undergoes further ethane elimination at room temperature. However, it undergoes further reaction at elevated temperatures to give a solid condensation product under slow ethane elimination (only half of the ethyl groups are lost from IV as ethane at a temperature of 50 °C). Thus, the reaction at elevated temperature yielding 2-hydroxymethylphenolatozinc 2-ethylzincoxyphenylmethoxide (V) according to eq. 5 seems plausible.

$$2\ \mathrm{IV} \longrightarrow \mathrm{Et}\left(\mathrm{ZnOC_6H_4CH_2O}\right)_2\mathrm{H} + \mathrm{EtH} \tag{5}$$

(V)

The relatively low rate of ethane elimination during the condensation of IV (eq. 5) is probably attributable to the lower reactivity of the ethyl group in the ethylzinc-oxygen compound than that of $ZnEt_2$ towards hydroxyl group, observed in other systems [7]. The reaction of IV with $ZnEt_2$ in molar ratio of 1/1 proceeds rapidly to give bis(ethylzinc) saligenate (VI) (eq. 6).

$$\mathrm{ZnEt_2} + \mathrm{IV} \longrightarrow \mathrm{EtZnOC_6H_4CH_2OZnEt} + \mathrm{EtH} \tag{6}$$

(VI)

The proportion of ethane evolved during the reaction of $ZnEt_2$ with SGN, in a molar ratio of 3/2, respectively, was nearly 100% based on the initial amount of hydroxyl groups in SGN, which indicates that the reaction takes place as follows (eq. 7):

$$3\ \mathrm{ZnEt_2} + 2\ \mathrm{SGN} \longrightarrow \mathrm{Zn(OCH_2C_6H_4OZnEt)_2} + 4\ \mathrm{EtH} \tag{7}$$

(VII)

Rapid evolution of ethane was observed until 75% of the hydroxyl groups had reacted with the zinc-bonded ethyl groups. This reaction step was accompanied by precipitation of the solid. Then the ethane evolution became slower and dissolution of the solid was observed. The resulting solution was found to contain zinc bis(2-ethylzincoxyphenylmethoxide) (VII) (Table 1). The structure of VII resembles that postulated for III. In view of the data obtained, the reaction according to eq. 7 probably involves a number of steps proceeding by eqs. 4, 6, and then 8.

$$\mathrm{IV} + \mathrm{VI} \longrightarrow \mathrm{VII} + \mathrm{EtH} \tag{8}$$

The last step (eq. 8) is slow since the ethylzinc group in VI, undergoing the ethane elimination, is bonded with the oxygen atom.

Conclusions

The results presented here show that reactions of diethylzinc with dihydric phenols such as pyrocatechol and saligenin in a molar ratio of 3/2, respectively, yield the novel ethylzinc-oxygen compounds which form monomeric species in 1,4-dioxane. These species, which contain zinc diphenoxide- or zinc dimethoxide-moieties complexed internally by ethylzinc groups have all the structural features required of an active species in a carbon dioxide/oxirane copolymerization catalyst [1].

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