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ON THE PRODUCTS OF REACTIONS OF ZINC DIALKYLS WITH PYROGALLOL

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Summary

Reactions of dialkylzinc compounds ZnR_2 (R = Me, Et) with pyrogallol (PG) have been carried out.

The reaction products obtained with mole ratios of reactants 3/1, 2/1 and 1/1, respectively, were characterized by means of IR, ^1H NMR spectroscopy, elemental analysis and cryometry.

The product formed from ZnR_2/PG 2/1 (the best known catalytic system for the alternating CO_2/propylene oxide copolymerization) was found to be 1,3,2-benzodioxazincol-4-alkylzincolate.

Introduction

It has previously been found [1] that the homogeneous $ZnEt_2$/pyrogallol (PG) 2/1 mole ratio catalytic system shows very high activity in the alternating copolymerization of carbon dioxide and propylene oxide, yielding high molecular weight poly(propylene carbonate). The corresponding systems consisting of $ZnEt_2$ and PG at mole ratios 3/1 and 1/1 were found to be inactive and slightly active, respectively, in the copolymerization [1]. In order to establish the nature of the active species formed in the ZnR_2/PG catalytic system the reactions of $ZnMe_2$ and $ZnEt_2$ with PG at reactant mole ratios of 3/1, 2/1 and 1/1 respectively, have been investigated.

As far as the present authors can establish, the reactions of dialkylzinc compounds or other related organometallic compounds, with PG have not yet been investigated. Some data concerned with the characterization of the products of the above reactions have been reported recently by us [2]. The reactions of $ZnEt_2$ with other polyhydroxybenzenes such as resorcinol, pyrocatechol, phloroglucinol have been investigated with respect to their catalytic activity in the copolymerization of carbon dioxide and propylene oxide [1,3].

Results

The reactions of $ZnMe_2$ and $ZnEt_2$ with PG at reactant mole ratios of 3/1, 2/1 and 1/1, respectively, were carried out in 1,4-dioxane. When a dioxane solution of PG was added dropwise to a stirred solution of dialkyl zinc, rapid evolution (within a few minutes) of the corresponding alkane was observed until a reactant mole ratio of ZnR_2/PG 2/1 was reached. Subsequent addition of the PG solution to the homogeneous reaction mixture obtained caused the elimination of the next portion of alkane but at a much lower rate than in the first stage (complete alkane evolution in a few hours), and the precipitation of a white product from the solution was observed. The reaction conditions and yields of evolved alkane are given in Table 1. Reaction products were isolated from each system and then characterized by means of elemental analysis, IR and ^1H NMR spectroscopy and cryoscopy. Results are given in Table 1.

Reactions of dialkylzinc with PG at a reactant mole ratio of 2/1, were investigated in various solvents. In each reaction evolution of the corresponding alkane was complete in a few minutes at room temperature. The alkane was always evolved in ca. 75% yield with respect to the alkyl groups introduced with ZnR_2.

TABLE 1

CHARACTERIZATION OF THE PRODUCTS OF REACTIONS OF ZnR_2 (R = Me, Et) WITH PYROGALLOL (PG)

Reaction [a]				Product					
Mole ratio ZnR_2/PG	R	Alkane evolved [b] (%)	System [c]	No.	Zn content (%)		IR characteristic bands (cm^{-1}) [e]		
					Found [d]	Calcd.			
3/1	Me	50	+	Ia					
3/1	Et	50	+	Ib	32.25	33.67	1580s	1293s	1250s
							1035s	873s	840m
							700w	655w	612s
2/1	Me	75	+	IIa	41.26	41.78	1583s	1300s	1153m
							787w	775w	707w
							487m	410m	305m
2/1	Et	75	+	IIb	39.84	39.99	1580s	1295s	1250s
							1045s	870s	840s
							612m	555w	507w
1/1	Me, Et	100	—	III	27.67	27.99	3500	2000(br)s	1575s
							1115s	1025s	869s
							710m	650m	550w

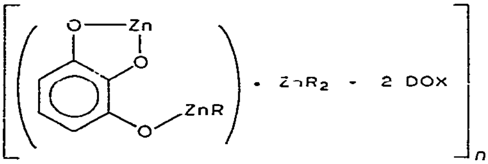
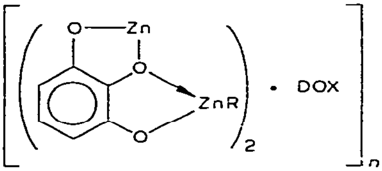
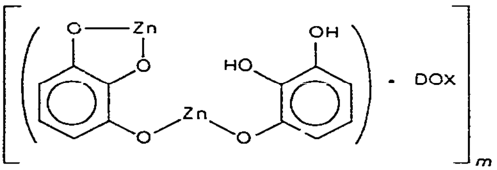
[a] In 1,4-dioxane (20 cm^3) (solution of PG added to the solution of ZnR_2); product concentration: 0.25 mol/l; room temp.; time, ca. 0.5 h. [b] Yield calculated with respect to the alkyl groups introduced with ZnR_2.

A list of the products formed together with some of their properties is given in Table 2.

When the order of mixing the reactants was reversed, i.e. when a solution of ZnR_2 was added to the PG solution, a white unidentified precipitate was formed immediately.

A comparison of the far IR spectra of dimethoxyzinc and diphenoxyzinc (whose molecules cannot form a ring structure) with the spectra of 1,3,2-benzodioxazincol (IV) and 1,3,2-benzodioxazincol-4-alkylzincolate (II) (where a five-membered ring closed by zinc is suggested) is given in Fig. 1. ^{1}H NMR spectra of ZnR_2/PG reaction products and of some related simple alkylzinc compounds were taken in 1,4-dioxane solutions at room temperature and in 1,3-dioxane at −40°C. The chemical shifts of the aromatic ring protons bonded to zinc via the oxygen atom and of protons of alkyl groups bonded directly to zinc were investigated. The internal chemical shift of the ethyl group bonded to the zinc atom was taken as well. The results are given in Table 3.

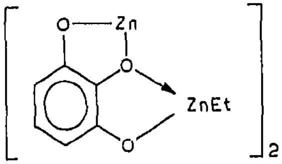
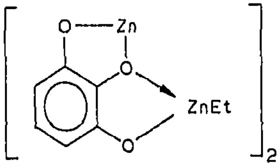
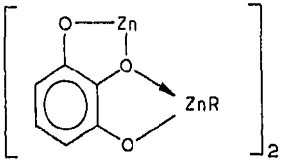
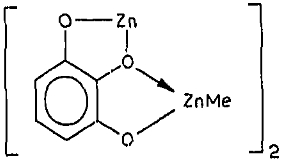
Molecular weight determinations of compounds Ib, IIa and IIb were carried out in 1,4-dioxane (the compounds investigated do not dissolve in benzene at concentrations of 1—2 weight percent). The lowering of freezing point was very

			Formula [f]
1155m 825m 510w	1123s 770m 330w	1075m 730m 283m(br)	
1030s 615m 280s	876m 557m	805m 512w	
1200m 779m 400w	1150m 720m 280m(br)	1120s 650w	
1290s 840m 490w	1240s 765m 300(br)w	1150m 735m	

[c] + = homogeneous; — = heterogeneous. [d] By conventional titration. [e] Nujol mull. [f] DOX = 1,4-dioxane, n = 4—6 (determined cryoscopically in 1,4-dioxane).

TABLE 2

REACTION OF ZnR_2 (R = Me, Et) WITH PYROGALLOL AT REACTANT MOLE RATIO 2/1 IN VARIOUS SOLVENTS [a]

Solvent [b]	DN [c]	Reaction system [d]	Zn content in product		IR characteristic bands (cm^{-1}) [e]	Formula [f]
			Found [g]	Calcd.		
$(CH_3O)_2CH_2$	24.0 [h]	—	40.24	40.74	1583s 1295s 1145s 1150m 1035s 925m 835m 775m 725s 633w 615m 555w 400w 280s	 · $(CH_3O)_2CH_2$
$(C_2H_5)_2O$	19.2	—	40.52	40.86	1582s 1290s 1243s 1150m 1033s 925w 833m 775m 725s 653w 617m 557w 519w 415w 283m	 · $(C_2H_5)_2O$
DOX	14.8	+	[i]	[i]	[i]	 · DOX
THF	20.0	+	37.49	38.34		 · THF

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[a] ZnR_2 5 mmol (solution of PG added to the solution of ZnR_2); product concentration 0.25 mol/l; room temp.; time ca. 0.5 h; yield of alkane evolved during reaction 75% with respect to alkyl groups introduced with ZnR_2. [b] DOX = 1,4-dioxane; THF = tetrahydrofuran. [c] DN = donor number of solvents [9]. [d] "+" = homogeneous, "—" = heterogeneous. [e] Nujol mull. [f] Coordination structure is omitted. [g] By conventional titration. [h] Value for $(CH_3OCH_2)_2$. [i] See Table 1.

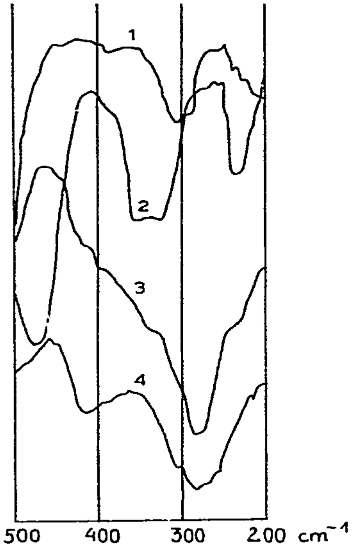
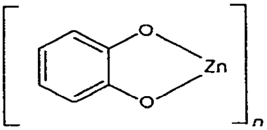


Fig. 1. Far IR spectra of zinc compounds: 1, $Zn(OCH_3)_2$; 2, $Zn(OC_6H_5)_2$; 3, $C_6H_4O_2Zn$ (IV); and 4, $C_6H_3(OZnR)O_2Zn$ (II).

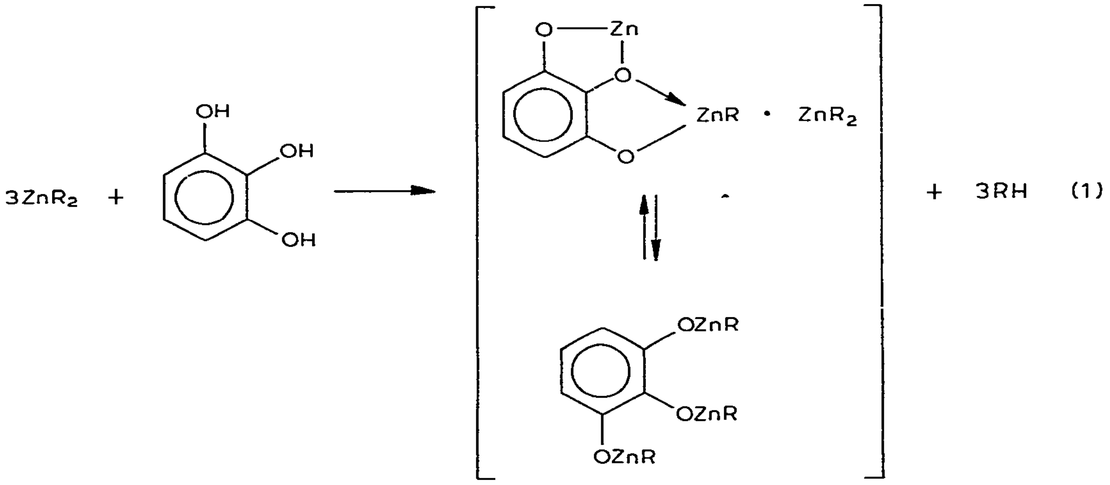


(IV)

small so only approximate data were obtained. These indicate that all compounds are strongly associated and the approximate degree of association is in the range 4—6 (Table 1).

Discussion

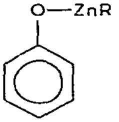
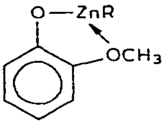
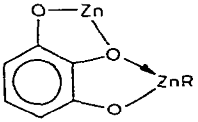
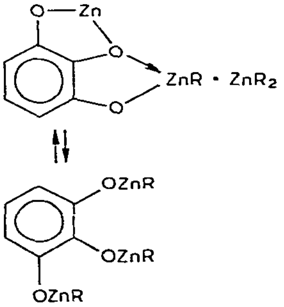
In the system ZnR_2/PG at a reactant mole ratio of 3/1, in which half the alkyl groups bonded to the Zn atom produce alkane (Table 1), the reaction course



(I)

TABLE 3

^1H NMR SPECTRA OF ORGANOZINC COMPOUNDS IN 1,4-DIOXANE AT ROOM TEMPERATURE

Compound[a]	R	Chemical shift[b] (τ ppm)			Internal chemical shift $\tau_{CH_3} - \tau_{CH_2}$ (ppm)
		Aromatic	CH_2	CH_3	
ZnR_2	Me			10.72	
	Et		9.86	8.86	−1.00
	Me	2.80 3.12		10.34	
	Et	2.74 3.10	9.46	8.60	−0.86
	Me	2.90 2.11		10.74	
	Et	2.85 3.05	9.81	9.04	−0.77
	Me(IIa)	3.43		10.55	
	Et(IIb)	3.17 3.50	9.61[c]	8.70[c]	−0.91
	Me(Ia)	3.83[d]		10.64[d]	
	Et(Ib)	3.49 3.64	9.71[c] 9.91[e]	8.71[c] 8.76[e]	−1.00

[a] Association via intermolecular coordination and complexation by solvent molecules are omitted in the formulas. [b] Integration of the signals showed correlations between the protons of alkyl and aromatic groups shown in the formulas of compounds. [c] A broad, fine structure only just visible. [d] In THF. [e] In 1,4-dioxane at −40°C.

shown in eq. 1 is suggested *. The reaction product I probably exists in two equilibrium forms. Since only one kind of alkyl group was observed in the ^1H NMR spectrum of I, even at −40°C (Table 3), fast exchange of alkyl groups between the complex and/or the tris(alkylzinc)pyrogallolate form may be suggested.

Subsequent addition of PG to the above described ZnR_2/PG reaction mixture, until the reactant mole ratio reaches a value of 2/1, results in an increase in the yield of alkane evolved during the reaction to 75% with respect to the alkyl groups introduced with ZnR_2 (Table 1). The reaction appears to proceed accord-

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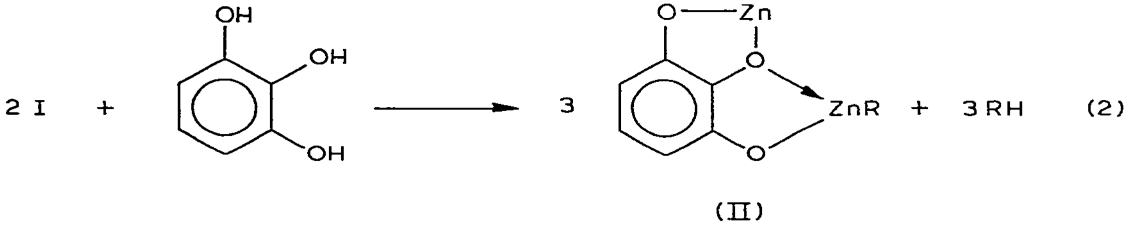
* Association of zinc compounds and their complexation by the solvent are omitted in the formulas.

ing to eq. 2. The structure of reaction product II which contains a five-membered heterocyclic ring appears to be analogous to that described in the literature for compounds of other metals with *ortho*-di- and tri-hydroxybenzenes (Sn [4]; Tl [5]; and Cu [6]). Analogous structures for zinc compounds have been proposed for zinc eugenolate * [7] and zinc 8-hydroxyquinolinate [8].



(2)

As can be seen from Fig. 1 there is an apparent difference in the low frequency spectra between the heterocyclic zinc compounds II and IV, and Zn(OR)$_2$. In the spectra of the heterocyclic compounds mentioned a broad, strong absorption band occurs at about 283 cm^{-1}. Taking into consideration the literature data [8] on the Zn—O stretching vibrations in chelate compounds one can assume that this absorption band is connected with the Zn—O stretching vibration in the heterocyclic rings of II and IV.

Comparison of the ^{1}H NMR spectra of some simple organozinc compounds and ZnR$_2$/PG reaction products (Table 3) shows τ_{CH_2} to be shifted to lower values in the series ZnEt$_2$, EtZnOC$_6$H$_4$OCH$_3$, EtZnOC$_6$H$_3$O$_2$Zn and EtZnOC$_6$H$_5$. This progressive shift is governed by two opposing effects. The introduction of an electronegative oxygen at zinc will result in a deshielding of the α-methylene hydrogens. On the other hand, coordination in the organozinc—oxygen compounds will counteract this influence. Apparently in EtZnOC$_6$H$_4$OCH$_3$ the effect of coordination dominates the inductive effect of the oxygen, whereas in EtZnOC$_6$H$_5$ the opposite situation exists. This is in agreement with the presence of an intramolecular coordinate bond in a sub-unit of EtZnOC$_6$H$_4$OCH$_3$: the same situation exists in EtZnOC$_6$H$_3$O$_2$Zn (II). In the latter case the effect of coordination also dominates the inductive effect of the oxygen atom. The result confirms the suggestion that intramolecular coordination exists in the sub-unit of II. Taking into consideration complete values for chemical shifts of the α-methylene protons it can be estimated that intramolecular bonding in the case of II is weaker than that of EtZnOC$_6$H$_4$OCH$_3$.

As can be seen from Table 3 the chemical shift of α-methylene protons in the Et$_2$Zn/PG 3/1 mole ratio reaction mixture (I) suggests that the effect of coordination dominates the inductive effect of oxygen.

Increased coordination of the zinc atom should lower its electronegativity and as a result the internal chemical shift of the ethyl group bonded to zinc should decrease. The internal chemical shifts of the ethyl group of the compounds investigated show, however, an order opposite to that expected (Table 3). This can be explained in terms of inter- and intra-molecular coordination of these compounds which involves an anisotropic effect of benzene ring on CH$_3$ group

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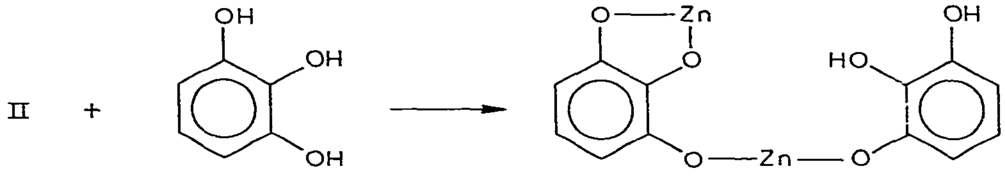
* Eugenol = 1-allyl-4-hydroxy-3-methoxybenzene.

protons and results in strong shielding of them (Table 3). Therefore CH_3 group protons cannot be taken as an internal standard for α-CH_2 protons and the correlation which usually exists between the internal chemical shift of the ethyl group bonded to the metal atom and the electronegativity of the metal is not valid.

The same changes take place in the case of methyl derivatives of the compounds investigated (Table 3), confirming the presence of an intramolecular coordinate bond in sub-units of $RZnOC_6H_4OCH_3$ and II. Investigations on the influence of the solvent on the reaction in ZnR_2/PG 2/1 mole ratio system (Table 2) and on the molecular weight determinations of the products (Table 1) show that intermolecular coordination plays a significant role in the systems studied. Table 2 shows that neither the solvent basicity nor whether the solvent is mono- or bidentate govern the solubility of the product formed in the ZnR_2/PG 2/1 system. It is worthwhile to note that the suggested heterocyclic compound (II) is soluble in cyclic ethers.

Subsequent addition of the PG solution to the solution of II results in further elimination of alkane and precipitation of a solid from the solution (Table 1). The reaction proceeds according to eq. 3. The white solid product III isolated from the post-reaction mixture is insoluble even in pyridine. This confirms that intermolecular coordination is very strong and plays a dominant role in the case of compound III.



(3)

(III)

Experimental

Materials

Dimethylzinc and diethylzinc (commercial grade reactants) were distilled under nitrogen before use. Pyrogallol (commercial grade reactant) was purified by sublimation under nitrogen. Solvents were purified according to known procedures.

All reactions were carried out under nitrogen. To a flask equipped with a stirrer containing 5 mmol of dialkylzinc in 5 ml of solvent, the required amount (see Tables 1 and 2) of pyrogallol in 15 ml of solvent was added dropwise. The contents of the flask were stirred vigorously. After completing addition of the pyrogallol solution, stirring was continued until the required amount of alkane was evolved. The alkane evolved during the reaction was collected in a gas burette.

Analysis

NMR spectra were recorded on 10% solutions of the compounds in dioxane using a JEOL C-100H spectrometer. IR spectra (Nujol mulls) of the compounds were recorded within the range 4000—200 cm^{-1} on a Perkin—Elmer 527 spectrophotometer. Molecular weights were measured cryoscopically in 1,4-dioxane using a standard freezing point depression apparatus modified so as to enable the measurements to be made in a nitrogen atmosphere.

Acknowledgement

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