

INVESTIGATIONS ON ORGANOZINC COMPOUNDS
IX*. COORDINATION CHEMISTRY OF ORGANOZINC COMPOUNDS
RZnX: ORGANOZINC DERIVATIVES OF *tert*-BUTANOL, SOME PHENOLS,
DIETHYLHYDROXYLAMINE AND SOME OXIMES

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(Received December 29th, 1967)

SUMMARY

The coordination chemistry of organozinc-oxygen derivatives RZnOR' in which R' stands for *tert*-Bu, C₆H₅, C₆Cl₅, C₆F₅, NEt₂, N=CMePh and N=CHPh has been studied. Depending on the nature of R' such compounds are dimeric (C₆Cl₅, C₆F₅), trimeric (*tert*-Bu), tetrameric (C₆H₅, N=CMePh), hexameric (NEt₂), or more highly associated (N=CHPh) in benzene solution. Plausible structures have been assigned to these compounds on the basis of spectroscopic (IR, PMR) and molecular weight data. The behaviour of these compounds in the presence of mono- and bidentate ligands is discussed.

INTRODUCTION

The reaction between organozinc compounds and alcohols has been described by Butlerow as early as 1864¹, but until quite recently very little was known about the constitution of the reaction products. In 1965 Coates and Ridley² published the results of an investigation of the reaction of dimethyl- and diethylzinc with various compounds containing reactive hydrogen. Methylzinc phenoxide and 2-methoxyethoxide and alkylzinc alcoholates in general were shown to be associated into tetramers for which a cubic structure with tetracoordinate zinc and oxygen atoms was proposed². An X-ray structure determination of methylzinc methoxide by Shearer and Spencer³ has meanwhile confirmed the cubic arrangement of the inorganic skeleton. Cubic structures have since been proposed for various other types of tetrameric organozinc derivatives⁴⁻⁶. More recently Coates and Ridley⁷ drew attention to the structural variations which may occur on changing the nature of the group bound to zinc via oxygen. Dimeric, trimeric and tetrameric products were obtained from the reaction of diorganozinc compounds with benzophenone, 2-dimethylaminoethanol and acetoxime⁷.

* For Part VIII see ref. 19.

Mono-organozinc compounds $RZnX$ in which X is a group bound to zinc via a hetero atom have been studied independently at our laboratory⁸⁻¹⁰. The present paper deals with organozinc derivatives of tert-butanol, some phenols, diethylhydroxylamine and some oximes. Aspects of the coordination chemistry of organozinc derivatives of a number of monoprotic, potentially bidentate hydroxyl-containing ligands will be reported separately¹¹.

RESULTS AND DISCUSSION

The organozinc-oxygen derivatives were readily available from the reaction of diphenyl- or diethylzinc with the appropriate hydroxyl derivative in hexane or benzene:



TABLE I

ORGANOZINC DERIVATIVES OF tert-BUTANOL, SOME PHENOLS, DIETHYLHYDROXYLAMINE AND SOME OXIMES

Compound	M.p. (°C)	Analysis found (calcd.) (%)		Molecular weight determination ^a			Degree of association (\bar{n})
		Zn	N	Conc. (%)	Molecular weight Observed	Calcd. for mon.	
(I) (tert-BuZnO-tert-Bu) ₃	169	32.70 (33.42)		0.83 4.22	587 597	195.6 195.6	3.00 ^b 3.06
(II) (EtZnOPh) ₄	177-178	35.18 (34.88)		2.58	750	187.5	4.01
(IIa) (EtZnOPh·py) ₂	190	24.38 (24.52)	5.53 (5.26)	3.64	527	533.2	1.98
(IIb) (EtZnOPh) ₂ ·TMED	214-215	26.18 (26.62)	5.46 (5.70)	2.60	486	491.2	0.99
(III) (EtZnOC ₆ Cl ₅) ₂	180	18.07 (18.18)		3.04	731	359.7	2.03
(IIIa) EtZnOC ₆ Cl ₅ ·TMED	78-80	13.56 (13.72)	5.83 (5.58)	0.63	511	475.9	1.07
(IIIb) EtZnOC ₆ Cl ₅ ·2py	210	12.48 (12.62)	5.32 (5.40)	3.06	495	518.1	0.96
(IV) (EtZnOC ₆ F ₅) ₂	113-115	23.71 (23.55)		5.15	570	277.5	2.09
(IVa) EtZnOC ₆ F ₅ ·TMED	69-70	16.75 (16.63)	7.45 (7.12)	7.32	403	393.7	1.02
(IVb) (EtZnOC ₆ F ₅ ·py) ₂	183-185	18.65 (18.31)	4.30 (3.93)	4.09	711	356.6	2.00
(V) (PhZnONEt ₂) ₆	168-169	28.37 (28.34)	5.98 (6.07)	2.19	1410	230.6	6.10
(VI) (EtZnON=CMePh) ₄	130-132	28.64 (28.60)	6.38 (6.13)	5.70	923	228.6	4.03
(VII) (PhZnON=CHPh) _{n=9}	115-140	25.00 (24.92)	5.32 (5.34)	3.55	2390	262.6	~9

^a Molecular weights were determined by ebulliometry in benzene unless otherwise stated. For all compounds with the exception of (VII) the mol. wt. observed was independent of the concentration; only one value is reported in the Table. ^b Cryometric determination.

The formation of bis-substituted products $\text{Zn}(\text{OR}')_2$ does not pose a problem. According to our results the recently proposed¹² equilibrium (2):



lies completely to the right side, reaction (2) being a useful preparative route to organozinc alkoxides. This is in accordance with the observation that most alkylzinc alkoxides can be sublimed without decomposition².

The various compounds prepared, together with the results of molecular weight determinations as well as analytical and melting point data are listed in Table 1.

tert-Butylzinc *tert*-butoxide (I)*

This compound which had been synthesized in order to check the influence of steric crowding on coordination behaviour was found to be a trimer in benzene solution both by cryometry and ebulliometry. The absence of dissociation even in refluxing benzene is indicated by the lack of concentration dependence of the molecular weight. Very recently, Coates and Roberts¹³ assigned a dimeric structure to this compound on the basis of cryometric mol. wt. determinations. As all other properties reported by these authors were identical with our results the molecular weight determinations were repeated. Since our earlier results were found to be completely reproducible the reported dimeric structure of *tert*-BuZnO-*tert*-Bu would seem to be in error.

The PMR spectrum of *tert*-BuZnO-*tert*-Bu in benzene shows two singlets of equal intensity at $\delta = 1.27$ ppm and $\delta = 1.32$ ppm (reported¹³: 1.28 and 1.34 ppm) for the *tert*-butyl and *tert*-butoxide protons. The observed coalescence of these signals into one singlet at 1.29 ppm upon raising the temperature to 70° is not readily explained. Dissociation is excluded by the mol. wt. data. An explanation based on the exchange of *tert*-butyl groups between zinc and oxygen would not seem very probable.

Steric effects will be responsible for *tert*-BuZnO-*tert*-Bu to occur as a trimer rather than the normal tetramer. The degree of association in the series EtZnOPh (II), EtZnOCHPh₂⁷, and PhZnOCPh₃⁷ is four, three, and two, respectively. Apparently, dimeric association is observed only in case of excessive steric crowding. The fact that *tert*-BuZnO-*tert*-Bu is nevertheless trimeric suggests that steric crowding is not as severe as in PhZnOCPh₃. If the plausible assumption is made that the Zn₃O₃ ring is not completely flat the six *tert*-butyl groups can arrange on both sides of the ring so as to minimize steric interaction.

Whereas tetrameric alkylzinc alkoxides do not react with pyridine² *tert*-BuZnO-*tert*-Bu forms a pyridine complex in accordance with the presence of coordinatively unsaturated zinc in the trimer. The complex which has 1:1 stoichiometry is monomeric and thus still contains coordinatively unsaturated zinc. These results are in accordance with those recently published by Coates *et al.*¹³. In spite of the fact that TMED** in general is a better complexing agent for organozinc compounds than pyridine (*cf.* ref. 10) TMED fails to form a complex with *tert*-BuZnO-*tert*-Bu as shown by cryometric experiments. Model studies indicate that severe steric crowding is responsible for the unusual behaviour of *tert*-BuZnO-*tert*-Bu.

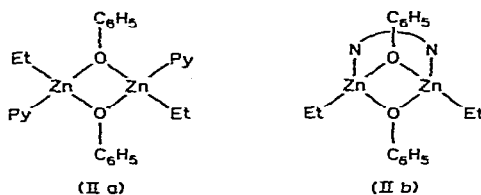
* Numbers correspond with those in Table 1.

** *N,N,N',N'*-tetramethylethylenediamine.

Ethylzinc phenoxide (II), pentachlorophenoxide (III) and pentafluorophenoxide (IV)

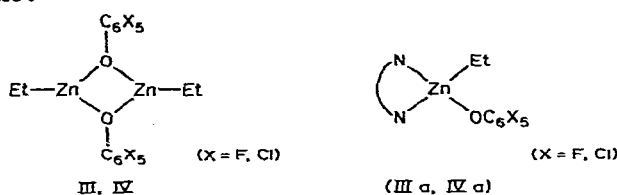
The study of these compounds was undertaken in order to check the influence of electronic effects on the coordination chemistry of organozinc-oxygen derivatives.

$\text{EtZnOC}_6\text{H}_5$ (II) has been found to be tetrameric in benzene suggesting the "normal" cubic structure^{2,3} with tetra-coordinate zinc and oxygen for this compound (cf. $\text{MeZnOC}_6\text{H}_5$)². The relatively weak donor character of the oxygens in the tetramer as a result of the $-I$ effect of the phenyl group appears from the fact that contrary to alkylzinc alkoxides² tetrameric $\text{EtZnOC}_6\text{H}_5$ is readily broken down by both pyridine and TMED with the formation of the binuclear complexes (II, a) and (II, b)*:



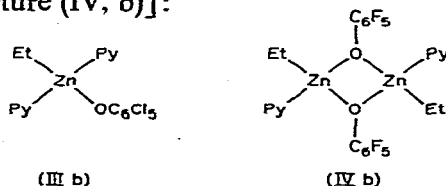
The formation of mononuclear complexes which would be favoured on entropy grounds is not observed, indicating that the Zn-O coordinate bonds in the dimers are strong.

In contrast, both $\text{EtZnOC}_6\text{Cl}_5$ (III) and $\text{EtZnOC}_6\text{F}_5$ (IV) are dimeric in benzene:



As a result of the much stronger $-I$ effect of the C_6Cl_5 and C_6F_5 groups the donating capacity of oxygen in these compounds apparently is too weak to allow face to face association of two dimer units into tetramers as observed for $\text{EtZnOC}_6\text{H}_5$. The strong $-I$ effect of the C_6Cl_5 and C_6F_5 groups is reflected in the relative weakness of the Zn-O coordinate bonds in dimeric $\text{EtZnOC}_6\text{Cl}_5$ and $\text{EtZnOC}_6\text{F}_5$. Both compounds form a mononuclear 1 : 1 complex with TMED [(III, a) and (IV, a)].

The dimeric structure of $\text{EtZnOC}_6\text{Cl}_5$ is likewise broken down by pyridine [structure (III, b)]. Interestingly, interaction of $\text{EtZnOC}_6\text{F}_5$ merely leads to coordination saturation of the zinc atoms, the Zn-O coordinate bonds remaining intact [structure (IV, b)]:



This result is in line with the somewhat greater $-I$ effect of the C_6Cl_5 group ($\text{p}K_a$ of $\text{C}_6\text{Cl}_5\text{OH}$: 5.26) as compared with that of the C_6F_5 group ($\text{p}K_a$ of $\text{C}_6\text{F}_5\text{OH}$: 5.32)¹⁴.

* In the formulae N-N represents the TMED ligand.

Phenylzinc derivative of diethylhydroxylamine (V)

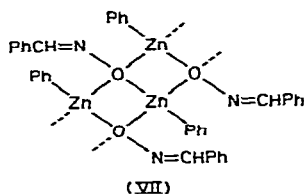
Crystalline PhZnONEt_2 (V) obtained from the reaction of Ph_2Zn with Et_2NOH was found to be hexameric in boiling benzene. In benzene solution no interaction with pyridine or TMED was observed.

The PMR spectrum in benzene (25°) shows the presence of two kinds of ethyl groups bound to nitrogen. The CH_2 protons appear as a very broad signal centered at 3.19 ppm whereas the CH_3 protons give rise to two relatively sharper triplets at 1.01 and 1.27 ppm. Upon raising the temperature to 70° the two triplets sharpen and the broad methylene signal splits into a multiplet. The position of the signals does not change indicating that no exchange takes place. The observation that the chemical shift difference between the methyl group signals is much greater than that between the methylene group signals must be ascribed to environmental influences, since differences in the electron-density at nitrogen would give rise to the opposite result. The broadening of the methylene group signals may be caused by conformational changes, *e.g.* hindered rotation around the oxygen-nitrogen bond. The PMR spectrum of parent Et_2NOH shows a sharp triplet at 1.10 ppm and a sharp quartet at 2.59 ppm. The low field shift of the methylene quartet in PhZnONEt_2 indicates decreased electron-density at nitrogen. A structure formed by two six-membered Zn-N rings coordinated face to face seems plausible. The available data do not allow a choice between inter-ring coordination via Zn-O or via Zn-N coordinate bonds.

Organozinc derivatives of acetophenoneoxime (VI) and benzaldoxime (VII)

$\text{EtZnON}=\text{CMePh}$ (VI) was found to be tetrameric in refluxing benzene. The PMR spectrum shows a downfield shift of the methyl protons ($\delta = 2.42$ ppm) relative to acetophenone oxime ($\delta = 2.07$ ppm). The IR spectrum contains the $\text{C}=\text{N}$ stretching vibration at 1259 cm^{-1} , a shift of 45 cm^{-1} to lower frequency as compared with $\nu(\text{C}=\text{N})$ in the parent oxime. These data suggest a structure involving Zn-N coordination similar to that of recently reported tetrameric $\text{MeZnON}=\text{CMe}_2$ which shows $\nu(\text{C}=\text{N})$ 40 cm^{-1} to lower frequency relative to acetoxime⁷. An X-ray crystallographic study of the latter compound has very recently revealed a cage-like structure containing fused zinc-oxygen-nitrogen rings with four-coordinate zinc atoms and three-coordinate oxygen and nitrogen atoms¹⁵. Intermolecular coordination in tetrameric $\text{EtZnON}=\text{CMePh}$ must be fairly strong, because both pyridine and TMED fail to interact with this compound.

$\text{PhZnON}=\text{CHPh}$ (VII) was found to be highly associated in refluxing benzene (*e.g.* $n \sim 9$ at 3.5 wt. %). The $\text{C}=\text{N}$ stretching vibration is observed at exactly the same position of 1546 cm^{-1} for $\text{PhZnON}=\text{CHPh}$ and $\text{HON}=\text{CHPh}$ suggesting that coordination through nitrogen does not take place. A structure containing Zn-O coordinate bonds only seems plausible:



The coordinate bonds must be strong as appears from the lack of interaction with both pyridine and TMED.

The electron-donating capacity of the nitrogen atom in $\text{PhZnON}=\text{CHPh}$ will be smaller than in $\text{MeZnON}=\text{CMe}_2$ because of the presence of the electron-withdrawing phenyl group instead of electron-donating methyl groups. This might explain the lack of nitrogen coordination in $\text{PhZnON}=\text{CHPh}$. It is, however, not clear why this compound prefers a polymeric structure over the tetrameric, cubic structure observed for organozinc alkoxides. The seemingly small change of replacement of a hydrogen atom by a methyl group is sufficient to completely modify the mode of coordination.

EXPERIMENTAL

General

All experiments were conducted in an atmosphere of dry, oxygen free nitrogen. Experimental techniques were essentially those described by de Liefde Meyer¹⁶ and Herzog¹⁷.

All starting materials were either P.A. grade or prepared according to published procedures. The solvents used were of P.A. grade and were distilled prior to use in a nitrogen atmosphere and stored on "Linde" molecular sieve no. 4A under nitrogen.

Spectroscopic measurements

PMR spectra were recorded on a Varian HR 100 spectrometer. IR spectra were run on a Grubb Parsons "Spectromaster" spectrometer.

Molecular weight determinations

All molecular weights reported were measured by cryometry or ebulliometry in benzene solution.

A Gallenkamp MW 120 ebulliometer was used, modified for operation in a nitrogen atmosphere as described by Mole¹⁸. The cryometric measurements were carried out in a double walled 50 ml vessel cooled in an ice/water mixture. Temperature differences were measured with a Philips E 205 CE thermistor incorporated in a bridge circuit, and recorded on a Philips PR 2210 potentiometric recorder.

The organozinc compounds were added as pellets pressed under a nitrogen atmosphere.

Synthesis of organozinc-oxygen compounds

Since the preparation of compounds of the type RZnOR' employs essentially the same procedure, only the synthesis of ethylzinc phenoxide and its complexes will be described in detail.

Ethylzinc phenoxide. To a stirred solution of 1.72 g (13.9 mmoles) of diethylzinc in 10 ml of benzene, cooled to 10°, was added slowly a solution of 1.04 g (11.0 mmoles) of phenol in 10 ml of benzene. During the exothermic reaction 245 ml of ethane (11.0 mmoles) were evolved. In order to complete the reaction the resulting clear solution was heated at 50° for 15 min. The excess of diethylzinc and the solvent were removed *in vacuo* and the crystalline residue recrystallized from n-hexane. Yield: 2.05 g (98% of the theory).

tert-Butylzinc tert-butoxide was obtained by refluxing for 1 hour tert-butanol with a slight excess of di-tert-butylzinc in n-pentane solution. The isolation of this compound was performed in the same way as that of ethylzinc phenoxide. Ethylzinc pentachlorophenoxide was recrystallized from benzene.

Complex of ethylzinc phenoxide with pyridine. 2 g of pyridine (25.2 mmole) were added to a solution of 2.05 g of ethylzinc phenoxide (10.9 mmole) dissolved in 10 ml of benzene. Upon standing for some minutes the complex crystallized out. After removal of the supernatant solution the residue was washed twice with 10 ml of benzene and dried in vacuo. Yield: 1.81 g (62% of the theory).

ACKNOWLEDGEMENTS

Financial support by the International Lead Zinc Research Organization, Inc. (Dr. S. F. RADTKE) and by Billiton-M and T Chemische Industrie N.V. is gratefully acknowledged. The authors wish to thank Professor G. J. M. VAN DER KERK for his stimulating interest.

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