ZINC AND CADMIUM

LITERATURE SURVEY COVERING THE YEAR 1978*

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Contents

Introduction

No significant shifts in interest have occurred in the field of organozinc and organocadmium chemistry. Also the yearly number of papers in this area of chemistry grows only slowly.
The following review articles have appeared this year:
i. The less familiar reactions of organocadmium compounds[1]
ii. Zinc and organic synthesis[2]

I. Preparation of organozinc and organocadmium compounds

When diethylzinc or dimethylzinc was reacted with pyrogallol in 2 : 1 molar ration, the 1,3,2-benzodioxazincol-4-alkylzincolates I were formed[3]:

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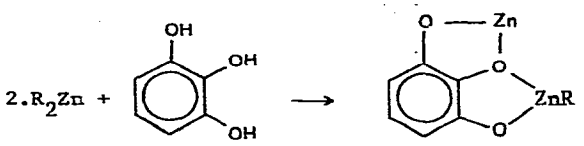
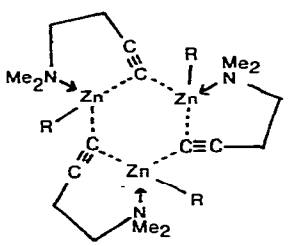
* Zinc and Cadmium; Annual Survey covering the year 1977 see: J. Organometal. Chem., Vol. 167 (1979) p. 1-17.



I (R = Me, Et)

Two types of functionally-substituted diorganozinc compounds have been described by Boersma, van der Kerk and co-workers[4,5].
ω-Functionally-substituted dialkylzinc compounds of the type $Zn[(CH_2)_nX]_2$ (n = 3, X = OMe, SMe, NMe_2; N = 4, X = OMe) are monomeric species in which exclusive intramolecular coordination between zinc and the terminal heteroatoms was established[4]. Complexation reactions of these compounds with N,N,N',N'-tetramethylethylenediamine and 2,2'-bipyridine showed that the strength of the intramolecular coordinate bonds decreases in the order NMe_2>SMe>OMe.
Ethyl(4-dimethylamino-1-butynyl)zinc has been prepared by metalation of 1-dimethylamino-3-butyne with diethylzinc[5]. The corresponding bis-alkynylzinc compound was made in a similar way from the acetylenic amine and diphenylzinc. Both compounds are trimers in benzene solution and association is believed to occur through both zinc-nitrogen and zinc-alkyne coordination:



R = Et, $Me_2N(CH_2)_2C{\equiv}C-$

The preparation and characterization of the pyridine complexes of ethylzinc hydride and phenylzinc hydride has been reported by de Koning et al.[6]. The complexes are formed when the corresponding diorganozinc compounds are reacted with zinc hydride in pyridine:

$$R_2Zn + ZnH_2 \xrightarrow{Py} 2RZnH.py$$

These compounds were also obtained from the pre-formed pyridine complexes of the parent diorganozinc compounds and zinc hydride in THF:

$$R_2Zn.2Py + ZnH_2 \xrightarrow{THF} 2\ RZnH.py$$

The complexes are trimers in benzene, probably associated through Zn-H-Zn bridges.

These organozinc hydrides rapidly reduce ketones and also excess pyridine. In the latter case, the pyridine is reduced exclusively to the 1,4-dihydropyridyl moiety.

The unexpected tetranuclear compound diethyl-tetrazinchexakis (N-phenylmethylcarbamate).2 benzene III has been obtained in crystalline form from a solution of ethylzinc-N-phenylmethylcarbamate[7]. It probably was formed through slight disproportionation of the latter compound:

$$2\ EtZnNPhCOOMe \longrightarrow Et_2Zn + Zn(NPhCOOMe)_2$$

$$2\ EtZnNPhCOOMe + 2Zn(NPhCOOMe)_2 \xrightarrow{C_6H_6} Et_2Zn_4(NPhCOOMe)_6.2C_6H_6$$

III

The crystal structure of III contains molecular units with pairs of benzene molecules in between. The molecular frame of each unit consists of a sixteen-membered $(ZnNCO)_4$-ring and an eight-membered $(ZnNCO)_2$-ring, sharing two zinc atoms. The three independent methylcarbamate groups, each with a zinc atom and a phenyl-carbon atom bonded to nitrogen, are approximately planar.

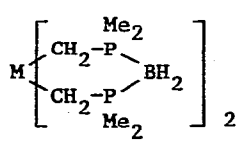
Unsolvated methyl- and ethylcadmium halides have been prepared by Habeeb and Tuck using the electrochemical oxidation of cadmium metal in the presence of methyl- or ethylhalide[8]. The compounds were stabilized by complexation with donor ligands like 2,2'-bipyridine, dioxane, DMSO and o-phenantroline. Oxidation of cadmium in the presence of bromopentafluorobenzene and acetonitrile yielded $C_6F_5CdBr.2CH_3CN$ initially, which dissociates via the equilibrium:

$$2\ C_6F_5CdBr.2CH_3CN \rightleftharpoons (C_6F_5)_2Cd.2CH_3CN + CdBr_2.2CH_3CN$$

supporting previous studies of solution equilibria involving R_2Cd and CdX_2 species.

The oxidation is thought to proceed via a free-radical mechanism in which radicals are generated at the cathode, followed by anodic processes.

Zinc and cadmium chelate derivatives of the borato(bis-dimethylphosphoniomethylide)anion have been described by Schmidbaur and co-workers[9]:



M = Zn,Cd

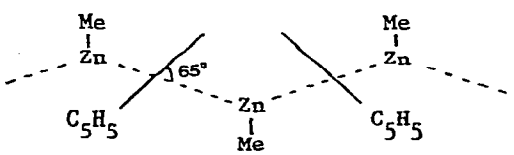
References p. 14

NMR spectra indicated fully symmetrical bonding of the chelating ligands to the metal atoms.

The first synthesis of bis(trimethylsilylmethyl)cadmium IV has been carried out by Heinekey and Stobart[10]. Liquid IV is very thermally stable, but as sensitive to oxidation as normal dialkylcadmiums. It forms a yellow 1 : 1 complex with o-phenantroline, whereas with 2,2'-bipyridine a very volatile adduct with the surprising Cd : Bipy ratio of 1 : 1.5 is formed. A crystallographic study of the latter complex shows that its molecular composition is $[(Me_3SiCH_2)_2Cd.Bipy].0.5$ Bipy. IR, Raman, and MS data of IV have been compared with those of its zinc and mercury analogs. The preparation of IV from trimethylsilylmethyllithium and cadmium chloride has been described by Al-Hashimi and Smith[11].

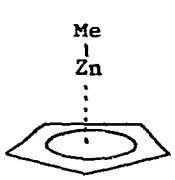
A zinc-copper mixture, prepared by heating a mixture of zinc and copper powder in 1 : 4 ratio for two hours at 400° under hydrogen has been used in the synthesis of dimethylzinc and diethylzinc[12]. When methyliodide was heated with an excess of this Zn/Cu mixture at 130° in an autoclave, dimethylzinc of 86.3% purity was formed in 10.7% yield. Under the same conditions, ethyliodide gave 30.1% of diethylzinc of 100% purity.

The crystal- and molecular structure of methyl(cyclopentadienyl)zinc has been determined by Wade and co-authors[13]. The structure may be described as consisting of puckered chains of zinc atoms, each carrying a methyl group, linked by bridging cyclopentadienyl groups inclined at an angle of 65° to the metal-metal vectors:



Since some incertainty remained in the orientation of the cyclopentadienyl groups within the ring plane, the structure is most realistically described in terms of highly disordered or rotating cyclopentadienyl groups. The hapticity of the cyclopentadienyl groups ranges from two to three, each pair contributing five electrons to the zinc atom between them.

In the gas phase, the same compound is monomeric and has a structure with C_5V symmetry, containing a pentahapto cyclopentadienyl ring[14]:

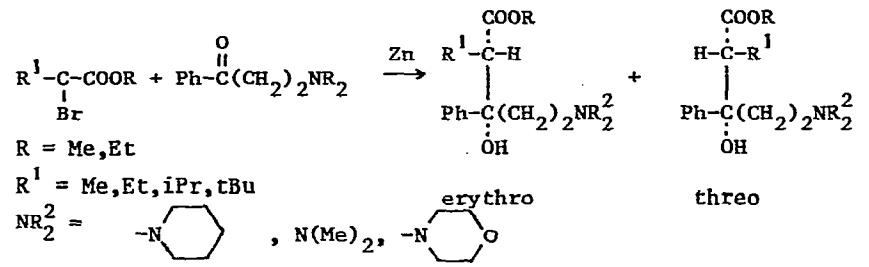


The zinc-cyclopentadienylcarbon vibrational amplitude is large, indicating a loose interaction. This, in turn, may be the reason for the polymerization of the compound in the solid state.

II. Reactions of organozinc- and organocadmium compounds

A. The Reformatski and related reactions

In a serie of papers, Lucas and Guetté have described asymmetric inductions in Reformatski reactions with Mannich-type ketones[15,16,17]:



In most cases, the erythro-isomers are formed in excess, contrary to the case of reactions of phenylalkylketones, in which normally threo-alcohols are obtained.

The authors attribute this inversion to participation of the nitrogen atoms. A bicyclic transition state is proposed in which steric influences determine the predominant formation of the erythro-alcohols and which also explains the variation of the stereoselectivity with the nature of the alkyl group in the Reformatski reagent.

The products of the reaction between zinc and N,N-diethylbromoacetamide in methylal (cf. also the work of Curé and Gaudemar[18]) have been investigated by Poller and Silver[19]. The authors propose the following reaction:

V

After two hours, only a single organometallic species appears to be present, possibly the bromine-free product VI, resulting from disproportionation of V:

VI

Compound V has been investigated as an alkylating agent for the group IV metals silicon, germanium and tin.

Erythro- and threo γ- and δ-amino-β-hydroxides VII have been prepared by Lucas and Guetté [20] by reacting

$$HOCPh(CHRCOOMe)(CH_2)_nNR^1_2$$

VII

R = Me,Et,iPr,tBu
NR^1_2 = morpholino, piperidino
R^1 = Me
n = 1,2

Reformatski reagents derived from compounds RCHBrCOOMe with α- and β-amino ketones. The influence of electronic and steric factors on the yields, which varied from 1 to 90%, was discussed.

Lapkin and co-workers have prepared α,α-dimethyl-β-ketoacid esters VIII in 75-85% yield by treating the Reformatski reagent $BrZnCMe_2COOEt$ with the compounds $RCOOCOCF_3$ (R = Me,Et,Pr) [21]:

$$RCOCMe_2COOEt$$

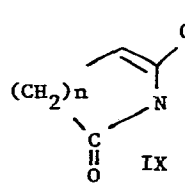
VIII

The same authors have used butyric anhydride as the substrate in reactions with a large variety of Reformatski reagents $BrZnCRR^1COOR^2$ [22]:

$(PrCO)_2CO + BrZnCRR^1COOR^2 \longrightarrow$ PrCOOCPr + CR^1COOR^2 42-71%
PrCOCHBuCOOBu 35%
R = H, R^1 = H,Me,Et,iPr,Bu; $PrCOCMe_2COOCHMe_2$ 55%
R = R^1 = Me; R^2 = Me,Pr,iPr,Bu,iBu

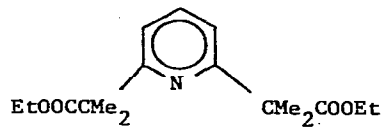
The Reformatski reaction of $BrZnCH_2COOR$ (R = Et, l-menthyl) with imines of the type $R^1CH = NR^2$ has been used as a primary step in the asymmetric syntheses of β-amino-acids and aspartic acid [23].

Lactams IX:



IX

n = 2,3



X

have been prepared via the Reformatski reaction of $BrZnCMe_2COOEt$ with aliphatic cyanoacids $NC(CH_2)_2COOH$. The analogous reactions of the butyl

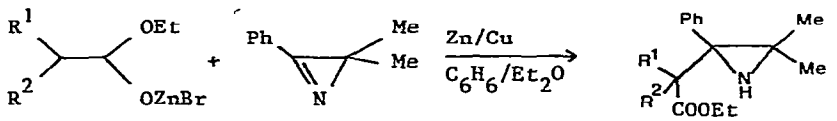
or trimethylsilyl esters afforded $(EtOOCCMe_2COCH_2)_2CH_2$ and the pyridine derivative X.

New C-4 substituted cephalosporins have been prepared from a 4-acetyl-3-cephem derivative using the Reformatski reagent $BrZnCH_2COOEt$[25].

The yield in a crucial step in the synthesis of (3S,4S)-4-amino-3-hydroxy-6-methylheptanoic acid has been greatly improved by carrying out a modified Reformatski reaction in which separately prepared enolate was added to a cooled solution of a blocked aldehyde[26]:

$$\text{PhtalylN-CH(R)-CHO} \xrightarrow{BrZnCH_2COOtBu} \text{PhtalylNCH(R)CH(OZnBr)CH}_2\text{COOtBu}$$

The Reformatski reaction of XI with dimethyl-3,3-phenyl-2-azirine yielded β-aziridino esters XII exclusively when the reaction was carried out in a benzene-diethylether mixture[27]:



XI XII

R^1 = H,Me
R^2 = H,Me

A similar reaction with the monomethylphenyl-azirine gave, apart from the aziridino esters, also small quantities of diazepinones.

B. Carbenoid reactions

Takakis and Rhodes have investigated the cyclopropanation reaction of some terminal, unsubstituted alkenes of the types:

$CH_2 = CHCH_2COOR$ and $CH_2 = CHCH_2CH_2OR^1$

R = H,Me, trideuteromethyl; R^1 = COMe, Me,H

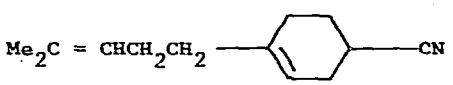
with a large excess of Simmons-Smith reagent (methyliodide/zinc-copper couple)[28]. In some cases, the initially formed cyclopropane derivatives reacted further to give ethers, formals and transesterification products. One of the reactions was developed into a convenient procedure for the preparation of symmetrical formals.

Two modified Simmons-Smith reagents have been studied by Takai and co-

workers[29]. Both modifications, i.e. the systems $CH_2I_2/Zn/Me_3Al$ and $CH_2Br_2/Zn/TiCl_4$, are effective carbonyl methylenation agents. The $CH_2I_2/Zn/Me_3Al$ system was very effective in the methylenation of aldehydes to terminal olefins:

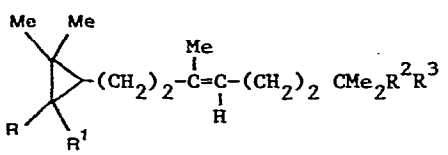
$$RCHO \xrightarrow{CH_2I_2/Zn/Me_3Al} RCH = CH_2$$

Even in those cases where double bonds were present in the substrate, e.g. in citral, no cyclopropanes were isolated. The active species in this system is thought to be $CH_2(ZnI)_2$.
The second system, i.e. $CH_2Br_2/Zn/TiCl_4$, appeared to be an excellent methylenation reagent for ketones. Both systems are complementary and the combination is a useful alternative for the Wittig reaction.
Only the terminal double bond in the cyclohexene carbonitrile XIII was converted into a cyclopropane ring upon reaction with the Simmons-Smith reagent[30]:



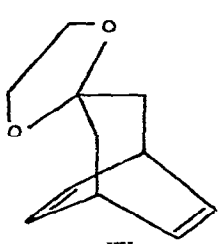
XIII

The same group of authors has prepared the cyclopropane terpenoids XIV using the Simmons-Smith reaction of geranylacetone with methyliodide as a first step[31]:

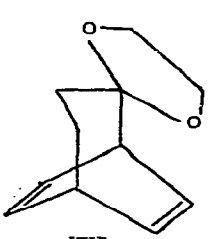


XIV

The stereochemistry of the Simmons-Smith reaction of the ketals XV and XVI

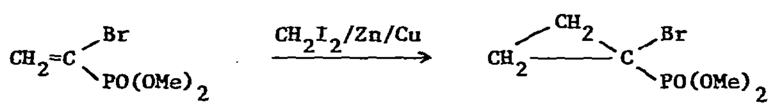


XV

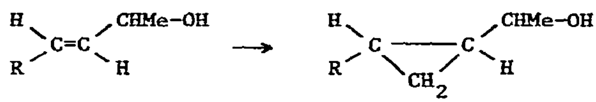


XVI

has been found not to be that required by intramolecular assistance of the type seen in similar reactions in earlier work[32]. The relative positions of the ketal groupings in XV and XVI are unfavourable for this type of intramolecular assistance. The authors warn against stereochemical assignments solely on the basis of stereoselective Simmons-Smith reactions. 1-Bromovinyl-1-phosphonic acid has been found to react with methylene iodide and zinc-copper couple to give 1-bromocyclopropane-1-phosphonic acid ester[33]:

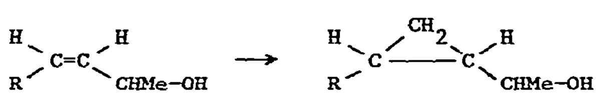


The Simmons-Smith reactions of the trans-acyclic allylic alcohols XVIII gave a mixture of threo- and erythro-isomers of the trans-1-(2-alkylcyclopropyl)ethanols[34]. Similar reactions of the corresponding cis-alcohols XVIII gave the erythro-isomers of the cis-alcohols predominantly:



threo + erythro

XVII



erythro

XVIII

C. Reactions of alkenyl- and alkynylzinc compounds

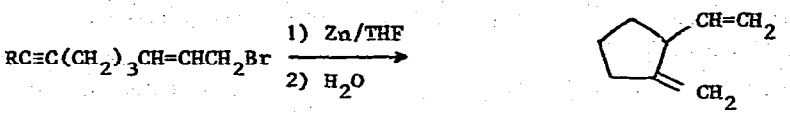
The reactivity of the α-ethylenic-γ-acetylenic organozinc compound $nC_4H_9C{\equiv}CCH{=}CHCH_2ZnBr$ towards aldehydes and ketones has been compared with that of the corresponding lithium and magnesium derivatives[35]. The zinc compound reacts with alkehydes and ketones to give nearly exclusively, except in the case of diisopropylketone, the alcohol resulting from attack on the central carbon atom of the enyne moiety:

$$nC_4H_9C{\equiv}CCH{=}CHCH_2ZnBr + RCOR^1 \longrightarrow nC_4H_9C{\equiv}C\underset{\displaystyle RC(OH)R^1}{CH}CH{=}CH_2$$

The reversibility of these reactions has been compared with that of the diene organometallics $CH_2{=}CH{-}CH{=}CH{-}CH_2M$ (M = ZnBr, MgBr, Li).
α-Ethylenic-ζ-acetylenic organozinc compounds:

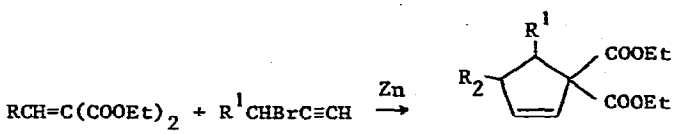
$$RC{\equiv}C(CH_2)_3CH{=}CHCH_2ZnBr \text{ (R = H, Me)}$$

undergo an intramolecular addition reaction, leading to cyclopentyl derivatives[36]:



R = H,Me

These reactions occur with allylic rearrangement and run more readily with zinc than with magnesium. A related intramolecular cyclization reaction, yielding cyclopentene derivatives, has been reported by Gaudemar et al.[37] When a diethylalkylidenemalonate XIX was reacted with an alkynylbromide and zinc in THF, and the reaction mixture was heated before hydrolysis, the cyclopentene derivatives XX were obtained:

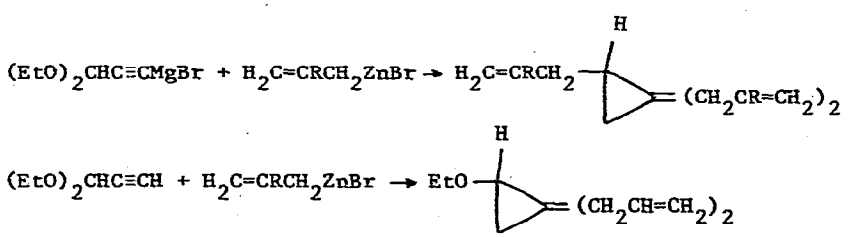


XIX XX

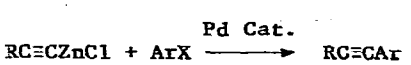
R = Me,Et,iPr; R^1 = H,Me

The reaction most probably occurs via thermal, in-situ cyclization of an intermediate adduct.

Bellasoued and Frangin have found that the reaction of 1-alkynes and 1-alkynylmagnesium halides with allylic zinc halides can be applied in the synthesis of substituted cyclopropanes, i.e.[38]:



A large variety of cyclopropanes has been prepared this way. A direct and selective synthesis of terminal arylalkynes using the palladium-catalyzed reaction of alkynylzinc reagents with aryl halides has been developed by King and Negishi[39]:

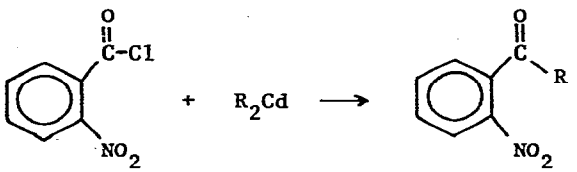


R = H,alkyl, aryl; X = I,Br

In the case of aryliodides or activated arylbromides, these reactions proceed cleanly without producing any other byproducts in significant amounts.

D. Miscellaneous reactions of organozinc- and organocadmium compounds

The classical ketone synthesis from acid chlorides and organocadmium compounds has been used in the first step of the direct synthesis of O-aminophenylalkylketones[40]:

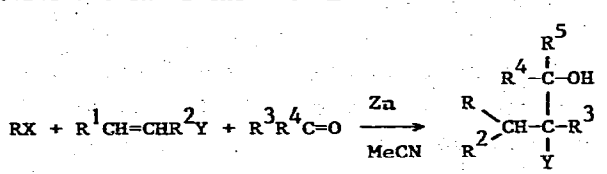


R = Me,Et,Pr,Bu, pentyl, hexyl

Yields in these reactions varied from 28 to 44%.
Autoxidation of dimethylcadmium gave MeCdOOMe and $Cd(OOMe)_2$[41,42]. When dimethylcadmium was treated with t-butylhydroperoxide, $MeCdOOCMe_3$ was formed. Hydrolysis of MeCdOOMe yielded the following products:

$$MeCdOOMe + H_2O \longrightarrow CH_4 + Cd(OH)_2 + MeOOH$$

The oxidation of diethylzinc and diethylcadmium by 3,5- and 3,6- di t.butyl-o-benzoquinones has been studied by EPR spectroscopy[43].
The electrochemical synthesis of tetraethyltin and lead, developed by Daolio and Mengoli, has been applied successfully to the preparation of tetrapropyl- and tetrabutyl derivatives of these two metals[44]. The method is based on electrolyzing an alkyl halide (preferably the iodide) between a zinc cathode and a tin or lead anode in an undivided cell. The process features cathodic zinc alkylation which supplies the zinc alkyl intermediate for the anodic reaction. A novel zinc-promoted one-step joining reaction of alkyl halides, activated olefins, and carbonyl compounds has been described by Shono et al.[45]. The reaction is thought to proceed through formation of an anionic species from the alkyl halide, followed by addition of the anion to the olefin and subsequent nucleophilic attack of the intermediate on the ketone:



A large variety of starting materials has been reacted together successfully.
The reaction of diarylzinc compounds with copper(I) salts has been found to be an excellent method for preparing stable arylcopper compounds in quantitative yields[46]:

$$R_2Zn + 2CuX \longrightarrow 2RCu + ZnX_2$$

R = Phenyl, o-tolyl, m-tolyl, p-tolyl, 2,6-dimethylphenyl

III. Organozinc compounds as polymerization catalysts

Kuznetsov and co-workers have studied the properties of the poly-(propylenesulfide) obtained in the presence of a diethylzinc/water catalytic system[47]. The polymer has an extremely high molecular weight, which was ascribed to the formation of polymer aggregates during the polymerization on the active sites of the catalyst. In a second paper[48], the modes of formation of the catalytic system were investigated.
A few papers have appeared which deal with the co-polymerization of carbon dioxide with cyclic ethers and sulfides in the presence of organozinc catalysts.
The polymerization of propylene sulfide with carbon dioxide by diethylzinc/resorcinol or diethylzinc/thioresorcinol systems yielded the homopolymer poly(propylene sulfide) almost exclusively[49]. In the presence of a 2 : 1 diethylzinc/pyrogallol system, however, 10 mol% of carbon dioxide was built in in the polymer. The incorporation of carbon dioxide lowered the yields and molecular weights of the polymers, suggesting that it acts as a chain-terminating agent.
True alternating co-polymerization of propylene oxide and carbon dioxide was brought about by a catalyst made by reacting diethylzinc with γ-aluminium oxide[50]. The authors suggest that the active sites are AlOZnEt units formed on the surface of the Al_2O_3.
Another system, active in the alternating copolymerisation of propylene oxide and carbon dioxide has been obtained by mixing poly(p-hydroxystyrene) with diethylzinc[51]. The highest catalytic activity was reached with a molar ratio of phenolic hydrogen to diethylzinc of 1 : 1. The presence of an ethylzinc species in the active centers has been established.
Tsuruta and co-workers have been investigating the stereoselective polymerization of propylene oxide by the well-defined zinc complex $Zn(OMe)_2 \cdot (EtZnOMe)_6$[52]. The complex has high catalytic activity. The diad and triad tacticity of the poly(propylene oxide) obtained suggests that the complex reacts very uniformly and stereoselectively.

A comparative study of triethylaluminium/water and diethylzinc/water catalysts in the polymerization of β-(2-acetoxyethyl)-β-propiolactone has been carried out by Araki et al.[53]. The Et_3Al/H_2O system, in which $(EtAlO)_n$ is the active species, acts via a normal ring-opening mechanism giving poly(β-esters):

$$[OCH(CH_2CH_2OAc)CH_2CO]_n$$

In the presence of the Et_2Zn/H_2O system, with $Et(ZnO)_nEt$ as the active species, the polymerization proceeds by a ring-opening mechanism accompanied by activation of the side-chain ester groups, giving a poly(δ-ester):

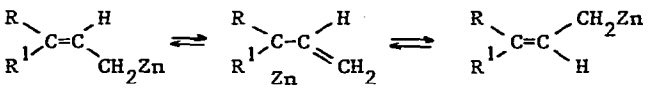
$$[OCH_2CH_2CH(OAc)CH_2CO]_n$$

IV. Physical and spectroscopic studies

Extensive ^1H NMR and kinetic measurements in the temperature range between -125^o and $+180^o$ have been used to determine the structure, thermal stability and decomposition reactions of bis-allylzinc compounds[54]:

$(RR^1C{=}CR^2CH_2)_2Zn$ (R,R^1,R^2 = H,H,H; H,H,Me; H,Me,H; Me,Me,H)

All four compounds are dynamic systems at room temperature and are best described as rapidly equilibrating mixtures of all isomeric σ-allyl forms:



Upon heating above 100^o, the allylzinc compounds decompose rapidly via radical pathways into coupling products. These coupling products exhibit CIDNP, confirming decomposition through random diffusion of alkyl radicals.
The electrochemical reduction of diethylzinc and diphenylzinc complexes with di-2-pyridylketone, 2,2'-bipyridine, and o-phenantroline showed two reductive waves and produced coloured radical anions[55]. EPR spectra of these anions indicated that in all cases the electron was mainly delocalized over the ligand π-orbitals.
The reactions of zinc and cadmium halides with Grignard reagents and methyllithium in THF have been investigated by voltammetric measurements using zinc and cadmium electrodes[56]. It was found that the reaction of zinc and cadmium halides with organomagnesium halides yields only the symmetrical compounds R_2Zn and R_2Cd. The reactions with methyllithium yield successively the symmetrical R_2Zn and R_2Cd compounds followed by ate-complexes like R_4CdLi_2 and R_4ZnLi_2. In the second part of the same paper, the basic properties of THF solutions containing mixtures of one molequivalent of R_2Zn or R_2Cd compound and two molequivalents of magnesium

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or lithium halide were studied. It appeared that the differences in reactivity of R_2Zn or R_2Cd in relation to the salt present are reflected in the basicities of the corresponding solutions.
The H, ^{13}C, ^{111}Cd, and ^{113}Cd NMR spectra of dimethylcadmium in isotropic and anisotropic phases have been recorded and analyzed[57]. The solvent dependence of the Cd-H and Cd-C coupling constants was studied and used in relativistic studies of the cadmium-carbon coupling tensor.

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