Zinc and Cadmium

Literature survey covering the year 1974

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Contents

In 1974 only a small number of papers dedicated to organocadmium chemistry has appeared. The topics treated are closely related to those studied in the field of organozinc chemistry. A separate annual survey of cadmium seemed, therefore, superfluous. This survey deals with papers in the area of organozinc and organocadmium chemistry published in 1974.

I. Preparation of organozinc compounds

Relatively few papers dealing with new organozinc compounds have appeared in 1974.

Moorhouse and Wilkinson described the synthesis of bis (trimethylsilylmethyl) zinc and bis(neopentyl) zinc and their use as alkylating agents in the formation of niobium and tantalum alkyls [1]. Their earlier findings in the case of bis (trimethylsilylmethyl) zinc [AS.83; 1] were confirmed. The reaction of bis (neopentyl) zinc with tantalum pentachloride did not afford readily purifiable products, although the known tris(neopentyl)tantalum dichloride was detected spectroscopically in the reaction mixture when an excess of alkylating agent was used. Both the colourless TMED complex and the red

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Zinc, Survey covering the years 1972–1973 see J. Organometal. Chem., 83(1974) 1–44; Cadmium, Survey covering the years 1972–1973 see J. Organometal. Chem., 83(1974) 45–53.

o-phenantroline and 2,2'-bipyridine complexes of bis (neopentyl) zinc were prepared and characterized. Another example of the use of a dialkylzinc compound for the preparation of an alkyl transition metal compound is the formation of methylvanadyl diisopropoxide in the reaction of dimethylzinc with triisopropyl vanadate in pentane [2]:

$$Me_2Zn + (Me_2CHO)_3\,VO \longrightarrow MeVO(OCHMe_2)_2 + MeZnOCHMe_2.$$

A new type of complex containing four zinc atoms was obtained when phenylzinc phenoxide was reacted with bis (2,2-dimethyl -3,5 -hexanedionato) zinc ($Zn(pac)_2$) [3]:

$$[PhZnOPh]_4 + 4\ Zn(pac)_2 \longrightarrow 2[PhZnOPh.Zn(pac)_2]_2$$

(I)

An X-ray crystal structure determination of (I) showed the presence of a doubly bridged eight-membered Zn_4O_4ring [3] (fig. 1).

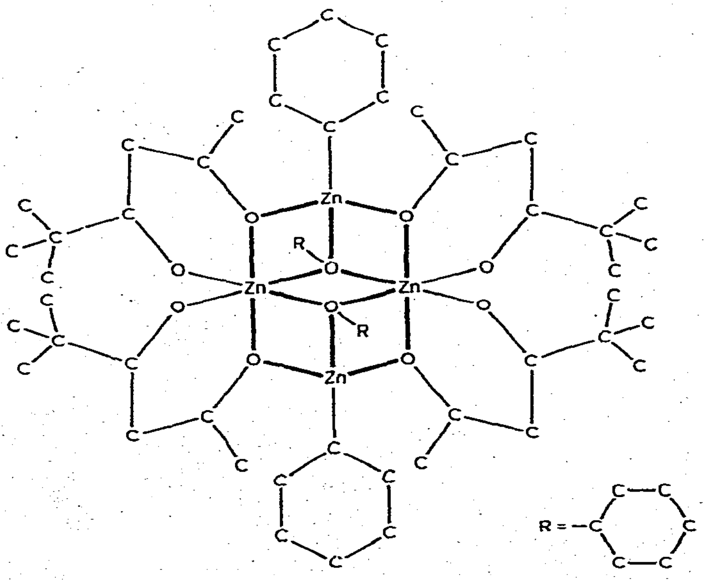


Fig. 1. The schematic structure of the $[PhZnOPh.Zn(pac)_2]_2$ complex. [From J. Boersma, A.L. Spek and J.G. Noltes, J. Organometal Chem., 81 (1974)7].

The dimeric structure contains four- and six-coordinate zinc atoms and two-, three-, and four-coordinate oxygen atoms.

An interesting compound containing both zinc and gold was obtained by de Graaf et.al.[4] from the reaction of diphenylzinc and gold(I)carbonylchloride:

$$4Ph_2Zn + 2Au(CO)Cl \longrightarrow \underset{(II)}{(Ph_3AuZn)_2} + 2\ PhZnCl + 2\ CO$$

The bright-red compound (II) is dimeric is benzene solution and spectral evidence suggests a structure with bridging phenyl groups.

The compound $Ph_2AuZnCl$ was obtained similarly using a 1/1 ratio of Ph_2Zn to Au (CO)Cl [4].

Bis (thioanisolyl) mercury, $[PhSCH_2]_2Hg$, reacts with metallic zinc in boiling xylene solution to give the corresponding organozinc compound. Bis (thioanisolyl)zinc yields thioanisol exclusively when acidolyzed in tetrahydrofuran. Upon heating, the compound tends to eliminate CH_2 leaving zinc thiophenolate $Zn(SPh)_2$[5].

II. Reactions of organozinc compounds

An extensive review on the application of organozinc compounds in organic synthesis has been published by Furukawa and Kawabata. It covers all aspects in this field and contains literature data from 1960 on [6]. Courtois and Miginiac reviewed recent advances in our knowledge of the reactivity of, among others, the allylic organometallic compounds of zinc and cadmium [7].

A. The Reformatsky reaction and related reactions.

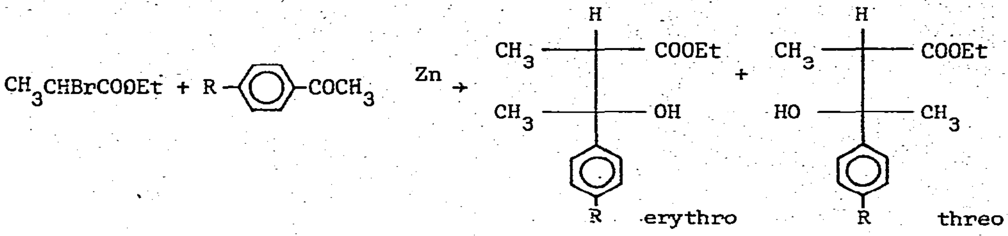
Also in 1974, numerous papers dealing with both the synthetic applications of the Reformatsky reaction, and with the nature of the reagents have appeared in the literature.

Ruppert and White carried out the Reformatsky reaction in a continuous-flow system using a heated column containing granular zinc. Yields of β-hydroxyesters, which were greatly improved as compared with those obtained by conventional methods, are reported. A main factor appears to be the limitation of contact-time between starting materials and products in the reaction zone [8].

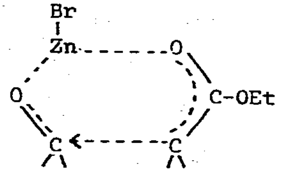
Two papers have appeared which deal with the stereochemistry of the Reformatsky reaction.

Mladenova et al. studied the influence of solvent, temperature, nature of the ester group, and nature of the metal, on the stereochemistry and the reversibility of the Reformatsky reaction of α-bromophenylacetates with benzaldehyde [9]. It appeared that both the amount of threo isomer and the reversibility of the reaction increase with the solvent polarity.

Balsamo et al. obtained direct evidence for equilibration in the Reformatsky reaction of ethyl α-bromopropionate with p-substituted acetophenones [10].



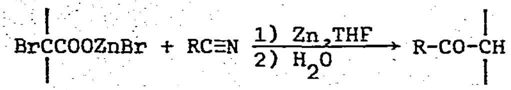
The erythro/threo ratio appears to increase with the reaction time until a constant value is obtained. This phenomenon is interpreted in terms of initial kinetic control and a slower equilibration of the diastereoisomers in the reaction medium. A six-membered transition state is proposed, in which the counter-ion $ZnBr^+$ coordinates with the two carbonyl-oxygen atoms:



The nature of the acetophenone substituent influences the initial isomer ratio, and greater electron-donating capacity increases the equilibration rate, but the erythro/threo ratio remains unaffected. In a later paper, the same authors describe the preparation of a series of erythro and threo-ethyl-3-hydroxy-2-methyl-3-(p-substituted phenyl) butyrates: $MeCH(COOEt)CMe(OH)C_6H_4$ R-p. (R = MeO, Me, H, F, Br, Cl) [11].

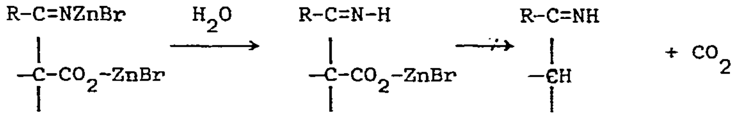
The PMR spectra are discussed and the observed chemical shifts are rationalized using the diamagnetic anisotropy of the phenyl group, and the deshielding effect of the carbonyl group as the main causes for the differences observed between the various possible diastereoisomers.

Bellasoued and Gaudemar have extended the use of the Reformatsky reagent of the bromozinc salt of an α-bromoacid [AS 83;10], instead of the usual α-bromoesters, to the reaction with nitriles [12]. Ketones are obtained in good yield after neutral hydrolysis:



$$\mathrm{Br\underset{|}{\overset{|}{C}}COOZnBr + RC{\equiv}N \xrightarrow[2)\ H_2O]{1)\ Zn,THF} R\text{-}CO\text{-}\underset{|}{\overset{|}{C}}H}$$

Also nitriles with particularly mobile α-hydrogen atoms, like benzylcyanide, which do not give addition products when reacted with Grignard reagents, react with these Reformatsky reagents to give the corresponding ketones. The authors tentatively suggest a reaction mechanism involving an imino-zinc salt which spontaneously decomposes into a ketimine, which subsequently hydrolyses to the product ketone:



$$\begin{array}{c}\mathrm{R\text{-}C{=}NZnBr}\\ |\\ \mathrm{-\underset{|}{C}\text{-}CO_2\text{-}ZnBr}\end{array} \xrightarrow{H_2O} \begin{array}{c}\mathrm{R\text{-}C{=}N\text{-}H}\\ |\\ \mathrm{-\underset{|}{C}\text{-}CO_2\text{-}ZnBr}\end{array} \longrightarrow \begin{array}{c}\mathrm{R\text{-}C{=}NH}\\ |\\ \mathrm{-\underset{|}{C}H}\end{array} + CO_2$$

In the Reformatsky reaction of ethyl α-bromoisovalerate with bis (n-butoxymethyl)-tert.-butylamine, a mixture of products is obtained [13]:

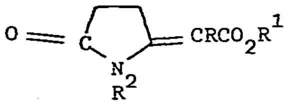
$$Me_2CBrCOOEt + (BuOCH_2)_2NCMe_3 + Zn \longrightarrow$$

$Me_3CNHCH_2CMe_2COOEt$	30%
$Me_3CNMeCMe_2COOEt$	7%
$Me_3CNMeCH_2CMe_2COOBu$	36%
$Me_2CHCOCMe_2CHCOOEt$	15%

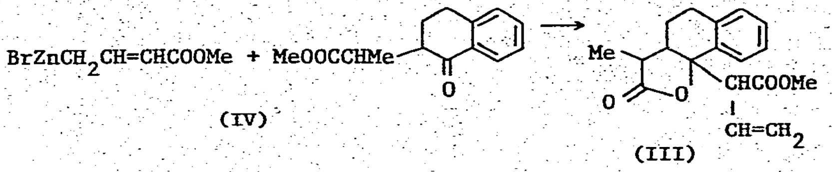
The reaction of ethylbromoacetate, zinc and 2,3-disubstituted acroleins yields unsaturated β-hydroxy acids [14]:

$$RCH{=}CR'CH{=}O + BrZnCH_2COOEt \longrightarrow R\text{-}CH{=}CR'\text{-}CHOH\text{-}CH_2COOH.$$

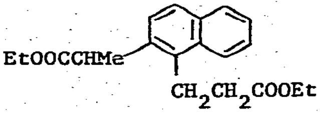
These acids were converted by decarboxylation and dehydration into the corresponding 3,4-disubstituted butadienes.
A series of eight enamido esters of the type:



(R = H, Me; R^1 = Et, t-Bu; R^2 = H) was obtained by the Reformatsky reaction on succinimide [15]. The lactone (III) was formed in the Reformatsky reaction of $BrCH_2CH{=}CHCOOMe$ with the 1-tetralone (IV) [16]:

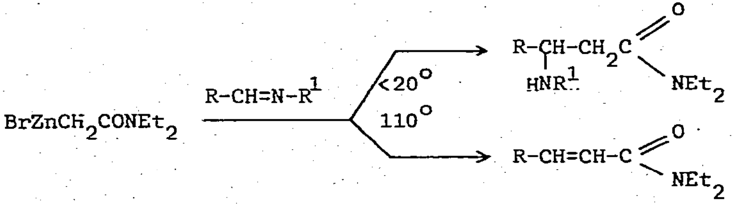


The product from the Reformatsky reaction of 1-(3-ethoxypropyl)-2-tetralone with ethyl bromoacetate gave only the naphthalene (V) on careful dehydration [16]:

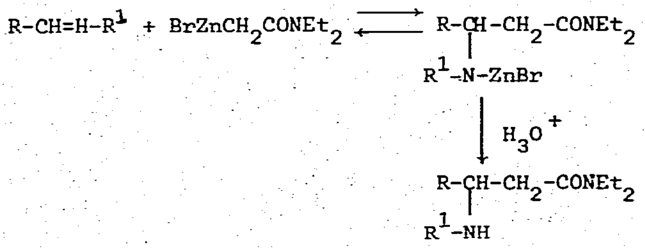


(V)

Gaudemar and co-workers have extended their research on Reformatsky-type reactions of α-bromoamides to the reaction with imines [17]. At low (< 20°) temperatures, β-aminoesters are obtained exclusively, whereas the reaction, when carried out at 110°, yields varying proportions of α-ethyleneamides, depending on the nature of the starting imine:

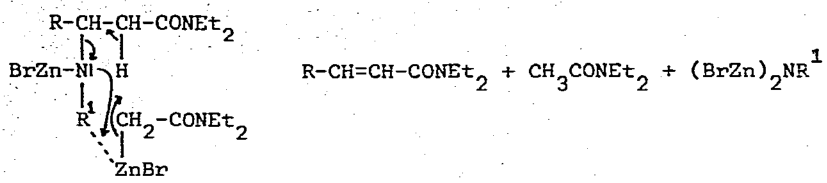


The formation of β-lactams, obtained when imines are reacted with normal Reformatsky reagents, was not observed. The authors propose a mechanism for the formation of both types of reaction products based on two subsequent reactions, i.e. 1) formation of an amino-amide:



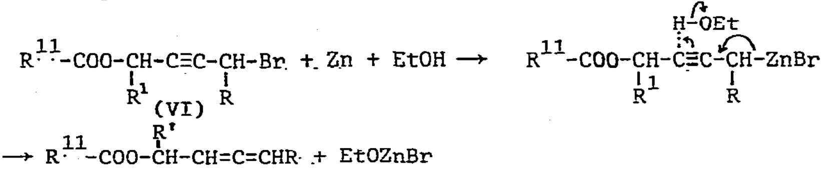
$$R\text{-}CH{=}H\text{-}R^1 + BrZnCH_2CONEt_2 \rightleftarrows \underset{R^1\text{-}N\text{-}ZnBr}{R\text{-}CH}\text{-}CH_2\text{-}CONEt_2 \xrightarrow{H_3O^+} \underset{R^1\text{-}NH}{R\text{-}CH}\text{-}CH_2\text{-}CONEt_2$$

2) deamination of the amino-amide:



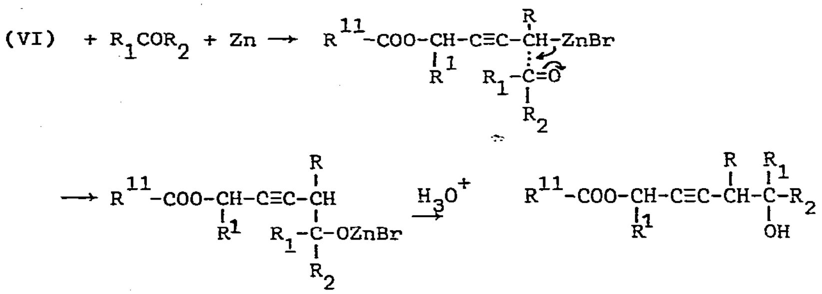
$$R\text{-}CH{=}CH\text{-}CONEt_2 + CH_3CONEt_2 + (BrZn)_2NR^1$$

Although no stable Reformatsky reagents could be obtained from esters of γ-halo-α-acetylenic alcohols, the esters react with zinc in the presence of ethanol giving esters of α-allenic alcohols which could be saponified to the corresponding alcohols [18]:



$$R^{11}\text{-COO-}\underset{R^1}{CH}\text{-C}\equiv\text{C-}\underset{R}{CH}\text{-Br} + Zn + EtOH \rightarrow R^{11}\text{-COO-}\underset{R^1}{CH}\text{-C}\equiv\text{C-}\underset{R}{CH}\text{-ZnBr} \rightarrow R^{11}\text{-COO-}\overset{R'}{CH}\text{-CH=C=CHR} + EtOZnBr$$

When the reactions were carried out in the presence of ketones, monoesters of α, β-acetylenic glycols were obtained:

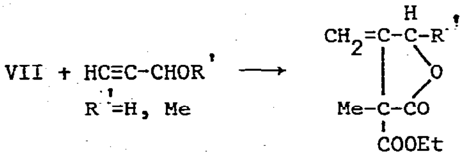


$$(VI) + R_1COR_2 + Zn \rightarrow R^{11}\text{-COO-}\underset{R^1}{CH}\text{-C}\equiv\text{C-}\overset{R}{CH}\text{-ZnBr} \rightarrow R^{11}\text{-COO-}\underset{R^1}{CH}\text{-C}\equiv\text{C-}\overset{R}{CH}\text{-}C(OZnBr)R_1R_2 \xrightarrow{H_3O^+} R^{11}\text{-COO-}\underset{R^1}{CH}\text{-C}\equiv\text{C-}\overset{R}{CH}\text{-}\underset{OH}{\overset{R_1}{C}}\text{-}R_2$$

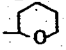
L. Miginiac and co-workers found that the Reformatsky-type reagent formed from ethyl (methylbromo)malonate and zinc, (VII), reacts easily with propargyl derivatives to give addition products of several types, depending on the nature of the propargyl substituent group [19]:

$BrZn\text{-}C(Me)(COOEt)_2 + HC\equiv C\text{-}R$:

(VII)



$\text{VII} + \text{HC}{\equiv}\text{C-CH}_2\text{OR}' \longrightarrow \text{CH}_2\text{=CH(CH}_2\text{OR}')\text{CMe(COOEt)}_2 +$

R' =Bu,  $+ \text{R}'\text{OCH}_2\text{-CH=CH-CMe(COOEt)}_2$

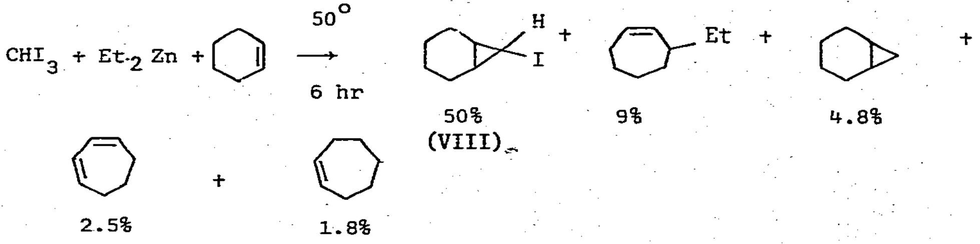
$\text{VII} + \text{HC}{\equiv}\text{C-CH}_2\text{-NHEt} \rightarrow$

$\text{VII} + \text{HC}{\equiv}\text{C-CH}_2\text{-NEt}_2 \rightarrow \text{CH}_2\text{=C(CH}_2\text{-NEt}_2)_2\text{-CMe(COOEt)}_2 +$

$+ \text{Et}_2\text{N-CH}_2\text{-CH=CH-CMe(COOEt)}_2$

B. Carbenoid reactions

Only one paper this year deals with carbenoid reactions. Miyano and Hashimoto described a convenient route for the synthesis of the rather unaccessible iodocyclopropanes [20]. When CHI_3 is reacted with Et_2Zn in neat cyclohexene at 0°, a 50% yield of 7-iodonorcarane is obtained, together with several by-products:



(VIII)

The byproducts were shown to be formed by reaction of EtZnX (X=Et or I) with the syn-form of (VIII).

The reaction was extended to other olefins and the corresponding iodocyclopropanes were obtained in yields varying from 34–70%.

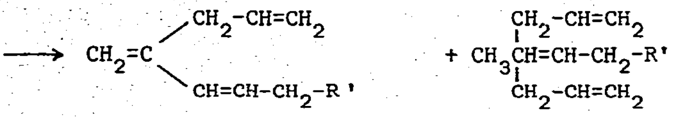
C. Reactions of alkenylzinc compounds with carbon-carbon and carbon-heteroatom unsaturated bonds.

This area of organozinc chemistry continues to attract attention, which is quite understandable in view of the interesting synthetic possibilities offered by these reagents (cf. also ref [7] of this Survey).

Courtois et al. have reacted allylzinc compounds with simple, and with α-substituted enynes [21]:

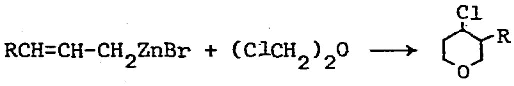
$$CH_2{=}CH{-}CH_2{-}ZnBr + HC{\equiv}C{-}CH{=}CH{-}CH_2{-}R' \longrightarrow$$

$R' = n\text{-}Pr, OH, OBu, NHEt, NEt_2$



(IX) (X)

Similar reactions were carried out with γ-substituted allylzinc bromides. Only single-, or double 3,4-addition is observed.
For R' = n-Pr and Bu, only product (IX) was formed.
In the other cases, mixtures of both products (IX) and (X) were formed.
Tetrahydropyrans were synthesized by the reaction of allyl halides with bis(chloromethyl)ether and zinc metal [22]:

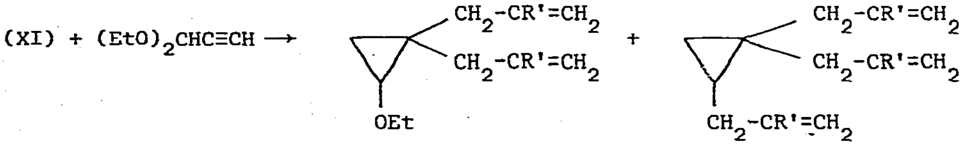


Frangin and Gaudemar studied the reactivity of allylzinc bromides (XI) towards alkynes, α-acetylenic acetals, alcohols and vinylmagnesium bromides [23]:

$$CH_2{=}CR'CH_2ZnBr + RC{\equiv}CH \longrightarrow CH_2{=}CRCH_2CR'{=}CH_2 + MeCR(CH_2CR'{=}CH_2)_2$$

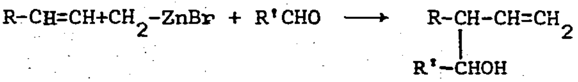
(XI, R' = H, Me)   (RC≡CMgBr)

$$(XI) + CH{\equiv}CCH_2OH \longrightarrow CH_2{=}CR'CH_2C(CH_2OH){=}CH_2$$



$$(XI) + CH_2{=}CHMgBr \longrightarrow CH_2{=}CR'{-}CH_2CH_2{-}CH{=}CHCH_2CH_2CR'{=}CH_2$$

When alkenylzinc reagents of the types $CH_2{=}CH{-}CH{=}CH{-}CH_2ZnBr$ and $C_6H_5{-}CH{=}CH{-}CH_2{-}ZnBr$ are reacted with aldehydes, only the branched alcohols are formed when the reaction is carried out at room temperature [24]:

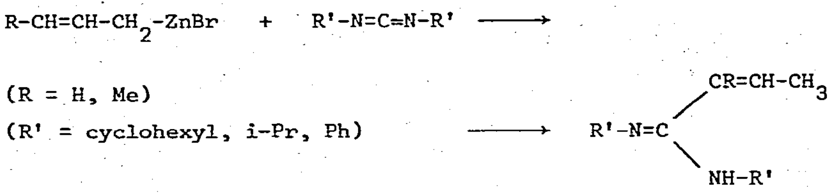


$$R{-}CH{=}CH{+}CH_2{-}ZnBr + R'CHO \longrightarrow R{-}CH(CH(OH)R'){-}CH{=}CH_2$$

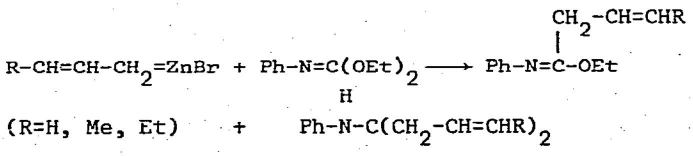
(R = Me, Ph)
(R' = Me, Et, n-Pr, i-Pr, n-Hex, Ph, Et-CH=CMe-)

Carrying out the reaction at elevated temperatures in polar solvents, produces the linear alcohols. The authors conclude that this conversion occurs via the reversed reaction and that the initial reaction is kinetically controlled. Similar reactions with ketones at ambient temperatures yield mixtures of branched and linear alcohols [25].
The amount of linear alcohol formed increases with the bulk of the alkyl groups of the ketone. Like in the foregoing case [25], heating of the reaction mixture produces the linear alcohols exclusively.

Allylzinc bromide and 2-butenylbromide react with carbodiimides giving amidines resulting from 1,4-addition, even in the presence of a large excess of organozinc reagent [26]:



The product amidines always have conjugated structures as a result of intermediate isomerization.
The same authors have compared the reactivities of similar alkenylzinc reagents and corresponding magnesium and lithium reagents, towards an iminocarbonate, an isourea and a guanidine derived from aniline [27]. In the case of zinc, only the isourea derivative reacts appreciably:



$$R\text{-}CH{=}CH\text{-}CH_2{=}ZnBr + Ph\text{-}N{=}C(OEt)_2 \longrightarrow Ph\text{-}N{=}\overset{\overset{CH_2\text{-}CH=CHR}{|}}{C}\text{-}OEt \qquad (XII)$$

$$(R=H,\ Me,\ Et) \qquad + \qquad Ph\text{-}\underset{H}{N}\text{-}C(CH_2\text{-}CH{=}CHR)_2 \qquad (XIII)$$

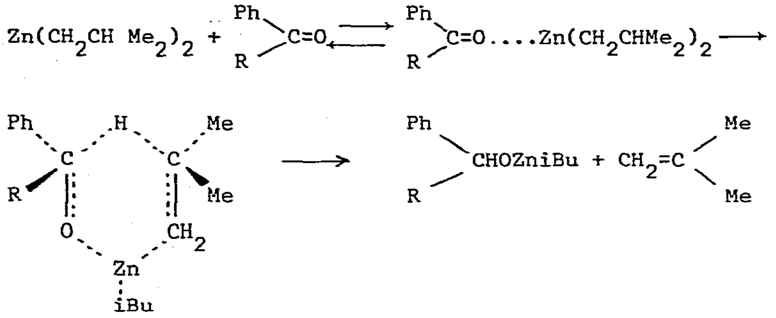
A mixture of (XII) and (XIII) was obtained only for R=H. In that case, also a small amount of a product (XIV) resulting from addition of 2 equivalents of allylzinc bromide was found:

$$C_6H_5\text{-}NH\text{-}C(CH_2\text{-}CH{=}CH_2)_2\text{-}(CH_2)_3\text{-}CH_2\text{-}CH{=}CH_2 \qquad (XIV)$$

In both other cases, (XII) was obtained exclusively.

D. Miscellaneous reactions of organozinc compounds.

Lardicci et al. have continued their work on the asymmetric reduction of ketones by chiral dialkylzinc compounds [28] [29] [AS. 83; 30]. The essential feature of this type of reduction appears to be the difference in chiral environment of the hydrogen atoms available for transfer to the carbonyl carbon atom of the ketone [28]. In a later paper, the reactivity of dialkylzinc compounds having β-branched alkyl groups towards a series of alkyl phenyl ketones was studied. At 86° in the absence of solvents the only product formed is the corresponding carbinol [29]. A cyclic six-membered transition state is assumed in these reductions:



The reactivity of dialkylzinc and dialkylcadmium compounds towards chiral alcohols has been investigated by Deffieux et al. [30].
Primary alcohols and 1,2-diols appear to be more reactive than secondary alcohols in the case of dialkylzinc compounds, whereas in the case of dialkylcadmium compounds secondary alcohols are more reactive than primary, but less reactive than 1,2-diols. The reaction kinetics were followed by polarimetry. Some reaction products of the type $[(EtZnOR)_6 . Zn(OR)_2]$ and $[(EtZnOR)_x . (Zn(OR)_2)_y]$ (x/y is ∿ 1) were identified by PMR spectroscopy.

Inoue and co-workers made the interesting observation that, contrary to what might be expected, the ethyl-zinc group in ethylzinc carboxylates is more reactive towards methanol and pyrrole than the ethyl group in diethylzinc [31]:

$$\text{"EtZnOOCR"} + CH_3OH \longrightarrow \text{"}CH_3OZnOOCR\text{"} + C_2H_6$$

$R = Me, CF_3, Ph$

Molecular weight determinations showed these "ethylzinc carboxylates" to be associated into trimers. The observed increased reactivity towards methanol and pyrrole is discussed in terms of the electron-withdrawing effect of the carboxylate group enhancing the ability of the zinc atom to coordinate with the incoming proton-active reagent.

Thermo- and photo-reactions of diphenylzinc with polychloromethanes were studied [32]. In the thermoreactions, diphenylzinc was reacted with chloroform and carbon tetrachloride at 80-100° to give the following product mixture:

$$\begin{array}{lllllllll} Ph_2Zn & + \ CHCl_3 & \xrightarrow{\Delta} & C_6H_6 & + \ Ph\text{-}Ph & + \ Ph_3CH & + \ PhZnCl & + \ ZnCl_2 & \\ \quad 1 & & & 0.51 & \quad 0.04 & \quad 0.45 & \quad 0.11 & \quad 0.89 & \text{mole} \end{array}$$

$$\begin{array}{lllllllll} Ph_2Zn & + \ CCl_4 & \xrightarrow{\Delta} & PhCl & + \ Ph\text{-}Ph & + \ Ph_4C & + \ PhZnCl & + \ ZnCl_2 & \\ \quad 1 & & & 0.15 & \quad 0.09 & \quad 0.25 & \quad 0.23 & \quad 0.77 & \text{mole} \end{array}$$

The presence of a carbene intermediate was detected by the formation of 7,7-dichloronorcarane after addition of cyclohexene to the reaction mixtures. The corresponding photoreactions were much cleaner:

$$Ph_2Zn + CHCl_3 \xrightarrow{h\nu} PhZnCl + PhH$$

$$Ph_2Zn + CCl_4 \xrightarrow{h\nu} PhZnCl + PhCl$$

"Ate" complexes of the type $CaZnR_4$ appear to be much more reactive than either R_2Zn or R_2Ca compounds towards ketones [33]. The yields and addition/reduction ratios are greater than those observed in mixed organocalcium compounds RCaI. The stoechiometry of the reaction corresponds to one equivalent of "ate" complex to two equivalents of ketone, i.e. two of the four ethyl groups present are available for reaction.

Similar "ate" complexes derived from zinc and calcium, strontium, and barium were used as anionic catalysts in the copolymerisation of butadiene with styrene [34]. Whereas the barium-based catalyst gave copolymers containing mainly _trans_-1,4 units, the calcium- and strontium-based catalysts gave predominantly copolymers with _cis_-1,4 units.

Mehta and Kapoor described a simple, non-reductive procedure for the dehalogenation of organic halides to hydrocarbons using zinc in DMF, followed by hydrolysis [35]. In the case of _gem_-dibromocyclopropanes, monobromocyclopropanes, allenes and fully saturated cyclopropanes are obtained [36]. Only in certain cases this procedure has preparative value.

III. Reactions of organocadmium compounds

Emptoz and Huet [37] found that when dimethylcadmium, diphenylcadmium, and di-p-tolylcadmium were reacted with benzyl halides in benzene or ether mainly substitution products of the type $PhCh_2R$ are obtained:

$$R_2Cd + PhCH_2X \longrightarrow PhCH_2R + RCdX$$

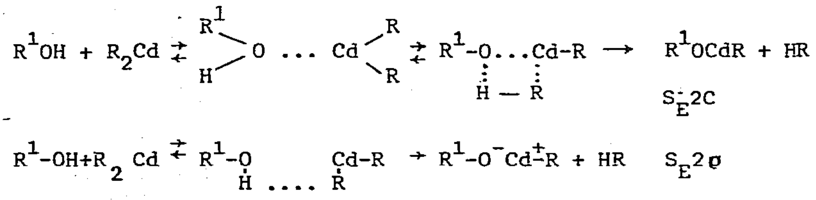
(R = Me, Ph, p-tolyl)
X = Cl, Br

Also, in some cases, small amounts of the coupling product $PhCH_2CH_2Ph$ were found. When the reactions were carried out in benzene solution, alkylation of the benzene was observed and the reaction rate increased considerably. The arylcadmium compounds appeared to be much more reactive than dimethylcadmium. The presence of magnesium bromide has an overall accelerating effect, but increases the coupling reaction.

The same authors made a comparative study of the acidolysis of diethyl compounds of magnesium, zinc and cadmium [38]. In the reaction with 1-hexyne, the order of increasing reactivity was found to be

$$Et_2Cd < Et_2Zn < EtMgX < Et_2Mg.$$

Also with iso-amylalcohol diethylzinc reacts much faster than diethylcadmium. Kinetic measurements show that the reaction of diethylcadmium with alcohols proceeds by an S_E2o mechanism in basic solvents like THF, dimethoxyethane and TMED. In diethyl ether, anisole or benzene, the mechanism is S_E2c:



When other, more acidic proton-active compounds are reacted, in most cases a S_E2o mechanism is observed.

New, stable compounds with tin-cadmium bonds were synthesized by the hydrostannolysis of diethylcadmium [39]:

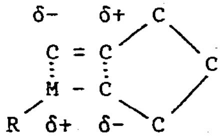
$$Et_2Cd + (Me_3CCH_2)_3SnH \longrightarrow [(Me_3CCH_2)_3Sn]_2Cd.$$

IV. Physical and spectroscopic studies of organozinc and organocadmium compounds.

Calculated and experimental values of $\Delta H^{o}f(g)$ and $\Delta H^{o}f(l)$ for a series of primary dialkylzinc compounds were given by Smith [40]. The agreement between calculated and experimental values is satisfactory. Shinkarev calculated thermodynamic functions (S^{o}, Cp^{o}, $G^{o}-H^{o}/T$ and $\Delta H/T$) for dimethylzinc and hexadeuterodimethylzinc using molecular and spectroscopic data [41]. An ideal-gas behaviour between 173° and 1500° was assumed.

A spin-trapping technique was used to study the model catalyst system Et_2Zn/cumene hydroperoxide [42]. ESR spectra were obtained when radical species were trapped by 2-methyl-2-nitrosopropane. An intense, stable nine-line signal was observed when the cumene hydroperoxide /Et_2Zn ratio was 0.5 to 2.2.

In a full paper (cf.AS.83;37), Denis et.al. reported on the PMR spectra of group II-metal derivatives of terminal alkenes [43]. Di-3-butenyl-and di-5-hexenylzinc in contrast with di-4-pentenylzinc, exhibit normal PMR parameters and the concept of metal-olefin association is not required to interpret these parameters. Most likely, the chain lengths are not appropriate for metal-olefin interaction. The occurrence of intramolecular cyclization in the di-5-hexenyl magnesium and zinc derivatives is thought to proceed via an internal addition-transition state:



Levy and de Loth made a UV-photoelectron spectroscopic study of the basicity of some cyclic aliphatic ethers and their coordination behaviour towards dimethylzinc [44]. The photoelectron spectra showed that the tetrahydropyran. 0.5 $ZnMe_2$ complex was more stable than the oxirane.0.5 $ZnMe_2$ complex, in agreement with the basicity predictions.

A comparative study by the same technique, of the complexation of the two Lewis acids $AlMe_3$ and $ZnMe_2$ with nitrogen, oxygen, and sulfur containing bases showed that $ZnMe_2$ is a "softer" acid than $AlMe_3$ [45].
The formation of both $ZnMe_2.L$ and $ZnMe_2.L_2$-type complexes could be detected.

In order to elucidate some of the factors influencing the catalytic activities of group IIB organometallic compounds, Tsuruta and co-workers measured the infrared frequency shifts of diethylcadmium in a variety of solvents, including oxygen- and sulfur-containing species [46]. Linear relationships were observed for the plots of the frequency shifts δV(C-Cd-C) versus δV(C-Zn-C) of diethylzinc and δV(C-Cd-C) versus δV(O-D) of MeOD.

Deviations of the plots for the systems containing diethylcadmium and cyclic sulfides were interpreted in terms of dative backbonding from the occupied 4d orbital of cadmium to the vacant 3d orbital of sulfur in solvent complexes. The enhanced reactivity of cadmium-sulfur compounds towards propylene oxide, as compared with that of cadmium-oxygen compounds, is considered to be also caused by backbonding, making the cadmium in the cadmium sulfur compound a "harder" acid.

Tamir et al. studied the photofragmentation dynamics of dimethylcadmium [47]. A theoretical analysis showed asymmetric dissociation to be the major decay mode. The experimental and computational results in the case of dimethylcadmium confirmed the theoretical analysis.

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