ZINC AND CADMIUM

LITERATURE SURVEY COVERING THE YEAR 1975

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Contents

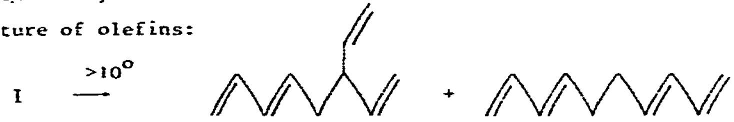
I. Preparation of organozinc compounds

Crystalline dipentadienylzinc-tetrahydrofuranate has been prepared by the reaction of pentadienyl potassium with zinc chloride in THF at low temperature [1]:

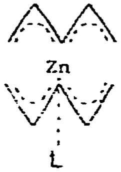
$$2KC_5H_7.THF \quad + \quad ZnCl_2 \xrightarrow[THF]{-20^\circ} \underset{I}{Zn(C_5H_7)_2.THF} \quad + \quad 2KCl$$

Zinc and cadmium, Literature Survey covering the year 1974, see J. Organometal. Chem., 115 (1976) 1-16.

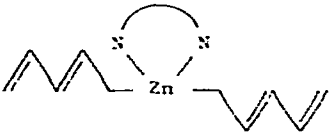
I is thermally unstable and decomposes at 10°C into metallic zinc and a mixture of olefins:



Complexes of I with strong donor ligands like trimethylamineoxide or with chelating ligands like TMED are stable up to 80°.
^{13}C NMR investigations showed that I and its complexes with Et_3N or Et_3NO are planar and have a W-shaped conformation with delocalized pentadienyl groups at 6°C:



In contrast, complexes with chelating ligands have a terminally σ-bonded configuration:



which at higher temperatures (80°C) changes reversibly into planar molecules having the W-shaped structure.

Dipentadienylzinc complexes add to ketones to give dienylalcohols after hydrolysis. The yield of products resulting from reaction at C 1 increased with the bulkiness of the alkylsubstituents bound to the carbonylgroup. With small ketones, only products were found which resulted from reaction at [illegible].

Lehmkuhl and Olbrysch have found that not only allylic organozinc compounds add across carbon-carbon double bonds, but that also tert. alkylzinc compounds, and to a much smaller extent also sec. alkylzinc compounds, show these reaction .

Di-tert-butylzinc adds to a large number of 1-alkenes and 1,3-diolefins between -20 and +75°C. The reaction with ethylene at 50-70° under 60 atmospheres of ethylene pressure yields bis(3,3-dimethylbutyl)zinc (II) in nearly quantitative yield:

$$((CH_3)_3C)_2Zn + CH_2{=}CH_2 \xrightarrow[60\ atm]{50-70^{o}} [(CH_3)_3CCH_2CH_2]_2Zn$$

II

II, being a primary dialkylzinc compound, does not react further. With terminal olefins, di-tert-butylzinc reacts nearly exclusively to give 1:1 addition products in which metal addition to C 2 of the olefin has occurred. Asymmetrically disubstituted olefins react only very slowly. 1,3-Butadiene reacts with di-tert-butylzinc in a 1,4 addition to give bis(5,5-dimethyl-2-hexenyl)zinc(III):

$$((CH_3)_3C)_2Zn \quad + \quad H_2C{=}CH{-}CH{=}CH_2 \xrightarrow{-20^{\circ}} [(CH_3)_3CH_2CH{=}CHCH_2]_2Zn$$

III

III is obtained as a mixture of cis and trans isomers in 1:2 ratio. The reaction of di-tert-butylzinc with styrene yields 1:1 adducts only when stoechiometric amounts of styrene are used at relatively low temperatures. In other cases, polystyrene, phenylalkanes and phenylalkenes are found after hydrolysis. The mechanism of this reaction probably consists of a combination of a stepwise-addition reaction and a radical-initiated polymerization reaction.

Bis(diphenylmethyl)zinc has been prepared by reacting diphenylmethylsodium as its dioxanate with zinc chloride in THF [3]:

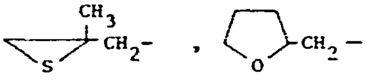
$$Ph_2CHNa.C_4H_8O_2 \quad + \quad ZnCl_2 \xrightarrow{THF} [Ph_2CH]_2Zn.THF \quad + \quad NaCl$$

IV

The crystalline THF complex IV is thermally unstable and decomposes within a few hours at room temperature into metallic zinc and tetraphenylethane. The THF-free dialkylzinc was obtained when the complex was evacuated at temperatures below 0°C. Its thermal stability is even less than that of IV. Complexation of bis(diphenylmethyl)zinc with nitrogen- and phosphorus containing ligands increases its thermal stability and decreases its sensitivity towards hydrolysis and oxidation.

The synthesis of phenylzinc alkoxides (V), in which the alkoxy group is an oxetane, or thietane derivative, was claimed in a patent [4]:

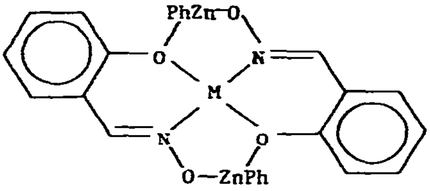
PhZnOR R=



etc.

V

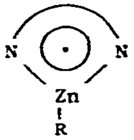
Salicylaldoxime complexes of Ni(II), Pd(II) and Cu(II) containing phenylzinc groups (VI) have been prepared by reacting diphenylzinc with the salicylaldoximates of the corresponding ions [5]:



M=Ni^{II}, Pd^{II}, Cu^{II}

VI

Paramagnetic monoalkylzinc species VIII, stabilized by 2,2'-bipyridine, are formed when LiBipy is reacted with various alkylzinc halides at -100°C [6].



VII

N N = 2,2'-bipyridine

R = Me, Et, iPr

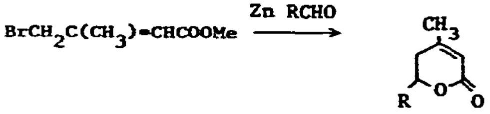
The observations that the half-life times of the radical species appeared to depend only on the nature of group R was used as a proof for the presence of species VII. The ESR spectra showed that the radicals contain symmetrical Bipy units. No hfs by zinc, or by the alkylgroup bound to zinc was found.

II. Reactions of organozinc- and organocadmium compounds

A. Reformatsky reaction and related reactions

Also this year, various papers illustrating the usefullness and versatility of the Reformatsky reaction have appeared.
Rieke and Uhm applied the very reactive zinc obtained by reducing a zinc salt with potassium metal in THF, in the Reformatsky reaction [7].
It appeared that with this type of zinc Reformatsky reactions can be carried out at 0°C in diethylether solution giving superior yields.
Also α-chloroesters can be used instead of α-bromoesters, although the yields are not nearly so high. Moreover, the yield of α-hydroxyesters appears to be very dependent on the nature of the anion of the zinc salt used in making the active zinc.

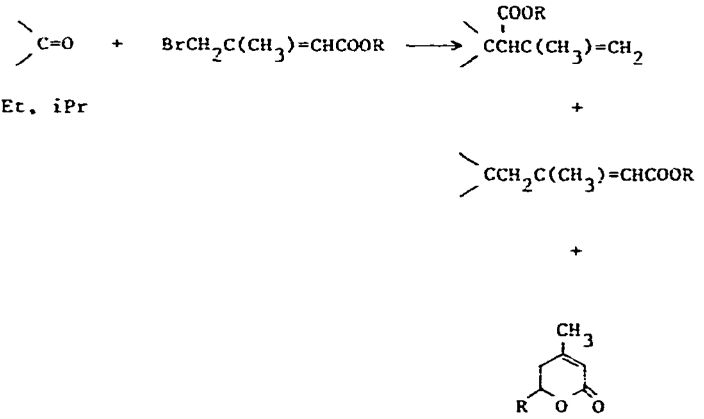
The reaction of a mixture of E and Z isomers of 4-bromo-3-methylbut-2-enoate (methyl-γ-bromosenecioate) with zinc and β-cyclocitral and similar aldehydes yields δ-lactones VIII as the main products [8]:



VIII

This indicates an E to Z inversion during the Reformatsky reaction. When these reactions were carried out with stereochemically pure E and Z-bromoesters, in both cases the same products were formed, disproving earlier reports, which claimed that only the Z isomers were responsible for the formation of the δ-lactones. An allylic rearrangement of the intermediate Reformatsky reagent, as proposed by Couffignal and Gaudemar (AS 83; 15) for zinc derivatives of γ-bromocrotonates, was thought to be responsible.

Couffignal and Gaudemar [9] investigated the same Reformatsky reagent but used ethyl- and isopropylesters instead of methylester. They compared condensations of carbonyl compounds both with preformed Reformatsky reagents in two-step reactions and with the γ-bromosenecioates in one-step reactions. In both cases the same products were obtained, i.e. one hydroxyester which has undergone an allylic rearrangement(IX), two , E and Z, hydroxyesters(X) and a lactone(XI):



$$>C{=}O \;+\; BrCH_2C(CH_3){=}CHCOOR \longrightarrow >C\overset{COOR}{CH}C(CH_3){=}CH_2$$

IX

R=Et, iPr

+

$$>CCH_2C(CH_3){=}CHCOOR$$

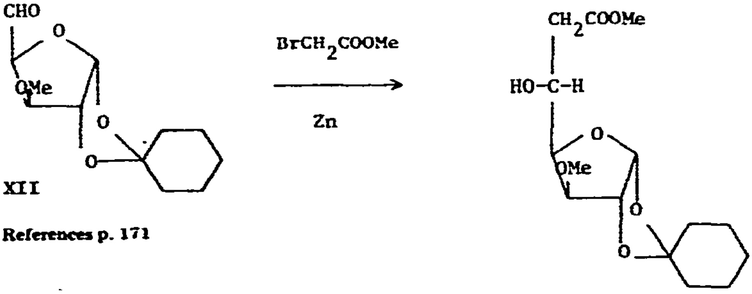
X

+

XI

Also here (cf. ref. 8) the cyclic lactone(XI)appeared to be the main, thermodynamically controlled, product. The influence of temperature, reaction time and nature of the carbonyl substrate were investigated.

The reaction of cyclohexylidenexylopentodialdofuranose (XII), with methylbromoacetate and zinc yielded the β-hydroxyester (XIII) [10]:



XII

XIII

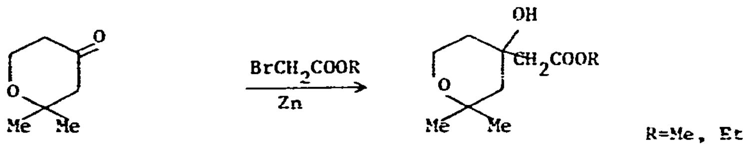
A large series of compounds of the type:

$PhCOCRR'CH_2SR''$ (R = Me, Et, Pr, Ph
R'= H, Me
R''= Bu, All, Pr, Et, i.Bu, iPr)

were prepared by reaction of PhCORR'ZnBr with chloromethylthioethers $ClCH_2SR''$ [11].

The syntheses of steroid dienes and analogs of isobufadienolides have been carried out using the Reformatsky reaction. [12]

The pyron XIV was reacted with zinc and alkylbromoacetates to give pyranacetates XV [13]:



R=Me, Et

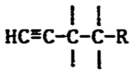
XIV XV

The reactions of carboxylic acid anhydrides with Reformatsky reagents have been used to prepare α-acyloxy-α,β-unsaturated esters [14]:

$$(RCO)_2O \xrightarrow{BrZnCHR'COOEt} RCO_2CR{=}CR'COOEt + RCOCHR'COOEt$$

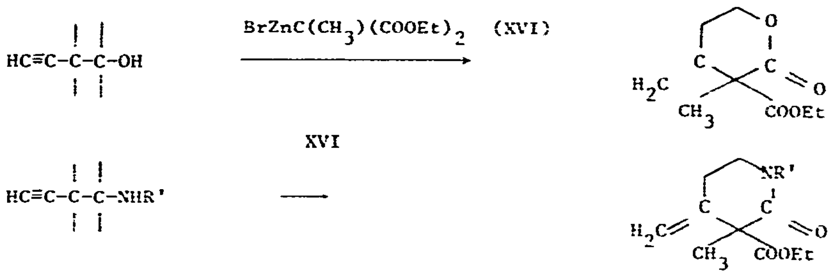
(R= Me, Et, Pr R'= Me, Et, iPr)

L. Miginiac and co-workers [15] have synthesized lactones and lactams by reacting the Reformatsky reagent derived from ethylmethylbromomalonate (XVI) with β-acetylenic compounds of the type:

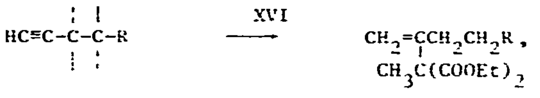


$HC{\equiv}C\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}R$ (R= OH, OR', NHR', NR'_2)

In the cases where cyclisation is possible, (R=OH, NHR') six-membered lactones and lactams were obtained:



When R =OR' or NR'_2, branched products are formed exclusively:

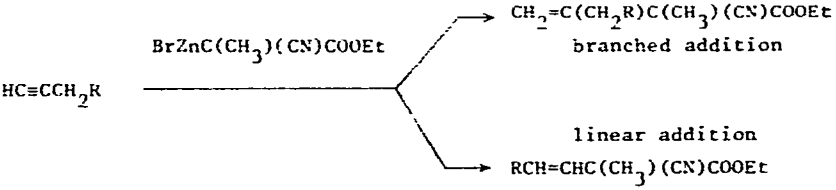


R = OR', NR'_2

The same authors [16] have investigated the addition of the zinc derivative of ethylmethylbromocyanoacetate to the triple bond of propargyl derivatives:

$HC{\equiv}CCH_2R$ (R = alkyl, OH, OR, NHR, NR_2)

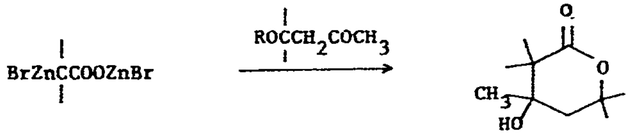
Although the orientation of these addition reactions is generally that observed in the addition to acetylenes, in which branched products are formed, sometimes also linear addition products are obtained if group R is bulky:



Also here, cyclisation to give lactones and lactams takes place if R= OH or NHR.

Bellascued and Gaudemar have extended their study of the reactivity of α-bromosalts of the type $Br{-}\overset{\diagdown\diagup}{C}{-}COOZnBr$ with zinc and carbonyl derivatives to the reactions with β-ketols [17] and benzaldehyde [18].

With β-ketols, these reactions yield mevalolactones (XVII) directly without the interfering secondary reactions observed in the corresponding reactions with normal Reformatsky reagents:

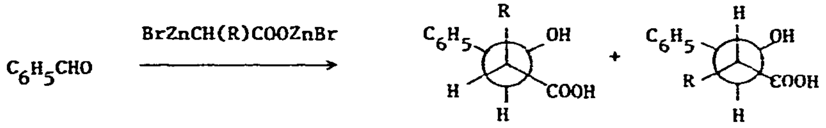


(R= acetyl, dihydropyranyl)

XVII

Although these reactions can be carried out in one step using OH-blocked β-ketols, preparation of the Reformatsky reagent prior to the addition of the ketol has the advantage that polymerisation of the β-ketol is avoided and that unblocked β-ketols can be used. In the latter case, two equivalents of Reformatsky reagent must be used.

The stereochemistry of the reaction of benzaldehyde with α-bromosalts and zinc, yielding α-hydroxy-acids, appears to be independent of the nature of the α-bromosalt, of the metal blocking the acidic function and of the reaction temperature [18]. In every case, the reaction is not very stereoselective and no equilibration between erythro and threo forms of the intermediate aldol stage is observed:



erythro threo

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

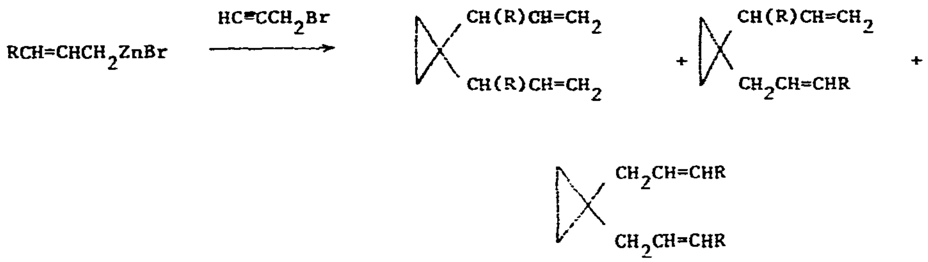
β,γ-Unsaturated organozinc compounds of the general type $RCH{=}CHCH_2ZnBr$ (R=alkyl, alkenyl) add to functionally substituted terminal acetylenes in a 1:1 reaction [19]:

$$RCH{=}CHCH_2ZnBr \xrightarrow{HC{\equiv}CCH_2R'} CH_2{=}C(CH(R)CH{=}CH_2)CH_2R' \quad \text{XVIII}$$

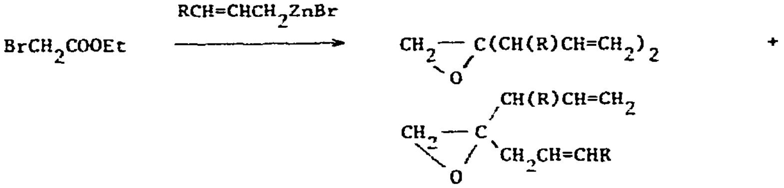
$$CH_2{=}C(CH_2CH{=}CHR)CH_2R' \quad \text{XIX}$$

(R'=alkyl, OH, Br, OMe, NMe_2
R =H, Me, Ph, $CH{=}CH_2$)

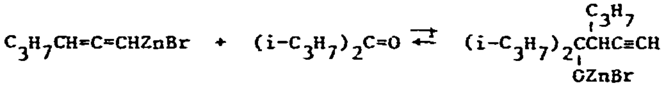
If R' is alkyl, OH, OMe or NMe_2, mixtures of XVIII and XIX are formed in varying proportions, XIX resulting from allylic rearrangement of the organozinc reagent.
If R' is OH, mainly XVIII is formed. Propargylbromide (R'=Br) forms an exception since in this case gem-disubstituted cyclopropanes are obtained as a result of di-addition followed by a 1,3-elimination:



The addition of allylzincbromides to the carbonyl group of α-halocarbonyl compounds has been used to prepare ethylenic halohydrines [20]. In some cases, especially when α-bromocarbonyl compounds were used, the corresponding epoxides were obtained, e.g.:



Moreau has investigated the reversibility of the addition of allenic organozinc compounds derived from $RCHBrC{\equiv}CH$ and $RC{\equiv}CCH_2Br$ to carbonyl compounds [21]. The presence of the equilibrium:

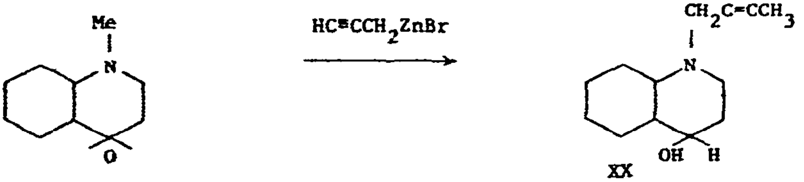


$$C_3H_7CH{=}C{=}CHZnBr + (i\text{-}C_3H_7)_2C{=}O \rightleftarrows (i\text{-}C_3H_7)_2\underset{OZnBr}{C}\overset{C_3H_7}{CH}C{\equiv}CH$$

has been established.

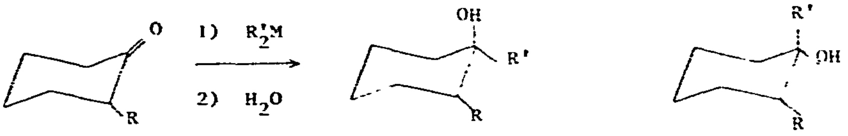
It appeared that the reversibility of these reactions is favoured by steric crowding both in the organozinc compound and in the carbonyl compound, and also by temperature elevation. A similar equilibrium was found in the case of organozinc compounds derived from $RC{\equiv}CCH_2Br$.

The decahydroquinolinol derivative XX was obtained from the reaction of propargylzinc bromide with methyl-1-decahydroquinolinone-4 [22]:



XX

Abenhaim [23] compared the stereochemistry of the addition of dicrotylzinc and of dicrotylmagnesium to methyl- and tert. butyl-substituted cyclohexanones. It appeared that both reagents react predominantly by equatorial attack:



XXI XXII

M = Zn, Mg

R = Me, t-Bu R' = crotyl

In the case of dicrotylzinc, the XXII / XXI ratio is smaller than in the case of dicrotylmagnesium, indicating that the zinc reagent is more stereoselective Some possible reaction mechanisms are discussed.

The reaction of α-ethylenic organozinc compounds with ethylchloroformate gives β-ethylenic esters in good yield [24]:

$$ClCOOEt \xrightarrow{RCH=C(R')CH_2ZnBr} CH_2=C(R')CH(R)COOEt$$

(R = H, Me, Et, Bu

R'= H, Me)

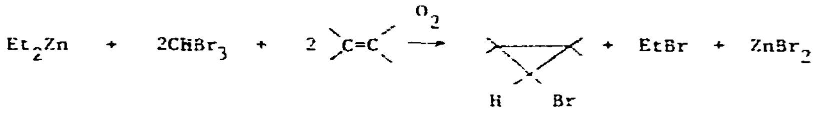
Pornet and L. Miginiac [25] have reacted O-alkylated arylaldoximes with, amongst others, allylzinc bromide. Only two of the five possible reaction products were observed in this case:

$$PhCH=NOEt \xrightarrow{C_3H_5ZnBr} PhCH(C_3H_5)NHOEt \quad (XXIII) \quad + \quad PhNHCH(C_3H_5)_2 \quad (XXIV)$$

XXIII is the result of addition of one allylzinc unit whereas XXIV results from the addition of two allylzinc units accompanied by a rearrangement.

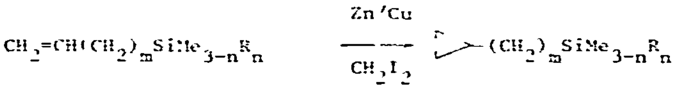
C. Carbenoid reactions of organozinc compounds

Miyano and Hashimoto [26] have continued their work on carbenoid reactions of organozinc compounds. They reported a convenient synthesis of monobromocyclopropanes from olefins using the zincbromocarbenoid reagent obtained from diethylzinc and bromoform in the presence of oxygen:



The yields in these reactions vary between 68 and 85%. Only in the case of styrene, the formation of the carbenoid reagent appeared to be inhibited, suggesting that it is formed by a free-radical chain mechanism. The same reagent is useful in the ring-expansion of alkylbenzenes (cf. A.S. 115; 8).

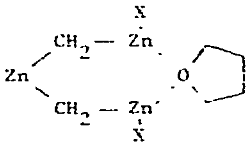
Organosilicon compounds containing a cyclopropyl group (XXV) have been prepared by reacting alkenyl silanes with methylene iodide and zinc/copper couple in a modified Simmons-Smith reaction [27]:



XXV

$m = 0-3$, $n = 0-2$,
$R = EtO, MeO, Cl, F, H$

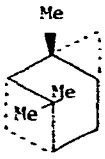
The formation of:



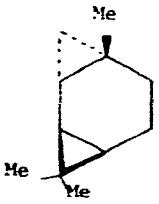
XXVI

from dihalomethanes and activated zinc -- either as a zinc/lead couple or by treatment with HCl -- in THF was claimed in a patent [28]. XXVI has been used to convert a series of 15 ketosteroids into methylene derivatives.

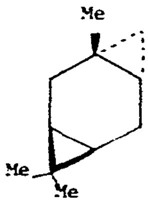
The Simmons-Smith reaction of α-pinene, 2-and 3-carene with methylene iodide and zinc/copper couple yielded XXVII, XXVIII and XIX, respectively [29]:



XXVII



XXVIII

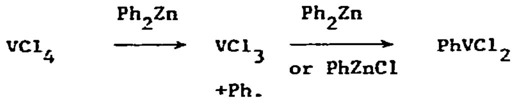


XIX

Similar reactions have been carried out with trans-isolimonene.

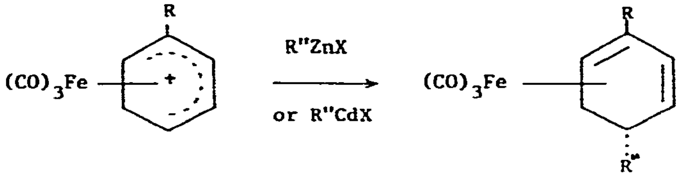
D. Miscellaneous reactions of organozinc and organocadmium compounds

Phenylvanadium compounds of the type $PhVCl_2.YZnCl_2$ in which Y varies from 0.6 to 1 have been obtained by reacting diphenylzinc with vanadium tetrachloride [30]. The phenylvanadium compounds could not completely be freed from zincchloride. The reaction is believed to run via initial formation of $PhVCl_3$ which decomposes immediately into VCl_3 and phenyl-radicals:



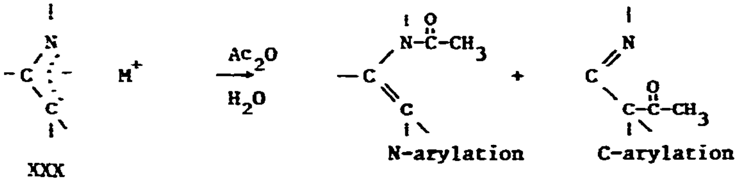
$$VCl_4 \xrightarrow{Ph_2Zn} \underset{+Ph.}{VCl_3} \xrightarrow[\text{or } PhZnCl]{Ph_2Zn} PhVCl_2$$

The direct alkylation of tricarbonylcyclohexadienyliron cationic complexes has been realized using organozinc or organocadmium reagents prepared in situ in ethanol or THF solution from the corresponding Grignard reagent with zinc or cadmium chloride [31]:

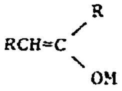


Similar reactions using organolithium or organomagnesium reagents fail because of reductive coupling reactions or decomposition. The organocadmium reagents give superior yields. The alkylation is regioselective in the 2-substituted salts and occurs on the opposite side of the ring to the tricarbonyliron group.

The reactions of acetic anhydride with Schiff bases which had been metallated by organozinc, -cadmium, and -magnesium reagents have been investigated by Thomas [32]:



It appeared that, whereas the nature of the solvent has no influence the nature of the metal is of prime importance. Substitution of magnesium by zinc, and especially cadmium, favours N-arylation over C-arylation. This phenomenon is discussed in terms of the nature of the ambident anions XXX, the species metallated by magnesium having structure XXXI, whereas with zinc, and particularly cadmium, structure XXXII is likely:



XXXI

$$\mathrm{R\underset{M}{\underset{|}{C}}H\underset{O}{\underset{\|}{C}}R}$$

XXXII

Ethylzinc iodide, prepared in THF solution, has been found to isomerize branched alcohols of the type XXXIII into the corresponding linear alcohols [33]:

$$CH_2{=}CHC(CH_3)_2C(OH)(R)(R') \xrightarrow[THF]{C_2H_5ZnI}$$

XXXIII

$$(CH_3)_2C{=}CHCH_2C(OH)(R)(R')$$

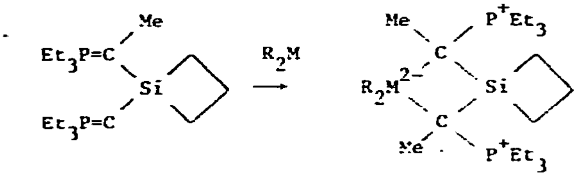
R, R' = Me, Et, nBu, iBu etc.

This way, linear tertiairy alcohols which are important intermediates in natural compound syntheses, can be obtained relatively easily in stereochemically pure form.

The reactions of diethylzinc with peroxides yielded ethane, alkoxy compounds and variable amounts of butane, depending on the nature of the peroxide [34]. Spin-trapping techniques showed the presence of ethyl radicals regardless of the experimental conditions. Alkoxy- or aryloxy radicals were observed in the presence of excess of peroxides. The polymerisation of vinylic monomers initiated by these radical-containing systems has been studied [35].

Lee and Zare [36] investigated the flame-emission spectra of the reactions of ozone with dimethylzinc and diethylzinc in a flow system at low pressure. The chemical behaviour of methyl- and ethyl radicals in the flame is discussed.

The bidentate chelating ligand character of difunctional silacyclobutyl-substituted phosphorylides has been confirmed by reacting one of these species with diethylzinc and dimethylcadmium [37]:



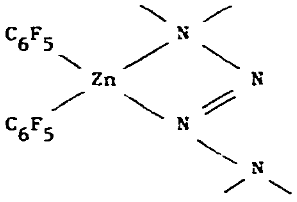
M = Zn, Cd
R = Et, Me

In both cases, 1:1 complexes were formed exclusively. Although both complexes should exist as cis/trans isomers, no evidence thereof could be obtained from NMR spectra. Apparently a rapid ligand-exchange process occurs.

Drago's theory has been applied to complexes of dimethylzinc with various Lewis bases like Et_3N, Et_2 S, Et_2O, Me_3P and THF [38]. A quantitative comparison of these complexes with those of group III A metals showed that dimethylzinc forms weaker complexes.

Structural studies

The structural chemistry of organic compounds of zinc, cadmium and mercury has been reviewed [39].
An X-ray crystal structure determination of bis(perfluorophenyl) tetramethyltetrazenezinc has been reported. The tetrahedrally surrounded zinc atom appeared to be bonded to a single carbon atom of each perfluorophenyl ligand and the 1- and 3-nitrogen atoms of the tetrazene ligand, which exists in the trans-form:



This structure contrasts with earlier reports of complexes of the tetramethyltetrazene ligand with related organometallic compounds. In these cases, a cis-ligand, 1,4-bonded to the metal was assumed. The PMR spectrum of the complex in toluene solution shows only one single absorption of the methyl groups bound to nitrogen in the temperature range from 25° to −75°. A rapid ligand exchange is thought to be responsible.

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