ZINC

LITERATURE SURVEY COVERING THE YEARS 1972 AND 1973

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CONTENTS

I. PREPARATION OF ORGANOZINC COMPOUNDS

The recent literature contains numerous references dealing with new organozinc compounds or new types of organozinc complexes.

So far, the so-called direct synthesis of organozinc compounds starting from zinc metal and organic halides had been restricted to alkylzinc compounds. The zinc powder obtained by Rieke et al. from the reaction of anhydrous zinc bromide with potassium in THF appears to be much more reactive than any form of zinc previously described in the literature in that this material undergoes the direct reaction in high yield with bromobenzene [1].

Zinc metal reacts directly with pentafluoroiodobenzene in a variety of coordinating solvents such as THF, DMA and DMSO to give almost quantitative yields of pentafluorophenylzinc iodide [2]. The reaction of 1,1,1-trifluorotrichloroethane with zinc in ether solvents (dioxan, DME, THF) affords 2,2,2-trifluorodichloroethylzinc chloride which crystallizes with one molecule of solvent and which in ether solution exists in equilibrium with the bis-organozinc compound [3]:

$$CF_3CCl_3 + Zn \xrightarrow{S} CF_3CCl_2ZnCl\cdot(S) \rightleftarrows (CF_3CCl_2)_2Zn + \\ + ZnCl_2\cdot(S)$$

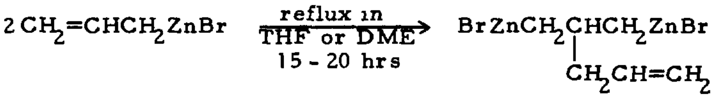
Klabunde et al. have prepared non-solvated fluoro-substituted organozinc compounds by the co-condensation of zinc atoms and fluoroalkyl iodides on a cooled surface. These non-solvated compounds are much more reactive and less stable than those formed in solution. Difluorocarbene is a decomposition product as shown by the presence of tetrafluoroethylene, and trapping with olefins [4].

Di-3-butenylzinc and di-4-pentenylzinc have been prepared by the reaction between the mercury analogs and zinc dust in evacuated sealed tubes in nearly quantitative yield [5]:

$$[H_2C{=}CH{-}(CH_2)_n]_2Hg + Zn \xrightarrow[20\ hrs]{120^\circ} [H_2C{=}CH(CH_2)_n]_2Zn + Hg \qquad (n = 2,3)$$

The preparation of diorganozinc compounds R_2Zn among which diphenylzinc by the reaction of electrolytic zinc dust with triorganoaluminium compounds R_3Al and organic halides RX (X = Cl, Br, I) at 90° - 140° has been claimed in a patent [6].

A novel compound with a bis-1,3-organozinc structure (I) has been obtained by Courtois and Miginiac via dimerisation of allylzinc bromide in refluxing THF or DME [7]:



$$2\,CH_2{=}CHCH_2ZnBr \xrightarrow[\text{15 - 20 hrs}]{\text{reflux in THF or DME}} BrZnCH_2CH(CH_2CH{=}CH_2)CH_2ZnBr$$

(I)

The complex (II) obtained from the 1/1 interaction of dicyclopentadienyldiphenyltitanium and phenyllithium reacts with zinc chloride to form the corresponding zinc complex (III) which is thermally unstable and decomposes at room temperature with the formation of diphenylzinc [8]:

$$\begin{tikzcd}
\underset{\text{(II)}}{2[(C_5H_5)_2TiPh_3]Li} + ZnCl_2 \arrow[r] & {[(C_5H_5)_2TiPh_3]_2Zn} \arrow[d, "\Delta"', "\text{(III)}"] \\
 & (C_5H_5)_2TiPh_2 + Ph_2Zn
\end{tikzcd}$$

Moorhouse and Wilkinson have applied the Grignard method to the preparation of bis(trimethylsilylmethyl)zinc:

$$2\,Me_3SiCH_2MgX + ZnX_2 \longrightarrow \underset{\text{(II)}}{(Me_3SiCH_2)_2Zn} + 2\,MgX_2$$

(II) forms adducts with N-ligands which are much less sensitive than (II), e.g. the 2,2'-bipyridyl and 1,10-phenanthroline complexes are unaffected by air for several days [9].

Reaction of tantalum pentachloride with (II) gives a mixture of $(Me_3SiCH_2)_2TaCl_3$ and $(Me_3SiCH_2)_3TaCl_2$, whereas niobium pentachloride gives mainly $(Me_3SiCH_2)_3NbCl_2$ [9]. An other example of the use of organozinc compounds for the preparation of alkyl transition metal halides involves the preparation of methylniobium(V) chlorides by Fowles et al. by the reaction of niobium(V) chloride and dimethylzinc which gives rise to an equilibrium mixture containing both mono- and di-methylniobium(V) chlorides. $MeNbCl_4$ has not been isolated, but its complexes with bidentate ligands were prepared. Me_2NbCl_3 as well as a series of complexes with mono- and bidentate ligands were obtained in this way [10].

Tebbe observed the occurrence of reversible complex formation between dicyclopentadienyltantalum hydride and diethylzinc:

$$Cp_2TaH_3 + Et_2Zn \rightleftharpoons Cp_2TaH_3ZnEt_2$$

Analogous adducts of dicyclopentadienylniobium hydride were detected by NMR spectroscopy at -20 to -50°, but at room temperature ethane is evolved with formation of a product the proposed structure of which is shown in Fig. 1 [11].

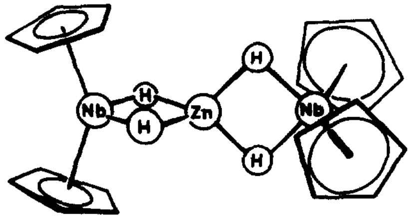


Fig. 1. The proposed structure of $[(C_5H_5)_2NbH_2]_2Zn$ [from F. N. Tebbe, J. Am. Chem. Soc. 95 (1973) 5413].

Thiocyanogen reacts with $Zn(CH_3)_2$, $Zn(C_2H_5)_2$, CH_3ZnOCH_3 and $C_2H_5ZnSC(CH_3)_3$ to form the corresponding hydrocarbon-insoluble zinc thiocyanates [12]:

$$ZnR_2 + (SCN)_2 \longrightarrow RZnSCN + RSCN$$

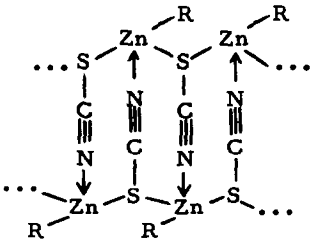
$$(R = CH_3,\ C_2H_5)$$

$$RZnX + (SCN)_2 \longrightarrow XZnSCN + RSCN$$

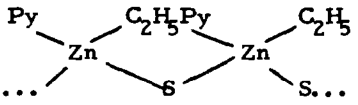
$$(R = CH_3,\ X = OCH_3)$$

$$(R = C_2H_5,\ X = SC(CH_3)_3)$$

Well-defined complexes with 1/1 (e.g. $C_2H_5ZnSCN \cdot Py$) or 1/2 (e.g. $CH_3OZnSCN \cdot 2\,Py$) stoechiometry have been isolated from pyridine solutions of these compounds. According to their properties and IR spectra the organozinc thiocyanates are coordination polymers (IV) with thiocyanate bridges which are partly broken down by pyridine (V) [12].



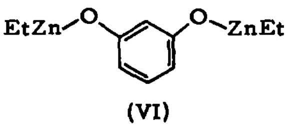
(IV)



(V)

A variety of organozinc compounds has been prepared by acidolysis-type reactions.

Kobayashi et al. have carried out a gas-volumetric study of the interaction of diethylzinc with a number of monohydric and dihydric phenols. Products such as bis(ethylzinc) resorcinolate (VI) and more complex products such as ethylzinc phenoxyzinc resorcinolate (VII) were prepared [13].



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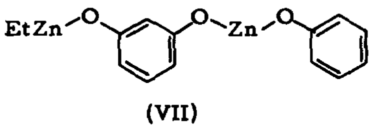


(VII)

Various alkylzinc alkoxides derived from tertiary alcohols (i.e. triphenyl-, diphenylmethyl- and dimethylphenylcarbinol) have been isolated and their degree of association has been determined [14]. The formation of triphenylsiloxy-substituted organozinc compounds via acidolysis of diorganozinc compounds with triphenylsilanol has been reported by Petukhov et al. [15]:

$$R_2Zn + Ph_3SiOH \longrightarrow RZnOSiPh_3 + RH \qquad (R = Et, Ph)$$

The hydrostannolysis reaction of zinc-carbon bonds in coordinatively saturated monoorganozinc compounds readily affords complexes containing a tin-zinc bond, e.g.:

$$Ph_3SnH + EtZnCl\cdot L \longrightarrow Ph_3SnZnCl\cdot L + EtH \qquad (L = Et_2O, DME \text{ or } TMED)$$

Uncomplexed $Ph_3SnZnCl$ has been obtained via removal of Et_2O from $Ph_3SnZnCl\cdot Et_2O$ by heating in vacuo [16].

The 2/1 reaction of triphenylgermane and triphenyltin hydride with coordinatively saturated dialkylzinc compounds affords the corresponding bis(triphenylgermyl)- or bis(triphenyltin)zinc complexes [17]:

$$2\,Ph_3GeH + Et_2Zn\cdot L \longrightarrow (Ph_3Ge)_2Zn\cdot L + 2\,EtH \qquad (L = Bipy, TMED)$$

$$2\,Ph_3SnH + Et_2Zn\cdot L \longrightarrow (Ph_3Sn)_2Zn\cdot L + 2\,EtH \qquad (L = THF, DME, Bipy, TMED)$$

Bychkov et al. have reported the selective acidolysis of one Zn-C bond of diethylzinc, if the reaction is performed in diglyme at room temperature:

$$Ph_3GeH + Et_2Zn \longrightarrow EtZnGePh_3 + EtH$$

Upon further reaction at 150° $(Ph_3Ge)_2Zn{\cdot}diglyme$ is obtained [18].

The reaction of organotin halides with zinc metal proceeds via the initial formation of reactive organotin-zinc compounds, the nature of the final reaction products depending entirely on the reaction conditions. In aprotic solvents, in the absence of strongly coordinating ligands, tetraorganotin compounds are formed via alkylation or arylation by intermediate organozinc compounds, produced by 1,2-intermetallic shifts of organic groups in the initial organotin-zinc reaction product [19]:

$$\begin{tikzcd}
R_3SnCl \arrow[r, "Zn(Cu)"] & R_3SnZnCl \arrow[r] & R_2Sn{\cdot}RZnCl \arrow[d, "R_3SnCl"] \\
 & & R_4Sn + [R_2Sn]
\end{tikzcd}$$

Strongly coordinating ligands prevent the 1,2-shift and hexaalkyl- or hexaaryldition compounds are formed [19], e.g.:

$$\begin{tikzcd}
Ph_3SnCl \arrow[r, "Zn(Cu)", "TMED"'] & Ph_3SnZnCl{\cdot}TMED \arrow[d, "Ph_3SnCl"] \\
 & Ph_6Sn_2 + ZnCl_2{\cdot}TMED
\end{tikzcd}$$

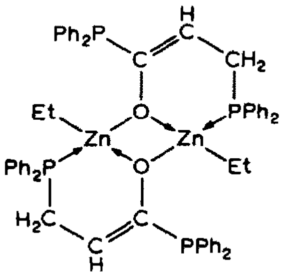
Burlitch and Hayes have obtained a series of tetrameric transition metal carbonyl zinc alkoxides via alcoholysis of transition metal carbonyl derivatives of zinc [20], e.g.

$$Zn[Co(CO)_4]_2 + CH_3OH \longrightarrow \tfrac{1}{4}[CH_3OZnCo(CO)_4]_4 + HCo(CO)_4$$

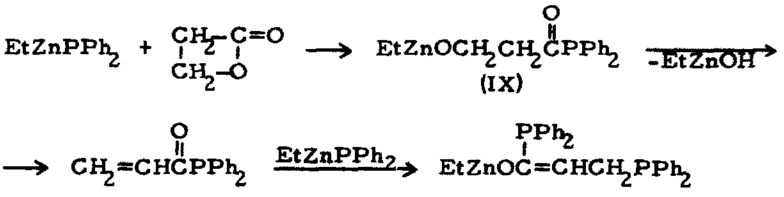
As judged by the ease of conversion in the pure alcohol, the observed order of reactivity $Zn[Fe(CO)_2Cp]_2 > Zn[Mn(CO)_5]_2 \approx Zn[Mo(CO)_3Cp]_2 >$ $> Zn[Co(CO)_4]_2$ generally parallels the pK_a values of the corresponding metal carbonyl hydrides [20].

A brief survey of the coordination chemistry of diorganozinc compounds R_2Zn and, in particular, of monoorganozinc compounds RZnX, with emphasis on research performed by the Utrecht group of Boersma and Noltes, has appeared in print [21].

In the course of their study of the interaction of monoorganozinc compounds RZnX with β-propiolactone (AS 70; 413) Boersma and Noltes isolated the unusual organozinc complex (VIII) (structure assigned on the basis of ^{1}H-, ^{31}P- and ^{13}C-NMR spectroscopy) from the reaction of β-propiolactone with ethylzinc diphenylphosphide [22]. The formation of this compound was rationalized in terms of acyl-oxygen cleavage of the lactone leading to the adduct (IX) which undergoes elimination with formation of (X). This compound then undergoes 1,4-addition with formation of (XI) which in benzene is a dimer [22]:



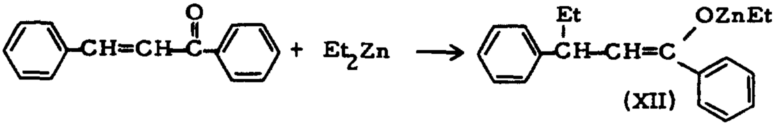
(VIII)



$$EtZnPPh_2 + \begin{array}{l}CH_2-C=O\\ |\qquad\ \ |\\ CH_2-O\end{array} \longrightarrow \underset{(IX)}{EtZnOCH_2CH_2\overset{O}{\overset{\|}{C}}PPh_2} \xrightarrow[-EtZnOH]{}$$

$$\longrightarrow \underset{(X)}{CH_2=CH\overset{O}{\overset{\|}{C}}PPh_2} \xrightarrow{EtZnPPh_2} \underset{(XI)}{EtZnO\overset{PPh_2}{\overset{|}{C}}=CHCH_2PPh_2}$$

Based on NMR results the reaction product of diethylzinc with phenylstyrylketone exists in benzene solution in the enolate form (XII) [23]:


(XII)

Ashby and Watkins have reported a convenient method for the preparation of complex metal hydrides of zinc involving the formation of an "ate"complex of zinc $M_nZn_mR_{2m+n}$ followed by reaction with either $LiAlH_4$, $NaAlH_4$ or AlH_3. The 1/1, 2/1 and 3/1 complexes of methyl lithium and dimethylzinc yield $LiZnH_3$, Li_2ZnH_4 and Li_3ZnH_5 upon reaction with $LiAlH_4$ in Et_2O, e.g.:

$$Me_2Zn + 2\,MeLi \longrightarrow Li_2ZnMe_4 \xrightarrow{2\,LiAlH_4} Li_2ZnH_4 + $$
$$+ 2\,LiAlMe_2H_2$$

The 1/1 and 1/2 reaction of KH with dimethylzinc in THF yields $KZnMe_2H$ and KZn_2Me_4H, respectively. Other complex hydrides reported in this paper are KZn_2H_5 resulting from the reaction of either $KZnMe_2H$ or KZn_2Me_4H with AlH_3 in THF and $KZnH_3$ resulting from the reaction of $KZnMe_2H$ with $LiAlH_4$ in THF [24, 25].

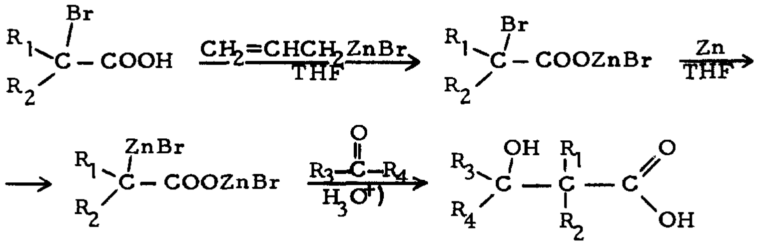
II. REACTIONS OF ORGANOZINC COMPOUNDS

A. Reformatsky reaction and related reactions

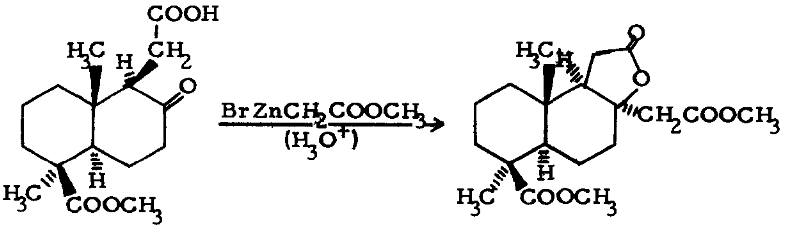
The chemistry of functionally substituted organozinc reagents has continued to attract attention. Many of the reagents prepared and syntheses performed with these reagents have only a remote connection with the original Reformatsky reaction. Considerable progress has been made with the elucidation of the nature of Reformatsky-like reagents. Numerous new synthetic applications of the Reformatsky reaction and related reactions have appeared in the literature.

Gaudemar has published an excellent review containing 543 references dealing with research connected with all aspects of the Reformatsky reaction (limited to reagents derived from α-bromoesters) published during the past thirty years [26].

In order to avoid secondary reactions occurring upon saponification of the conventional Reformatsky reaction product Bellasoued et al. have applied the Reformatsky reagent of the bromozinc salt of an α-bromoacid in stead of the usual α-bromoester for the synthesis of a large variety of β-hydroxyacids [27, 28]:



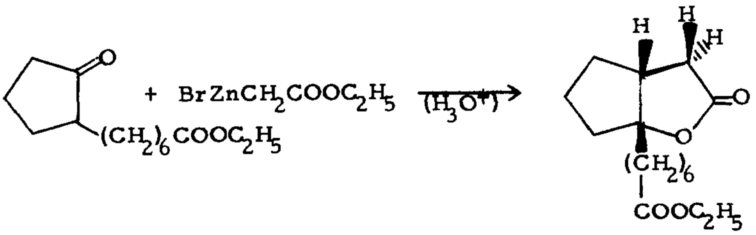
The yield of the lactone-diester (XIV) formed by the Reformatsky reaction of the ester-ketone (XIII) can be increased to over 90 %, if a 3/1 benzene/dimethoxyethane solvent mixture is used [29]:



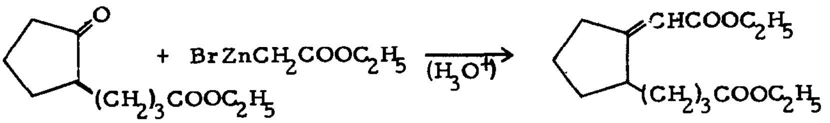
(XIII)

(XIV)

Bicyclic γ-lactones were found among the products of the reaction of two 2-substituted cyclopentanones with the Reformatsky reagent [30]:

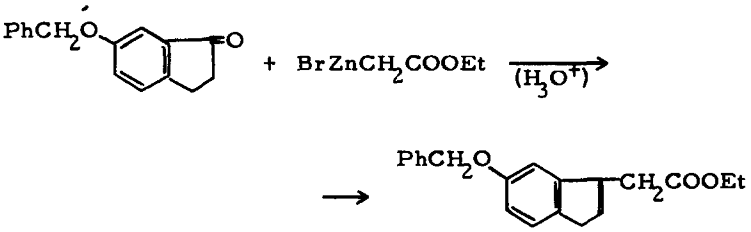


However, the cyclopentanone (XV) afforded the 1-(carbethoxymethylene)-substituted cyclopentane (XVI) [31]:

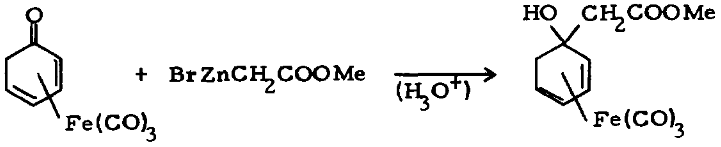


(XV) (XVI)

Indene-3 acetic acid derivatives have been prepared via the Reformatsky reaction of 6-benzyloxy-1-indanone [32]:

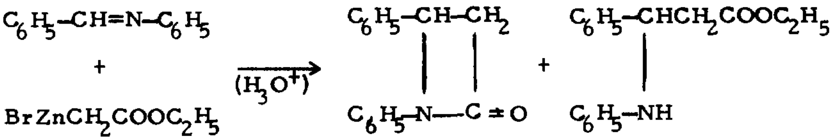


The tricarbonyliron complexes of cyclohexa-2,4-dienone and cyclohepta-2,4-dienone undergo the Reformatsky reaction with methyl α-bromoacetate and zinc to afford the expected β-hydroxy esters [33]:

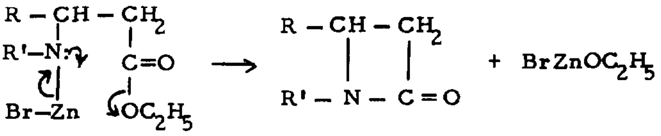


The configuration of the various β-hydroxyesters formed in the reaction of the organozinc reagent of methyl α-bromopropionate with 2-phenylpropanal [34] and with α-phenylethyl-methylketone [35] has been elucidated.

The reaction of the Reformatsky reagent with Schiff bases may give rise to the formation of β-lactams or of β-aminoesters, e.g.:

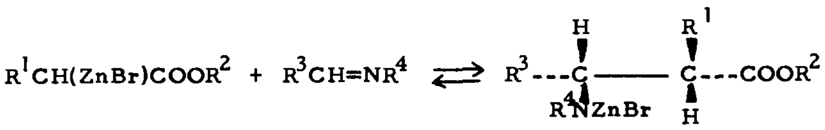


Dardoize et al. have studied the various factors disfavouring ring-closure of the intermediate (XVII) leading to the formation of β-lactams:



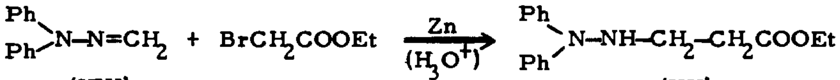
(XVII)

Conditions (low reaction temperature, short reaction times) have been developed for the Reformatsky synthesis of a variety of β-aminoesters [36]. The results of a study of the stereochemistry of the condensation reaction were in accord with those of Luche and Kagan (AS 71; 83) in that the reaction is stereospecific with nearly quantitative formation of the aminoester with *erythro*-configuration (XVIII). Evidence has been presented that the condensation reaction is reversible [37]:



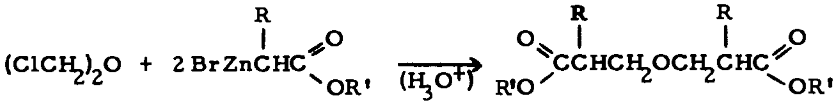
(XVIII)

The Reformatsky reaction with N-methylene-N',N'-diphenylhydrazine (XIX) produces the β-hydrazinoester (XX) in good yield [38]:



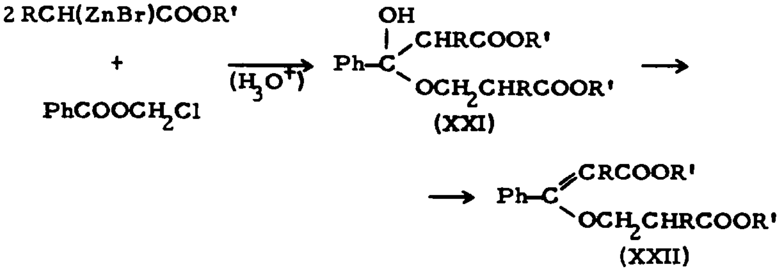
(XIX) (XX)

A variety of β,β'-dialkyl-β,β'-dicarbalkoxydiethylethers has been obtained by the Reformatsky reaction of α-bromoesters with bis(chloromethyl)ether [39]:



(R = i-Pr, Bu;
R' = Me, Et, Pr, Bu)

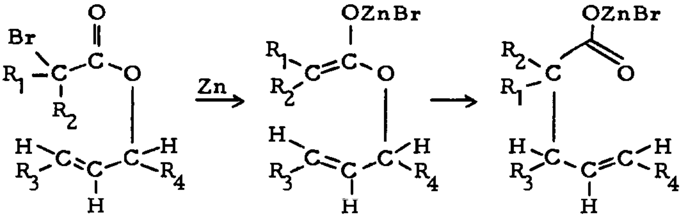
More recently, a complete analysis of the products formed in this type of reactions has been published [40]. The interaction of Reformatsky reagents with chloromethyl benzoate has been used to prepare a variety of hydroxyesters of type (XXI) which readily dehydrate to give α,β-unsaturated esters of type (XXII) [41]:



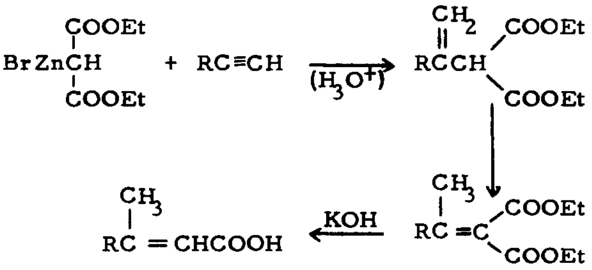
(R = i-Pr Bu;
R' = Me, Et, Pr, Bu)

The Reformatsky reaction has been applied to the synthesis of branched 2-deoxyaldonic acids [42].

The [3,3]-sigmatropic rearrangement of the zinc enolate obtained from α-bromoesters derived from allylic or acetylenic alcohols provides a useful synthesis of γ,δ-unsaturated acids [43]:

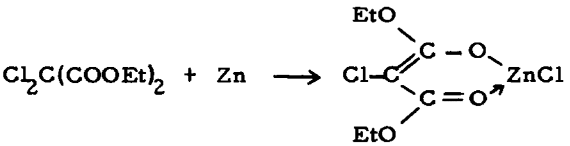


The organozinc reagent derived from diethyl α-bromomalonate adds exothermally to the carbon-carbon triple bond of terminal acetylenes enabling the synthesis of a variety of β-methyl-α,β-unsaturated carboxylic acids [44]:



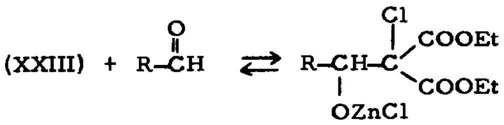
(R = n-Pr, Ph, p-MePh, p-MeOPh)

The reaction of diethyl dichloromalonate with zinc in methylal solution (reflux) or in THF (rapid at 20°) affords a reagent which based on IR--spectral data has been assigned the enolate structure (XXIII) [45]:

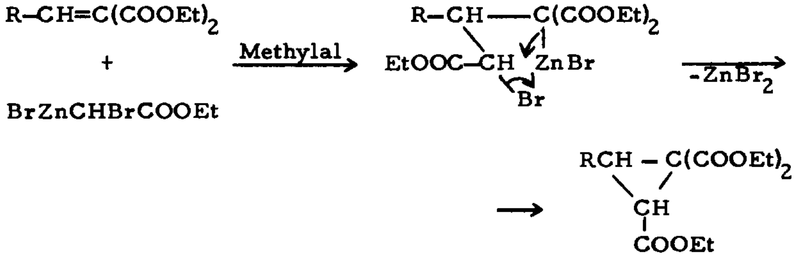


(XXIII)

(XXIII) appears to be quite unreactive towards organic halides, but in methylal solution undergoes condensation with isobutyraldehyde [45]:

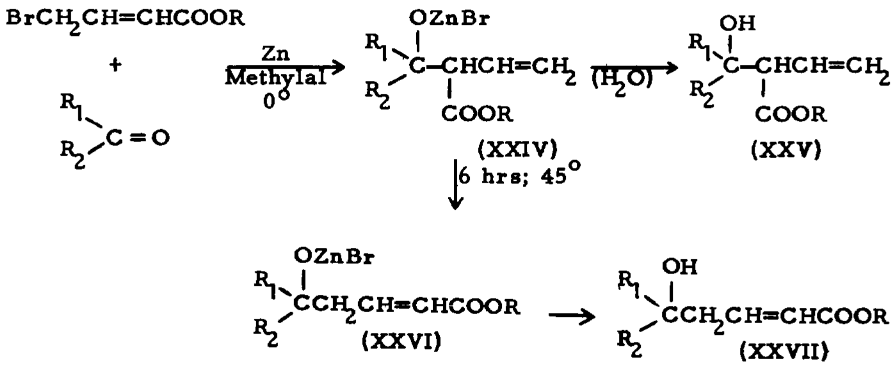


The reaction of the organozinc reagent derived from ethyl dibromoacetate with diethyl alkylidenemalonates results in cyclization of the primary adduct leading to cyclopropane-1,1,2-tricarboxylic esters [46]:



The reaction with ethyl trichloroacetate affords the not hitherto reported 3-alkyl-2-chloro-1,1,2-triethoxycarbonylcyclopropanes [46].

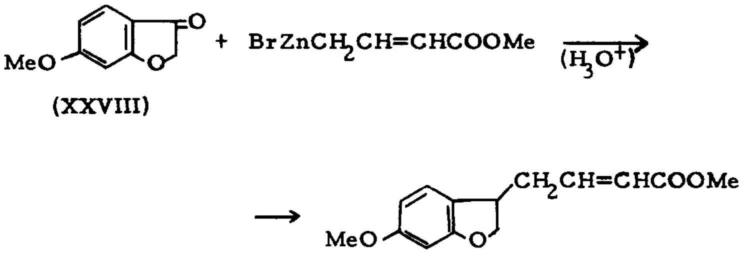
The Reformatsky reaction of methylisopropylketone with isopropyl-γ-bromocrotonate carried out in methylal at 0° affords exclusively the β-hydroxyester (XXV) after hydrolysis. Hydrolysis following heating of the adduct (XXIV) affords exclusively the δ-hydroxyester (XXVII) corresponding with the thermodynamically more stable adduct (XXVI) [47]:



(XXIV) (XXV) (XXVI) (XXVII)

The reversibility of the various reactions has been investigated and conditions have been developed for obtaining either the branched (allylic rearrangement) or the linear alcohol from this type of reaction [47].

The Reformatsky reaction of 7-methoxy-2-methylchroman-4-one and of 6-methoxycoumaran-3-one (XXVIII) with methyl-γ-bromocrotonate yields methyl-γ-(7-methoxy-2-methylchromanylidene-4)-crotonate and methyl γ-(6-methoxybenzofuran-3)-crotonate (XXIX) [48]:

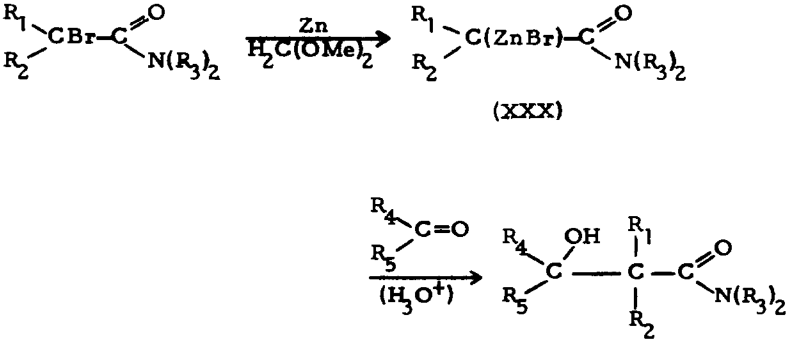


(XXVIII)

(XXIX)

The same organozinc reagent has been used in the synthesis of miltirone, a diterpenoid quinone [49].

The reaction of α-bromoamides with zinc powder in refluxing methylal gives rise to the nearly quantitative formation of the corresponding organozinc reagents (XXX) which undergo the usual condensation reaction with aldehydes and ketones, thereby affording a facile route to β-hydroxyamides (XXXI) [50]:

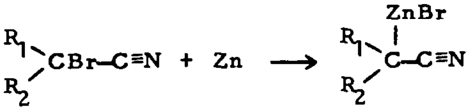


(XXX)

(XXXI)

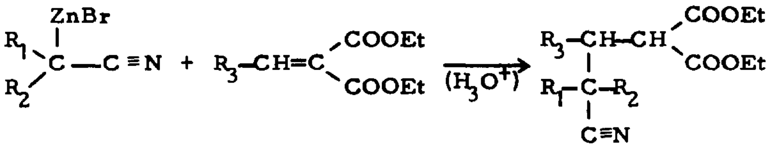
The condensation reaction is stereospecific with predominant formation of the isomer with erythro-configuration [50].

Similarly, the reaction of α-bromonitriles with zinc in THF at 20° yields quantitatively the corresponding organozinc reagent which is present (IR, NMR) in the C-metalated form [51]:



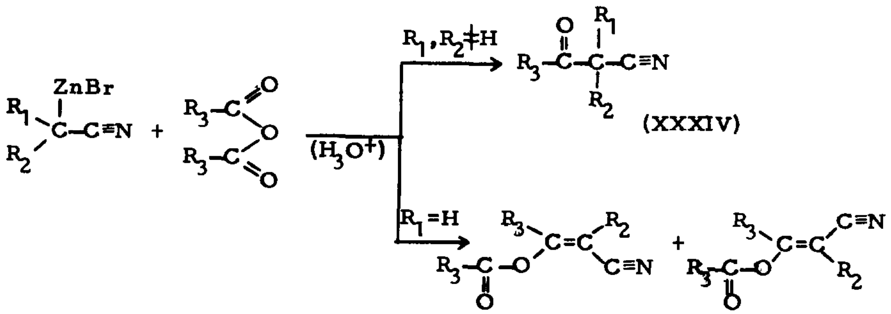
(XXXII)

(XXXII) condenses normally with aldehydes and saturated ketones providing a convenient route to β-hydroxynitriles, the nature of the solvent having little influence on the stereochemistry of the reaction (predominant formation of isomer with erythro-configuration). The reaction with alkylidene malonates produces the 1,4-adducts (XXXIII) in good yield [51]:



(XXXIII)

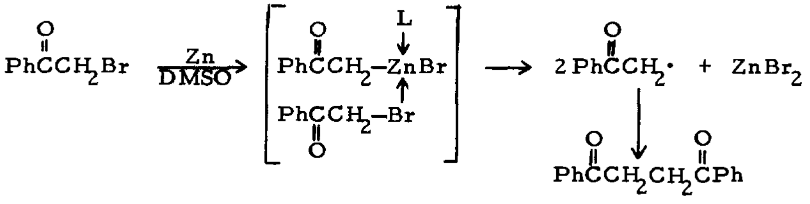
The condensation of (XXXII) with acid anhydrides depending on the nature of R_1 and R_2 produces either β-ketonitriles (XXXIV) or the cis- and trans-enol esters (XXXV, XXXVI) [52]:



(XXXIV)

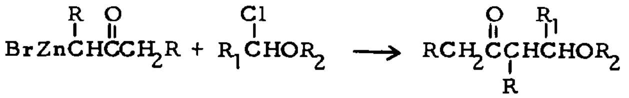
(XXXV) (XXXVI)

Intermolecular one-electron transfer with the formation of phenacyl radicals takes place upon reacting phenacyl bromide with zinc in DMSO [53]:



$$PhC(O)CH_2Br \xrightarrow[DMSO]{Zn} \left[\begin{array}{c} PhC(O)CH_2-\overset{L\downarrow}{Zn}Br \\ \uparrow \\ PhC(O)CH_2-Br \end{array}\right] \longrightarrow 2\,PhC(O)CH_2\cdot + ZnBr_2 \;;\; 2\,PhC(O)CH_2\cdot \downarrow PhC(O)CH_2CH_2C(O)Ph$$

Organozinc reagents derived from aliphatic α-bromoketones have been successfully applied to the synthesis of β-alkoxyketones [54]:



$$BrZnCH(R)C(O)CH_2R + R_1CH(Cl)OR_2 \longrightarrow RCH_2C(O)CH(R)CH(R_1)OR_2$$

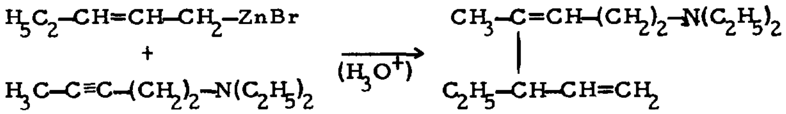
B. Reactions of alkenylzinc compounds with carbon-carbon and carbon-heteroatom unsaturated bonds

The group of L. Miginiac and Ph. Miginiac at Poitiers have continued their extensive studies concerning the reactivity of 2-alkenylzinc compounds towards carbon-carbon and carbon-heteroatom unsaturated bonds. This research has produced a number of valuable synthetic procedures.

The addition of alkenylzinc compounds to unsaturated (ethylenic, acetylenic and allenic) amines constitutes a general method for the synthesis of mono- and di-ethylenic amines [55], e.g.:

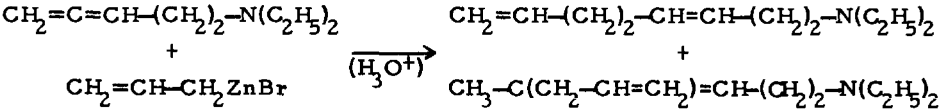
$$\begin{array}{ccc} HC{\equiv}C{-}(CH_2)_n{-}N(C_2H_5)_2 & & CH_2{=}CH{-}CH_2{-}CH{=}CH{-}(CH_2)_n{-}N(C_2H_5)_2 \\ + & \xrightarrow[(H_3O^+)]{} & + \\ CH_2{=}CH{-}CH_2{-}ZnBr & & CH_2{=}C(CH_2{-}CH{=}CH_2){-}(CH_2)_n{-}N(C_2H_5)_2 \end{array}$$

Addition reactions with the organozinc reagent derived from 1-bromopentane-2 involve allylic rearrangement, e.g.:



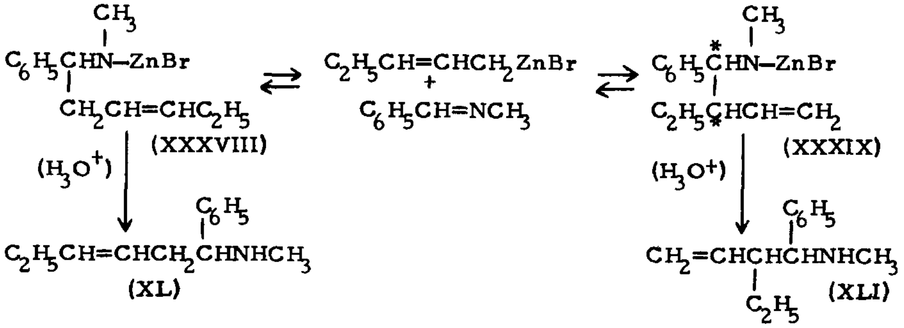
$$\begin{array}{c} H_5C_2{-}CH{=}CH{-}CH_2{-}ZnBr \\ + \\ H_3C{-}C{\equiv}C{-}(CH_2)_2{-}N(C_2H_5)_2 \end{array} \xrightarrow[(H_3O^+)]{} \begin{array}{l} CH_3{-}C{=}CH{-}(CH_2)_2{-}N(C_2H_5)_2 \\ \quad\;\; | \\ C_2H_5{-}CH{-}CH{=}CH_2 \end{array}$$

With allenic amines addition takes place at the terminal double bond [55], e.g.:



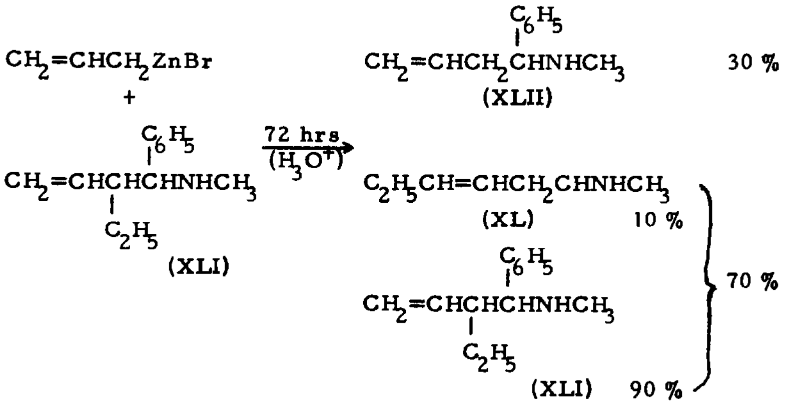
$$\begin{array}{c} CH_2{=}C{=}CH{-}(CH_2)_2{-}N(C_2H_5)_2 \\ + \\ CH_2{=}CH{-}CH_2ZnBr \end{array} \xrightarrow[(H_3O^+)]{} \begin{array}{c} CH_2{=}CH{-}(CH_2)_2{-}CH{=}CH{-}(CH_2)_2{-}N(C_2H_5)_2 \\ + \\ CH_3{-}C(CH_2{-}CH{=}CH_2){=}CH{-}(CH_2)_2{-}N(C_2H_5)_2 \end{array}$$

The reaction of α-ethylenic organozinc compounds with aldimines in general affords a mixture of branched and linear amines (e.g. XL and XLI). Mauzé et al. have shown that the adduct (XXXIX) resulting from the addition (with allylic rearrangement) of pentenylzinc bromide to N-methylbenzaldimine is slowly converted into the thermodynamically more stable adduct (XXXVIII):



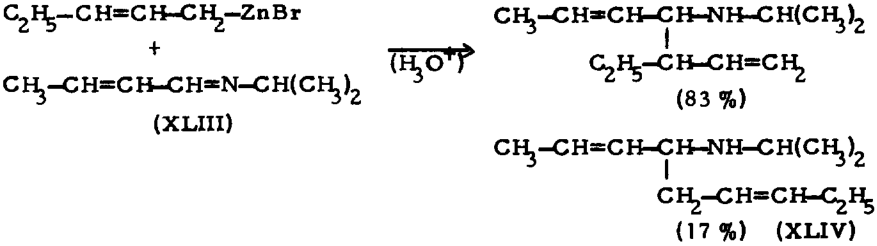
$$\begin{array}{ccccc} \begin{array}{l} \quad\;\; CH_3 \\ \quad\;\; | \\ C_6H_5CHN{-}ZnBr \\ \quad\;\; | \\ \quad CH_2CH{=}CHC_2H_5 \end{array} & \rightleftarrows & \begin{array}{c} C_2H_5CH{=}CHCH_2ZnBr \\ + \\ C_6H_5CH{=}NCH_3 \end{array} & \rightleftarrows & \begin{array}{l} \qquad\;\; CH_3 \\ \qquad\;\; | \\ C_6H_5\overset{*}{C}HN{-}ZnBr \\ \quad\;\; | \\ C_2H_5\overset{*}{C}HCH{=}CH_2 \end{array} \\ \text{(XXXVIII)} & & & & \text{(XXXIX)} \\ \downarrow (H_3O^+) & & & & \downarrow (H_3O^+) \\ \begin{array}{l} \qquad\qquad\quad C_6H_5 \\ \qquad\qquad\quad | \\ C_2H_5CH{=}CHCH_2CHNHCH_3 \end{array} & & & & \begin{array}{l} \qquad\quad\; C_6H_5 \\ \qquad\quad\; | \\ CH_2{=}CHCHCHNHCH_3 \\ \qquad\; | \\ \qquad C_2H_5 \end{array} \\ \text{(XL)} & & & & \text{(XLI)} \end{array}$$

That the formation of adduct (XXXIX) is reversible and that rupture of the $\overset{*}{C}{-}\overset{*}{C}$ bond of (XXXIX) is involved is evidenced by the isolation of the mixture of amines (XL), (XLI) and (XLII) upon reacting the amine (XLI) with allylzinc bromide for 72 hrs at 20°:



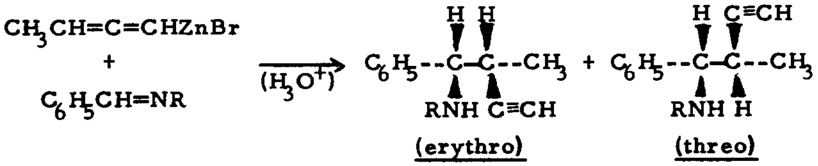
The results of a study concerning the reversibility of adduct-formation with a variety of aldimines is reported [56].

Contrary to pentenyllithium which undergoes selective 1,4-addition with (XLIII), the reaction of pentenylzinc bromide with the α,β-unsaturated aldimine (XLIII) involves exclusively 1,2-addition.



A product analysis for the addition reaction of pentenylzinc bromide with three other α,β-unsaturated aldimines is presented [57]. Like the additions with non-conjugated aldimines [56] adduct-formation of this type is reversible. With increasing reaction time the proportion of the amine (XLIV) derived from the thermodynamically more stable adduct (no allylic rearrangement) increases [58].

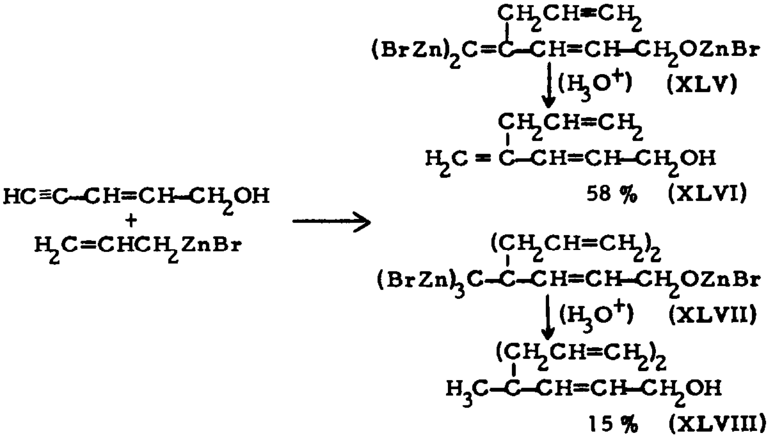
The reaction of the organozinc reagent derived from 3-bromo-1--butyne with aldimines proceeds in a stereoselective fashion. In the mixture of diastereoisomeric acetylenic amines obtained the isomer with threo-configuration strongly predominates [59]:



R = Me (THF) 15 : 85

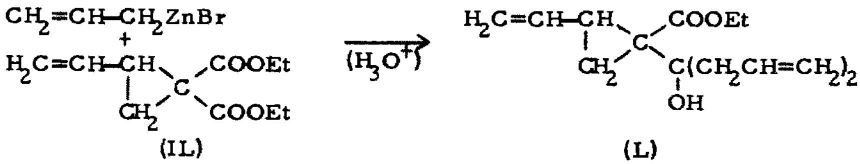
R = Et (THF) 7 : 93

Whereas both allyllithium and allylmagnesium bromide add to the double bond, allylzinc bromide adds exclusively to the triple bond of penten-2-yn-ol-1:

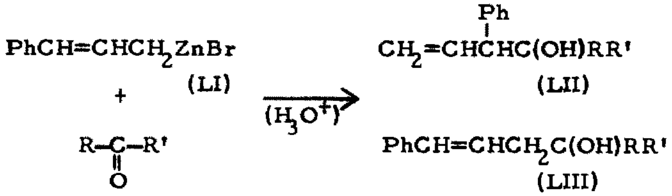


The formation of (XLVI) and (XLVIII) results from hydrolysis of the ω,ω-bis-bromozinc and ω,ω,ω-tris-bromozinc compounds (XLV) and (XLVII), respectively, as evidenced by the formation of the corresponding deuterated alcohols upon deuterolysis of the reaction mixture [60].

The reaction of allylzinc bromide with the vinylcyclopropanedicarboxylic ester (IL) affords exclusively the product (L) resulting from 1,2-addition to one of the ester functions [61]:

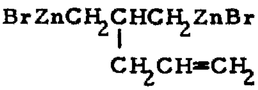


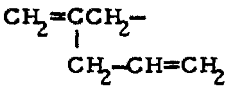
The reaction of the cinnamyl organozinc reagent (LI) with aldehydes and ketones produces a mixture of branched (allylic rearrangement) and lineal alcohols (LII) and (LIII) after hydrolysis:



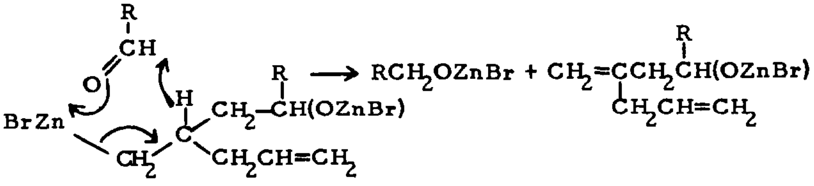
The condensation reaction has been shown to be reversible. By applying elevated reaction temperatures and longer reaction times the product composition becomes thermodynamically controlled enabling in some cases the exclusive synthesis of alcohols (LIII) [62].

The bis-organozinc reagent (LIV) formed by heating a solution of allylzinc bromide at reflux temperature is reactive towards aldehydes, ketones, gem-chloroethers and acyl halides, but is unreactive towards esters, nitriles and aldimines [7]. The alcohols resulting from the

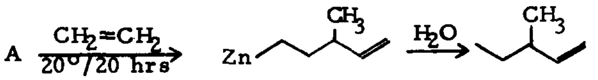

(LIV)

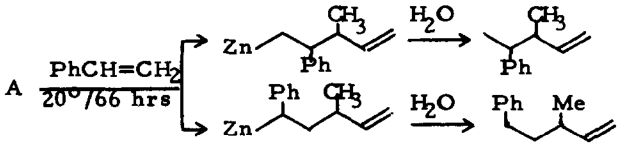

(LV)

reaction with carbonyl compounds contain the group (LV) suggesting that a primary condensation step is followed by a reduction step [7]:



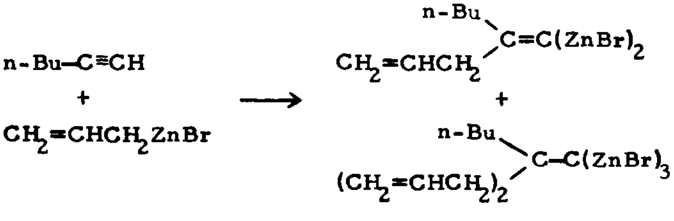
Addition reactions of dicrotylzinc (A) with simple olefins and dienes have been reported by Lehmkuhl and Nehl [63]. Although according to ^{1}H-NMR spectroscopy dicrotylzinc occurs exclusively in the 2-butenyl form the addition products obtained from olefins are derived from the 1-methyl-2-propenyl form, e.g.:





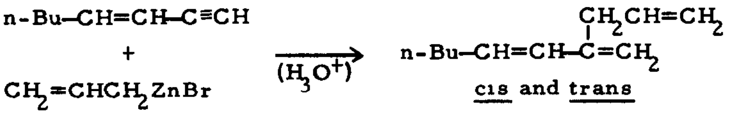
In the addition to butadiene products derived from the 2-butenyl form are obtained as well [63].

The reaction of allylzinc bromide with terminal acetylenes results in a mixture of mono- and bis-addition products depending on the reaction conditions [63]:



$$\text{n-Bu–C}\equiv\text{CH} + \text{CH}_2\text{=CHCH}_2\text{ZnBr} \longrightarrow (\text{n-Bu})(\text{CH}_2\text{=CHCH}_2)\text{C=C(ZnBr)}_2 + (\text{n-Bu})(\text{CH}_2\text{=CHCH}_2)_2\text{C–C(ZnBr)}_3$$

Pentenylzinc bromide undergoes mono-addition only, but two isomeric products are formed as a result of partial allylic rearrangement. Allylzinc bromide undergoes exclusive mono-addition with the triple bond of enynes [63]:



$$\text{n-Bu–CH=CH–C}\equiv\text{CH} + CH_2\text{=CHCH}_2\text{ZnBr} \xrightarrow[(H_3O^+)]{} \text{n-Bu–CH=CH–}\overset{\overset{\textstyle CH_2CH=CH_2}{|}}{C}\text{=}CH_2$$

cis and trans

C. Carbenoid reactions of organozinc compounds

The carbenoid reactivity of appropriate organozinc compounds has continued to attract attention and further examples of their application in organic and organometallic synthesis have appeared in the literature.

Considerable further research has been carried out concerning the zinc carbenoid reagent generated from diethylzinc and gem-dihaloalkanes first introduced by Furukawa et al. (AS 69; 225).

Chloroiodomethane/diethylzinc was found to be a useful methylene source for the cyclopropanation of olefins (70 - 100 % yield) provided the reaction is carried out in the presence of oxygen, of radical generators such as AIBN or under irradiation with UV light. The methylene addition to cis- and trans-2-butene proceeds in a stereospecific manner in the presence of oxygen. The reactivity order of dihalomethanes towards diethylzinc ($CH_2I_2 > CH_2ClI > CH_2Br_2 > CH_2BrCl$) is the same as that of radical halogen-abstraction reactions from dihalomethanes. A free-radical mechanism for the formation of the zinc-carbenoid reagent is proposed with the methylene-transfer step being a conventional one-step, three-centered carbenoid reaction [65, 66]:

$$\text{EtZnR} \xrightarrow[\text{or } h\nu]{\text{Initiator}} \text{Et}\cdot$$

$$\text{Et}\cdot + CH_2IX \longrightarrow \text{EtI} + \cdot CH_2X$$

$$\cdot CH_2X + \text{EtZnR} \longrightarrow XCH_2\text{ZnR} + \text{Et}\cdot \text{ etc.}$$

(X = Cl or I; R = Et or X)

Olefins inhibit the formation of the zinc-carbenoid reagent from Et_2Zn and $ClCH_2I$, the order of the inhibitory effect following the order of the reactivity of the olefin towards radicals. This result is consistent with the proposed radical-chain mechanism for the formation of the zinc-carbenoid reagent, more reactive olefins being more effective in trapping intermediate ethyl or chloromethyl radicals [66, 67].

Whereas bicyclo [4.1.0] heptane was obtained as the major product of the reaction of cyclohexene with diethylzinc and methylene iodide, the yield is considerably reduced if the reaction is performed in the presence of lithium or magnesium halides. The presence of large amounts of n-propyl and n-butyl iodide was interpreted in terms of insertion of the zinc carbenoid reagent into the carbon-iodine bond of ethyl and n-propyl iodide [68]:

$$Et_2Zn + CH_2I_2 \xrightarrow{\text{fast}} EtI + \underset{\text{(A)}}{EtZnCH_2I}$$

$$\text{(A)} + EtI \longrightarrow n\text{-}PrI + EtZnI$$

$$\text{(A)} + n\text{-}PrI \longrightarrow n\text{-}BuI + EtZnI$$

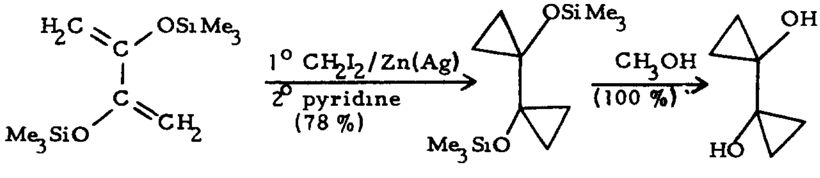
Seyferth and coworkers have introduced the ethylzinc iodide/methylene iodide reagent as a very useful alternative for the previously used $Zn(Cu)/CH_2I_2$ reagent for nucleophilic iodomethylene-group transfer to heavy metal atoms. The homogeneous solution of iodomethylzinc iodide produced by reaction of equimolar quantities of EtZnI and CH_2I_2 in THF has been used to prepare Me_3SnCH_2I, $Me_2Sn(CH_2I)_2$ and $Hg(CH_2I)_2$ in good yield. Recently prepared Me_3SiCHI_2 and Me_3SnCHI_2 likewise react with EtZnI to give $Me_3SiCHIZnI$ and $Me_3SnCHIZnI$, respectively, which show nucleophilic reactivity comparable to that of ICH_2ZnI [69]:

$$Me_3SnCHI_2 \xrightarrow{EtZnI} Me_3SnCHIZnI \xrightarrow{Me_3SnCl} \underset{(83\ \%)}{(Me_3Sn)_2CHI}$$

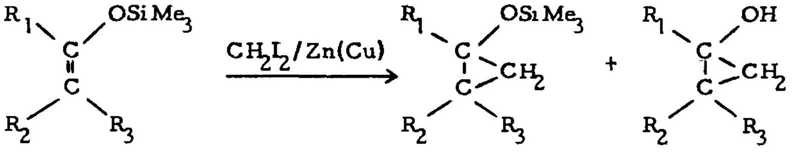
Whereas the 1/1 reaction of Me_3SiCX_2H (X = Br, I) with ethylzinc iodide or with zinc-copper couple yields $Me_3SiCHXZnX$ (X = Br, I), the reaction of $Me_3SiCHBr_2$ with zinc-copper couple in a 1/2 ratio affords a product which upon hydrolysis affords Me_4Si and, therefore, is believed to be the gem-dizinc reagent (LVI) [70]:

$$Me_3SiCHBr_2 + 2\,Zn(Cu) \xrightarrow[5\ hrs;\ 60^\circ]{THF} \underset{(LVI)}{Me_3SiCH(ZnBr)_2}$$

Denis, Girard and Conia have reported two modifications of the conventional Simmons-Smith reaction which result in improved yields, particularly with functionally substituted olefins. A zinc-silver couple is used in stead of a zinc-copper couple and work-up involves the addition of an amine (e.g. pyridine) in order to remove zinc salts. Numerous examples of successful methylenation reactions of olefinic esters, aldehydes, ketones and ethers by the new procedure are provided and the results are compared with those employing the conventional $CH_2I_2/Zn(Cu)$ reagent and hydrolytic work-up [71]. The great utility of this reagent is for example illustrated by the synthesis of 1,1'-dihydroxydicyclopropyl via cyclopropanation of bis-2,3(trimethylsiloxy)butadiene followed by methanolysis [72]:

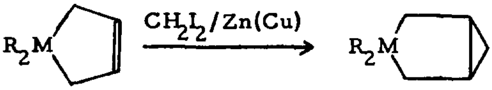


The reaction of trimethylsilyl enol ethers with the Simmons-Smith reagent affords a mixture of trimethylsilyl cyclopropyl ether (LVII) and cyclopropanol (LVIII). The yield of (LVII) is improved employing cold, rapid work-up, whereas enrichment in (LVIII) occurs upon work-up at ambient conditions [73]:



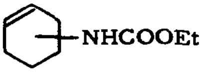
(LVII) (LVIII)

3-Sila- and 3-germabicyclo [3.1.0]hexanes with various substituents at the metal atom have been obtained in good yield by applying the Simmons--Smith reaction to unsaturated five-membered metallacyclic compounds [74]:

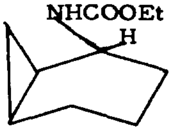


(R = Me; M = Si (65 %); M = Ge (65 %)
R = Ph; M = Si (76 %); M = Ge (74 %))

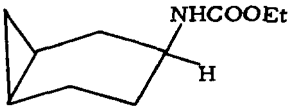
The Simmons-Smith reaction applied to the cyclohexynyl urethanes (LIX, 3- and 4-position) gave the syn-isomers (LX) and (LXI) with 95 % stereospecificity and 75 - 95 % yields [75].



(LIX)



(LX)



(LXI)

Partially optically active trans-(1 R, -2 R)(-)-2-phenylcyclopropanecarboxylic acids have been obtained via asymmetric Simmons-Smith methylenation of (-)-menthyl trans-cinnamate [76].

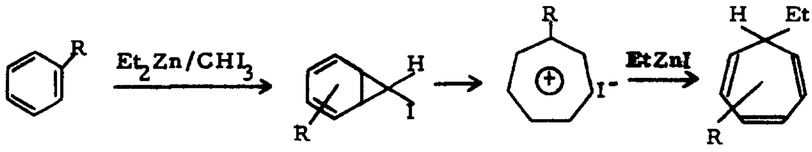
The Simmons-Smith reaction has been applied to various hexenopyranosides [77, 78, 79].

Simmons-Smith methylenation of 5,6-unsaturated steroids leads to a mixture of both epimeric cyclopropane derivatives. Contrary to the results of Templeton and Wie (AS 71; 101) influence of the configuration of an hydroxylgroup at C(3) on the stereochemical course of the reaction was not observed [80, 81]. 15α,16α-Methylenetestosterone has been obtained by a multi-step process including a Simmons-Smith methylenation step [82].

Miyano et al. observed that the zinc-carbenoid reagent obtained from the Zn/CH_2I_2 reaction (1/2 ratio) does not afford methyl iodide on hydrolysis, but does yield methylene iodide upon reaction with iodine. This result together with the formation of styrene in the reaction with benzaldehyde suggests that $CH_2(ZnI)_2$ is the reacting species [83].

Reactions of α-haloacrylic esters with organozinc compounds resulting in the formation of cyclopropane derivatives will be mentioned under section D of this review [94,95].

The reaction of benzene with the iodocarbenoid reagent formed from diethylzinc and iodoform results in ring-expansion. The reaction of alkylbenzenes with this reagent affords a novel route to alkyl-substituted 7-ethylcyclohepta-1,3,5-trienes. It is proposed that the intermediate alkyl tropylium ions, formed from the adduct of the iodocarbenoid reagent and the alkylbenzene, react to form the product [84, 85]:



D. Miscellaneous reactions

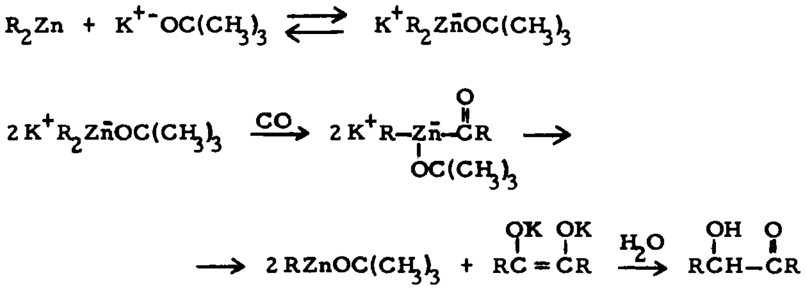
Acidolysis-type reactions have been used for preparing a variety of zinc compounds of the type RZnX and ZnX_2 (cf. Section I of this Survey; Refs. 13 - 18). Inoue et al. have studied the influence of coordinating ligands on the reactivity of the Zn—C bond in this type of reactions [86, 87]. N,N,N',N'-Tetramethylethylenediamine (TMED) has an accelerating effect on the reaction of Et_2Zn with pyrrole. 2,2'-Bipyridine (Bipy) has a similar, but much larger effect. The reactivity of di-n-propylamine, diphenylamine, pyrrole, indole and carbazole towards Et_2Zn is much the same in spite of the considerable difference in their acidities indicating that coordination of the amine to zinc is an important factor [86]. From the observation that the reaction of Et_2Zn with cyclopentadiene (pK_a 15), indene and fluorene is much slower than with nitrogen acids such as pyrrole (pK_a 16.5) or with ethanol (pK_a 18) the conclusion was drawn that in acidolysis reactions of dialkylzinc compounds σ-type coordination, which is possible for ethanol and pyrrole, but not for the acidic hydrocarbons, plays an important part [87].

Bis(trifluoromethyl)phosphine reacts with dimethylzinc to form a new four-membered P–C–P–C heterocycle:

$$2(CF_3)_2PH + 2Me_2Zn \longrightarrow 2CH_4 + 2MeZnF + (CF_3PCF_2)_2$$

The proposed intermediate $MeZnP(CF_3)_2$ and the MeZnF reaction product were not isolated [88].

Di-n-butylzinc and di-isopropylzinc react with carbon monoxide at atmospheric pressure in the presence of potassium t.butoxide to furnish after hydrolysis the corresponding acyloins. The presence of base is essential for reaction to occur suggesting the following reaction sequence [89]:



$$R_2Zn + K^{+-}OC(CH_3)_3 \rightleftarrows K^+R_2\bar{Zn}OC(CH_3)_3$$

$$2K^+R_2\bar{Zn}OC(CH_3)_3 \xrightarrow{CO} 2K^+R-\underset{OC(CH_3)_3}{\bar{Zn}}-\overset{O}{\overset{\|}{C}}R \longrightarrow$$

$$\longrightarrow 2RZnOC(CH_3)_3 + R\overset{OK}{C}=\overset{OK}{C}R \xrightarrow{H_2O} R\overset{OH}{C}H-\overset{O}{\overset{\|}{C}}R$$

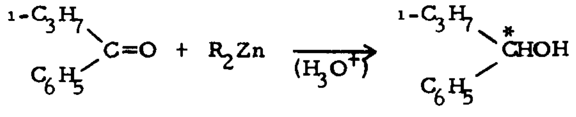
Benzoin is not formed in the reaction of diphenylzinc the only identified product being biphenyl [89].

The reaction of carbon dioxide with diethylzinc has been found to be specifically accelerated by N-methylimidazole.

$$Et_2Zn + CO_2 \xrightarrow[\text{complexing agent}]{\text{benzene; } 20^{\circ}} EtCOOZnEt$$

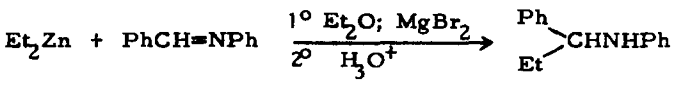
The enhancement of the reactivity of diethylzinc is believed to result from σ- as well as π-coordination with N-methylimidazole. This reaction has been related to the carbon dioxide/water reaction catalyzed by the metalloenzyme carbonic anhydrase which contains one zinc atom per molecule. The suggestion has been put forward that coordination of the imidazole group of histidine to the zinc atom in this enzyme makes an important contribution to the high catalytic activity of the enzyme [90].

The reaction of alkylphenylketones with optically active dialkylzinc compounds R_2Zn such as (+)-di[(S)-2-methylbutyl]zinc, (+)-di[(S)-3-methylpentyl]zinc and (+)-di[(S)-4-methylhexyl]zinc produces as the main product optically active carbinols with (S)-configuration, the stereoselectivity of the reaction decreasing with increasing distance of the chiral carbon atom in the alkyl group to the zinc atom [91]:



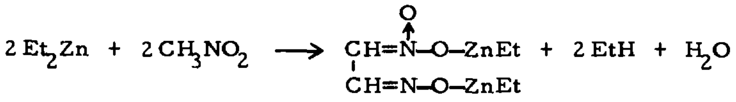
$$(i\text{-}C_3H_7)(C_6H_5)C{=}O + R_2Zn \xrightarrow[(H_3O^+)]{} (i\text{-}C_3H_7)(C_6H_5)\overset{*}{C}HOH$$

Diethylzinc is less reactive than diethylcadmium towards Schiff bases, but the reactivity is enhanced in the presence of magnesium bromide, the yield of adduct with benzalaniline increasing from 12 to 57 %, if the amount of $MgBr_2$ present during the reaction is increased from 10 to 200 mole % [92]:



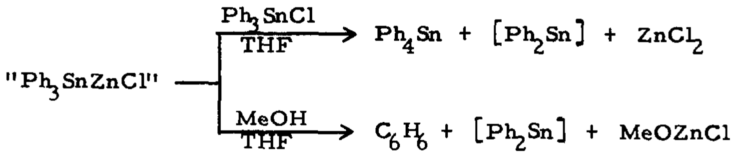
$$Et_2Zn + PhCH{=}NPh \xrightarrow[2^{\circ}\ H_3O^+]{1^{\circ}\ Et_2O;\ MgBr_2} (Ph)(Et)CHNHPh$$

The reaction of diethylzinc with nitroalkanes has been reported to involve the formation of the ethylzinc salt of methazonic acid, ethane and water which reacts further with diethylzinc [93]:

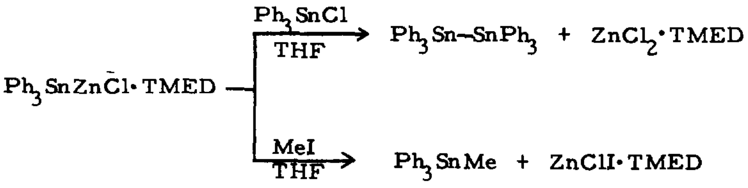


$$2\,Et_2Zn + 2\,CH_3NO_2 \longrightarrow \begin{array}{l} CH{=}\overset{O}{\overset{\uparrow}{N}}{-}O{-}ZnEt \\ | \\ CH{=}N{-}O{-}ZnEt \end{array} + 2\,EtH + H_2O$$

The reactivity of uncomplexed triphenyltin zinc chloride differs from that of e.g. its TMED-complex in that it acts as a phenylating agent and, therefore, suggests that in the absence of strongly coordinating ligands 1,2-intermetallic migration of a phenyl group from tin to zinc has occurred [16]:

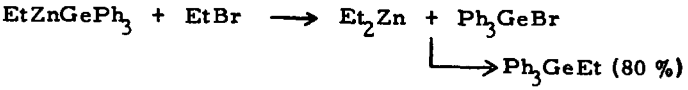


$$\text{"}Ph_3SnZnCl\text{"} \begin{cases} \xrightarrow[THF]{Ph_3SnCl} Ph_4Sn + [Ph_2Sn] + ZnCl_2 \\ \xrightarrow[THF]{MeOH} C_6H_6 + [Ph_2Sn] + MeOZnCl \end{cases}$$



$$Ph_3SnZnCl{\cdot}TMED \begin{cases} \xrightarrow[THF]{Ph_3SnCl} Ph_3Sn{-}SnPh_3 + ZnCl_2{\cdot}TMED \\ \xrightarrow[THF]{MeI} Ph_3SnMe + ZnClI{\cdot}TMED \end{cases}$$

Ethyl(triphenylgermyl)zinc has been reported to undergo specific Ge–Zn bond cleavage upon reaction with ethylbromide at 100° [18]:



$$EtZnGePh_3 + EtBr \longrightarrow Et_2Zn + Ph_3GeBr \longrightarrow Ph_3GeEt\ (80\ \%)$$

The 1/1 reaction of the diglyme complex of bis(triphenylgermyl)zinc with acetic acid results in selective cleavage of one Ge–Zn bond, if the reaction is carried out at room temperature:

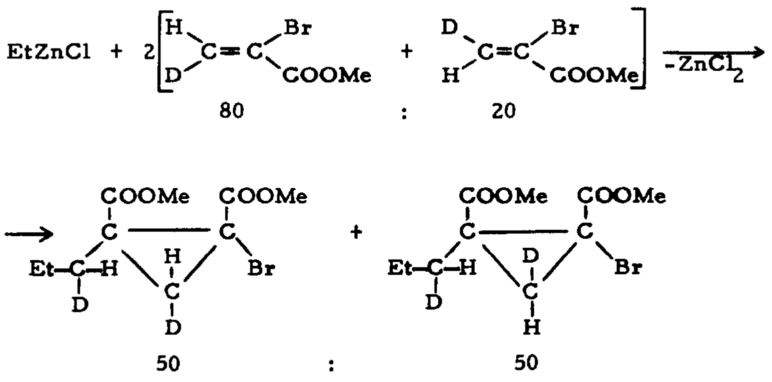
$$(Ph_3Ge)_2Zn + HOAc \xrightarrow{20^{o}} Ph_3GeZnOAc + Ph_3GeH$$

At 100° both Ge—Zn bonds react [18].

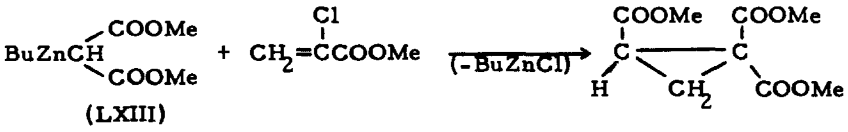
The thermal decomposition of ethyl(triphenylsiloxy)zinc involves migration of a phenyl group from silicon to zinc and further decomposition by a radical mechanism. Reaction of (LXII) with carbon tetrachloride or chloroform yields an unstable trichloromethylzinc compound which decomposes with the formation of triphenylsiloxyzinc chloride and dichlorocarbene [15]:

$$\underset{(LXII)}{EtZnOSiPh_3} \xrightarrow[CHCl_3]{CCl_4 \text{ or}} \left[Ph_3SiOZnCCl_3\right] \xrightarrow[-:CCl_2]{} Ph_3SiOZnCl$$

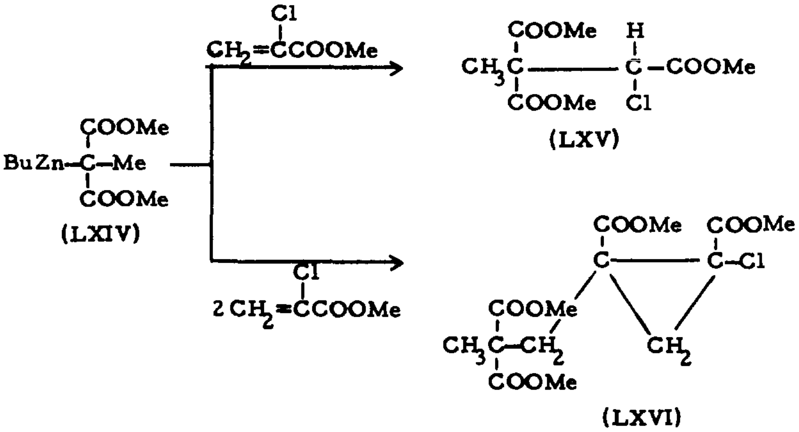
The stereochemistry of ring-formation in the reaction of two molecules of α-halogenoacrylic ester with ethylzinc chloride (AS 71; 93) has been studied using β-deuterated α-bromoacrylic ester. The mode of



the C=C double bond opening was found to be cis and trans in a 50/50 ratio. The use of chiral alkylzinc alkoxides allows the asymmetric synthesis of cyclopropanedicarboxylic esters [94]. If instead of EtZnCl the alkylzinc chelate compound (LXIII) is reacted with methyl α-chloroacrylate, the reaction proceeds in a different fashion with only one molecule of acrylate participating in the ring closure:



However, if the α-H is replaced by methyl as in (LXIV) the normal 1/2 reaction with α-haloacrylate takes place with formation of (LXVI). In this case the product of the first-step 1/1 addition (LXV) can be isolated [95]:



III. ORGANOZINC COMPOUNDS AS POLYMERIZATION CATALYSTS

Several publications providing details on the catalytic properties of organozinc compounds in polymerization reactions have appeared. Abstracts of patent applications and patents describing multi-component polymerization catalysts containing organozinc compounds as one of the components of the catalytic system, which have appeared in Chemical Abstracts, will not be surveyed here.

A brief survey of the research of the Utrecht group concerned with the application of organozinc compounds as catalysts for the cyclotrimerization of isocyanates and the polymerization of aldehydes and β-lactones has appeared in print. Emphasis is on investigations aiming at elucidating the initiation and propagation mechanism of these organozinc-catalyzed reactions [21].

Tsuruta has given an excellent account of the state of the art in the area of stereoselective and asymmetric-selective (or stereoelective) polymerizations in a review with 142 references. The author who has made substantial contributions in this area deals extensively with the role of organozinc-based catalyst systems in this type of polymerizations [96].

Several alkylzinc alkoxides derived from tertiary alcohols were found to be active in the polymerization of epoxides, the catalytic activity decreasing in the series ethylzinc triphenylmethoxide > ethylzinc diphenylmethylmethoxide > ethylzinc dimethylphenylmethoxide and,therefore, with decreasing acid strength. The alkylzinc alkoxides containing the (+)-2-methylbutylzinc group induced the asymmetric-selection polymerization of DL-propylene oxide with formation of optically active poly(propylene oxide). The asymmetric-selection efficiency increases with increasing phenyl--substitution of the alkoxide (increasing σ^*-constant) [14].

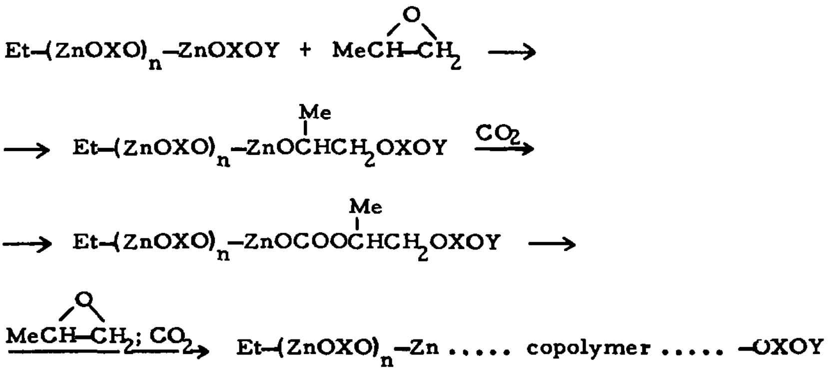
Tani et al. have published the details of their study of the stereospecific polymerization of propylene oxide and its α-deuterated analog using N,N-bis(ethylzinc)-tert.butylamine as the catalyst. Only in the presence of a small amount of water is isotactic poly(propylene oxide) obtained. It was concluded that at least two kinds of catalytically active species are present, one for the atactic and one for the isotactic polymerization and that the main reaction occurring in the presence of water is represented by [97]:

$$2\,\mathrm{EtZnNBu^tZnEt} + \mathrm{H_2O} \longrightarrow 2\,\mathrm{EtZnNHBu^t} + \mathrm{EtZnOZnEt}$$

The system diethylzinc/nitromethane has been reported to exhibit a very high catalytic activity for the polymerization of a variety of alkylene oxides. The reaction of Et_2Zn with nitromethane in addition to the zinc salt of methazonic acid produces water which upon reaction with Et_2Zn produces the catalytically active species [93].

Inoue and Tsuruta have continued their investigations concerned with the organozinc-catalyzed alternate copolymerization of carbon dioxide and epoxides [cf. AS 71; 108].

The differences between the catalyst systems diethylzinc/water and diethylzinc/methanol has been examined in relation to the elementary processes of the copolymerization. Both catalysts react with CO_2 to produce XZnOCOOR, where X = OCH_3 for the $Et_2Zn/MeOH$ system and X = $(OZn)_nOH$ or $(OZn)_nEt$ for the Et_2Zn/H_2O system. The reactivity of XZnOCOOR with propylene oxide depends on X and the difference between the two systems can be explained by the presence or absence of repeating Zn–O bonds [98]. The combination diethylzinc/dihydric phenol is a particularly effective catalyst for the copolymerization reaction. The catalytic activity of these systems is believed to be connected with the presence of the ZnOXOZn group, where X may be phenylene, naphthylene, etc. One aromatic group (–OXO–) is incorporated into the copolymer chain in the initial stage of the copolymerization [13]:



$$\mathrm{Et{-}(ZnOXO)_n{-}ZnOXOY} + \overset{O}{\mathrm{MeCH{-}CH_2}} \longrightarrow$$

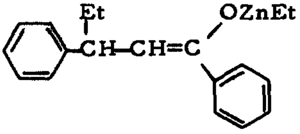
$$\longrightarrow \mathrm{Et{-}(ZnOXO)_n{-}ZnO\overset{Me}{C}HCH_2OXOY} \xrightarrow{CO_2}$$

$$\longrightarrow \mathrm{Et{-}(ZnOXO)_n{-}ZnOCOO\overset{Me}{C}HCH_2OXOY} \longrightarrow$$

$$\xrightarrow{\overset{O}{\mathrm{MeCH{-}CH_2}};\ CO_2} \mathrm{Et{-}(ZnOXO)_n{-}Zn}\ \ldots\ldots\ \text{copolymer}\ \ldots\ldots\ \mathrm{{-}OXOY}$$

Another active copolymerization catalyst consists of the combination of dialkylzinc with dicarboxylic acids or hydroxycarboxylic acids. Especially Et_2Zn/isophthalic acid 1/1 and Et_2Zn/m-hydrobenzoic acid 1/1 gave higher yields than the Et_2Zn/resorcinol system. Active species of the type $Et{-}(ZnOOCRCOO)_n{-}H$ and $Et{-}(ZnOOCRO)_n{-}H$ are probably involved [99].

Tsuruta has studied ethylzinc 1,3-diphenyl-1-pentene-olate (LXVII) as a model compound for the growing end in the anionic polymerization of phenylvinylketone [23]:



(LXVII)

IV. STRUCTURAL, SPECTROSCOPIC AND PHYSICAL STUDIES

A. Structural studies

An X-ray crystal structure determination of ethylzinc iodide has been reported [100]. This compound is a coordination polymer in the solid, Fig. 2 showing the arrangement of the molecules in the projection along b and Fig. 3 the relationship between the polymeric structure and the theoretical cubane-type arrangement.

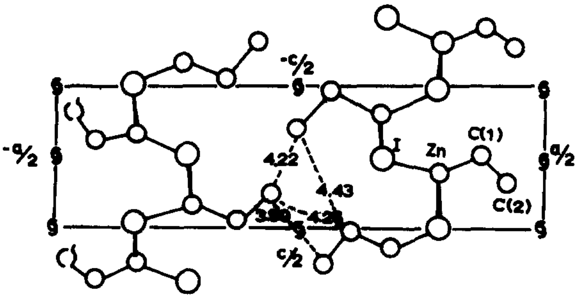


Fig. 2. Arrangement of ethylzinc iodide molecules in the projection along b [from P. T. Moseley and H. M. M. Shearer, J. Chem. Soc., Dalton Trans., 1973, 64].

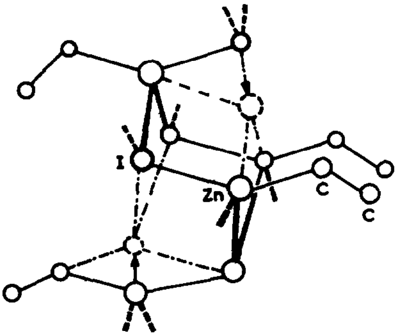


Fig. 3. The relationship between the polymeric structure and the theoretical cubane-type structure for ethylzinc iodide [from P. T. Moseley and H. M. M. Shearer, J. Chem. Soc., Dalton Trans., 1973, 64].

B. Spectroscopic studies

Evans and Phillips have concluded from ^{19}F-NMR spectroscopic measurements (p-fluorine region) that the species present in solutions of pentafluorophenylzinc iodide in THF can be represented by a predominantly monomeric Schlenk equilibrium:

$$(C_6F_5)_2Zn + ZnI_2 \rightleftarrows 2C_6F_5ZnI$$

The calculated value for the equilibrium constant K is 7.5 ± 0.9 at 35°. The activation energy for pentafluorophenyl exchange was found to be ca. 70 kJ mol^{-1} [2]. K_{eq} values for a variety of solvents are given.

Pentafluorophenylzinc bromide in THF behaves similarly with K_{eq} 16.0 ± 3.0 at 35° [2].

The 60 MHz ^{1}H-NMR spectral parameters for a series of divinylmetal compounds (Zn, Cd, Hg) have been reported by Visser and Oliver. The change in the chemical shifts and coupling constants have been discussed as a function of the central metal atom [101]. The 60 MHz ^{1}H-NMR parameters for di-3-butenylzinc and di-4-pentenylzinc have been reported by Denis et al. The data for the latter compound have been interpreted in terms of a weak intramolecular interaction between the zinc atom and the double bond. A dipole-dipole interaction as a result of the inherent polarity of the Zn—C bond and the polarity of the double bond is proposed [5].

Stability constants for the complex formation between dimethylzinc and diethylsulphide (K = 3), diethylether (K = 20) and triethylamine (K ≈ 200) have been determined by an NMR technique [102]. NMR spectroscopic data for a variety of alkylzinc alkoxides derived from tertiary carbinols have been reported by Nakaniwa et al. [14].

The transient monomethylzinc radical has been generated by flash photolysis of dimethylzinc and its UV absorption spectrum has been recorded and interpreted. Two absorption systems occur at 3790 - 4180 Å and 2600 - 2740 Å [103].

Dimethylzinc has been included in a molecular structure study of dimethylmetal compounds (M = Zn, Cd, Hg). A normal coordinate analysis is presented and the normal frequencies and eigenvectors have been calculated [104].

IR and Raman spectra have been presented for solid methylzinc borohydride and methylzinc deuteride. The vibrational modes of the CH_3Zn^+ ion have been assigned assuming local C_{3v} symmetry. The Zn—C stretch (557 cm^{-1}) occurs at the average of the symmetric (503 cm^{-1}) and asymmetric (610 cm^{-1}) stretches of $(CH_3)_2Zn$ [105].

The 2,2'-bipyridyl complex of bis(triphenylgermyl)zinc and of bis-(triphenylstannyl)zinc displays charge-transfer absorptions in the visible spectrum, λ_{max} of which decreases with increasing polarity of the solvent [17].

The consistently lower metal-metal stretching frequency (ν_{as} MZnM) in $(Ph_3M)_2Zn{\cdot}Bipy$ complexes as compared with in $(Ph_3M)_2Zn{\cdot}TMED$ complexes (M = Ge, Sn) has been explained in terms of Zn ⟶ Bipy charge transfer [17].

Alkylzinc thiocyanates RZnSCN display the Zn—C stretching absorption at 558 cm^{-1} ($R = CH_3$) and 530 cm^{-1} ($R = C_2H_5$), respectively [12]. Bis(trimethylsilylmethyl)zinc $(Me_3SiCH_2)_2Zn$ according to the IR and Raman spectra possesses the expected linear structure. The single Zn—C stretch occurs at 508 cm^{-1} (polarized) [9].

C. Miscellaneous studies

Measurements of the optical rotation (α_D^{25} in benzene solution) have revealed that the transfer of (S)-2-methylbutyl groups from zinc to aluminium in the (+)-di[(S)-2-methylbutyl]zinc/tri-isobutylaluminium system proceeds without significant racemization [106].

Philipp et al. have developed an improved procedure for the quantitative determination of $C_1 - C_5$ alkylzinc compounds [107]. The bis-THF complex of dimethylzinc has been applied as the reagent for the quantitative gas-volumetric determination of surface hydroxyl groups in amorphous silica [108].

Guest et al. have included dimethylzinc in their theoretical study of the bonding in a number of methylmetal compounds (Li, B, Zn) based on semi-empirical and ab initio molecular orbital calculations. The carbon atoms are approximately sp^2 hybridized, the Zn—C bonds have negligible π character and the zinc 3d orbitals are essentially non-bonding in character [109]. A topological equivalent orbital approach has been applied by Cox to a variety of polynuclear organozinc species such as $(RZnSR')_4$ and $(MeZnS\text{-}iPr)_8$ [110].

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