ZINC

ANNUAL SURVEY COVERING THE YEAR 1971

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CONTENTS

I. PREPARATION OF ORGANOZINC COMPOUNDS

    The 1971 literature contains relatively few references dealing with new organozinc compounds or new types of organozinc complexes.

Lorberth has published the details of his synthesis of Group II B metal derivatives of diazoalkanes. Such compounds were obtained by acidolysis of the very reactive bis(trimethylsilylamino) derivatives with diazomethane or ethyl diazoacetate [1]:

$$Zn[N(SiMe_3)_2]_2 + CH_2N_2 \xrightarrow{Et_2O} [ZnCN_2]_n + 2HN(SiMe_3)_2$$

$$Zn[N(SiMe_3)_2]_2 + 2HC(N_2)COOEt \xrightarrow{Et_2O} Zn[C(N_2)COOEt]_2 +$$

$$+ 2HN(SiMe_3)_2$$
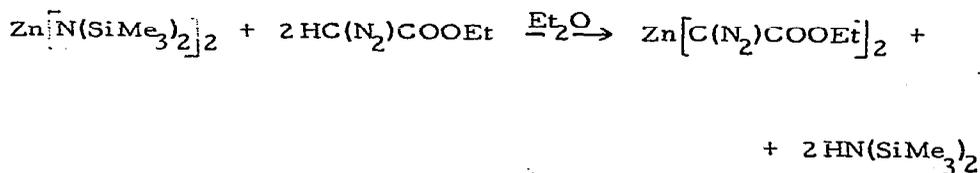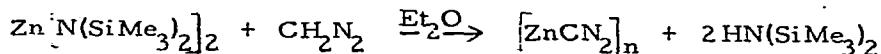
Novel trinuclear phenylzinc β-diketonate complexes have been characterized by Boersma et al. Complexes of type (I) are formed via spontaneous disproportionation of the Ph_2Zn/β-diketone 1/1 reaction

$$Ph_2Zn + Hacac \xrightarrow{benzene} [PhZn\,acac] + PhH$$

$$2[PhZn\,acac] \longrightarrow Ph_2Zn + Zn(acac)_2$$

$$2[PhZn\,acac] + Zn(acac)_2 \longrightarrow [PhZn\,acac]_2 \cdot Zn(acac)_2$$
$$(I)$$
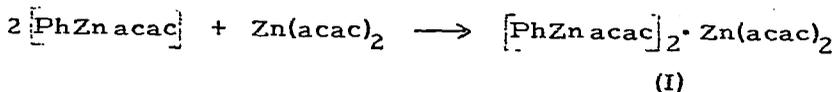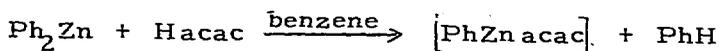
product or by a stoechiometric reaction which allows the isolation of mixed complexes:

$$2PhZn\,pac + Zn(acac)_2 \longrightarrow [PhZn\,pac]_2 \cdot Zn(acac)_2$$
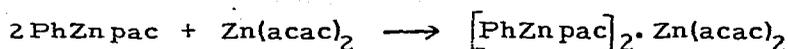
For (I) a structure with one hexacoordinate central zinc and two tetra-
coordinate terminal zinc atoms has been proposed [2].
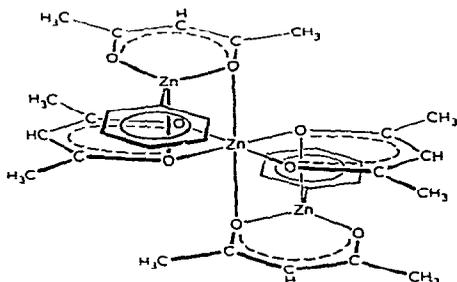
Kawakami and Tsuruta have reported a study (analytical, molecular
weight, IR and NMR data) of the products formed by the interaction of
n-butylzinc compounds (Bu_2Zn as well as BuZnX) with active methylene
compounds, e.g.:

$$BuZnOMe + CH_2(COOMe)_2 \longrightarrow MeOZnCH(COOMe)_2 + BuH$$
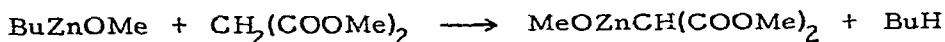
Such products were shown to undergo a Michael-type 1,4-addition with
α, β-unsaturated carbonyl compounds [3].

Aminophosphine derivatives of organozinc compounds have been
synthesized using an acidolysis-type reaction [4]:

$$Ph_2Zn + RNHPPh_2 \xrightarrow{Et_2O} PhZnNRPPh_2 + PhH$$

(R = $2,3$-$Me_2C_6H_3$,4-MeC_6H_4,2-pyridyl)
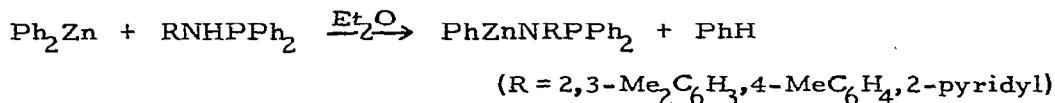
Crystalline 1/1 complexes in which bis-trimethylphosphinimo-
-dimethylsilane acts as a 1,3-bidentate ligand to the tetracoordinate
zinc atom of dimethyl- and diethylzinc have been reported by Schmid-
baur and Wolfsberger [5]:

$$R_2Zn + (Me_3P=N)_2SiMe_2 \longrightarrow Me_3P=N \diagdown \begin{matrix} Me \diagdown \diagup Me \\ Si \\ \diagup \diagdown \\ \diagdown Zn \diagup \\ \diagup \diagdown \\ R \quad R \end{matrix} \diagup N=PMe_3$$
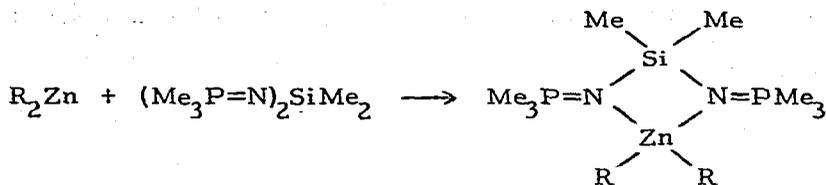
Various reports dealing with the synthesis of anionic alkylzinc or hydridozinc complexes have appeared.

Tsuruta et al. have investigated the synthesis and reactivity towards carbon tetrachloride and a variety of saturated and α, β-unsaturated ketones of calciumzinc tetra-n-butyl $CaZn(n-Bu)_4$ [6].

Greenwood and Travers have reported anionic zinc, cadmium and mercury complexes of the dodecahydro-_nido_-decaborate(2-) ion [7]. The zinc complexes which were isolated as the bis-(trimethylammonium) or the bis-(methyltriphenylphosphonium) salts are readily obtained by ionization in water of the neutral compound which according to new analytical results is a bis-ether complex:

$$2\,ZnB_{10}H_{12}\cdot 2\,Et_2O \xrightarrow{H_2O} Zn^{2+} + Zn(B_{10}H_{12})^{2-} + 4\,Et_2O$$
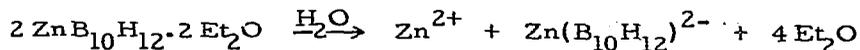
The reaction of methylzinc iodide with sodium hydride in THF yields a compound of the composition $NaZn_2(CH_3)_2H_3$ for which the

$$2\,CH_3ZnI + 3\,NaH \longrightarrow NaZn_2(CH_3)_2H_3 + 2\,NaI$$

$$(II)$$
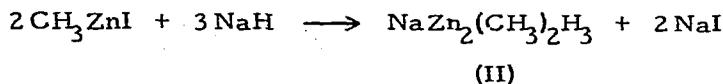
following structures were considered [8]:

$$\left[\begin{matrix} CH_3 \diagdown \quad \diagup CH_3 \\ Zn-H-Zn \\ H \diagup \quad \diagdown H \end{matrix}\right]^- \quad \left[\begin{matrix} CH_3 \diagdown \quad \diagup H \\ Zn-H-Zn \\ CH_3 \diagup \quad \diagdown H \end{matrix}\right]^- \quad \left[\begin{matrix} H \\ \diagup \diagdown \\ CH_3-Zn-H-Zn-CH_3 \\ \diagdown \diagup \\ H \end{matrix}\right]^-$$
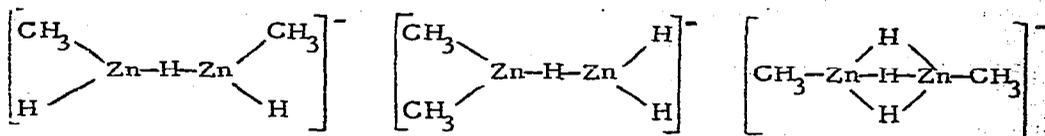
Reductions with this hydride afford results similar to those obtained
with $LiAlH_4$, reductions of nitriles being particularly facile. (II) is a
precursor to the first ternary hydride of zinc. Moderate heating under
high vacuum converts (II) into $NaZnH_3$:

$$Na_2Zn(CH_3)_2H_3 \cdot x\ THF \longrightarrow NaZnH_3 + (CH_3)_2Zn + x\ THF$$
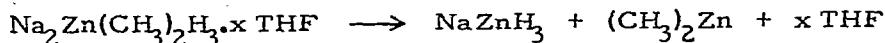
$NaZnH_3$ has somewhat greater thermal stability than ZnH_2 [8].

The quaternary zinc hydride K_2ZnH_4 has been obtained by Ashby
and Beach by the reaction of potassium hydride with di-sec.butylzinc
in benzene or THF and by the hydrogenation of the anionic complex
$KZn(sec-Bu)_3$ in THF [9]:

$$4\ KH + 3\ (sec-Bu)_2Zn \longrightarrow K_2ZnH_4 + 2\ KZn(sec-Bu)_3$$

$$2\ KZn(sec-Bu)_3 + 3\ H_2 \longrightarrow K_2ZnH_4 + Zn + 6\ C_4H_{10}$$
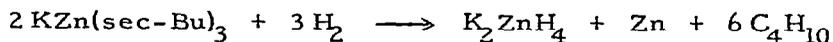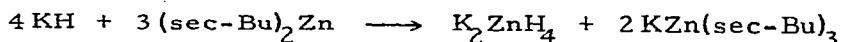
In contrast to ZnH_2 K_2ZnH_4 is quite thermally stable [9].

Russian authors found the reaction of zinc iodide with $LiAlH_4$ in
diethylether at $-45-50°$ unsuitable as a route to zinc hydride [10].
From a kinetic study of the thermal decomposition of zinc hydride in
diethylether an activation energy of 27.9 Kcal/mole was obtained for
this reaction [11].

II. REACTIONS OF ORGANOZINC COMPOUNDS

A. Reformatsky reaction and related reactions

The chemistry of functionally substituted organozinc reagents
has remained the single most active area of organozinc research. In
this research, which has been largely the domain of French chemists,
organic rather than organometallic aspects are emphasized. In the
past year numerous new synthetic applications of the Reformatsky
reaction and related reactions have appeared in the literature. Stereo-
chemical aspects have also received attention.

The Reformatsky reaction is normally conducted at reflux tem-
perature in benzene or benzene-ether solvents. Rathke and Lindert
observed that reaction proceeds readily at room temperature and, more
important, that nearly quantitative yields may be obtained when a sol-
vent mixture containing trimethylborate is used. The advantage of this
procedure is most apparent when the carbonyl compound is especially
susceptible to base-catalyzed condensation [12].

The use of trimethylsilyl α-bromoesters instead of alkyl α-
-bromoesters allows a facile synthesis of β-hydroxyacids. The primary
β-hydroxy trimethylsilyl esters are hydrolyzed under extremely mild
conditions, e.g. [13]:

$$\text{Ph-C(=O)-Et} + \text{BrZnCH}_2\text{C}(=O)\text{OSiMe}_3 \longrightarrow \left[\text{Ph}\diagdown\underset{\text{Et}}{\overset{}{C}}\diagup\overset{\text{CH}_2\text{COSiMe}_3}{\underset{\text{OZnBr}}{}} \right]$$

$$\xrightarrow[\text{HCl}]{\text{dilute}} \underset{\text{Et}}{\overset{\text{Ph}}{\diagdown}}\text{C(OH)CH}_2\text{COOH} \quad (80\%)$$
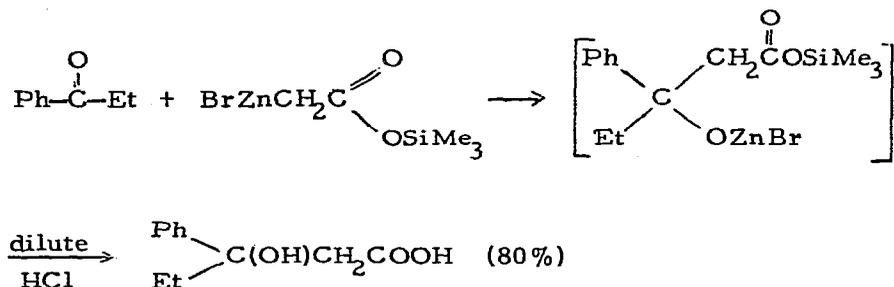
The Reformatsky reaction has been applied for the introduction
of the carbaethoxymethyl group in organosilicon [14], organogerma-

nium [15] and organotin [14] compounds:

$$\geq MX + ZnBrCH_2COOEt \longrightarrow \geq MCH_2COOEt + ZnBrX$$
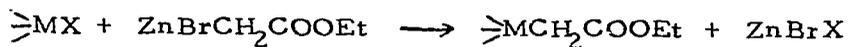
Nitrones may be applied as carbonyl analogs when tetrahydro-
furan is used as the solvent and the reaction temperature is controlled.
E.g. N-methyl-C-arylaldonitrones react with zinc and α-bromoesters
to yield the corresponding 2-methyl-3-aryl-5-isoxazolidones (III) [16]:

(III)
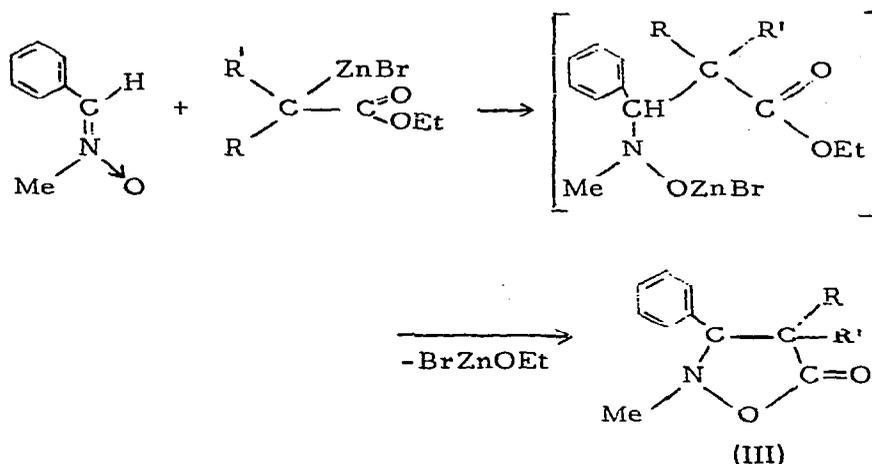
Several studies have dealt with stereochemical aspects of conden-
sation reactions with Reformatsky reagents.

Luche and Kagan have investigated the stereochemistry of the
reaction with Schiff bases. The preformed reagents at -18° react with
nearly quantitative formation of aminoesters with erythro-configuration
(IV). At reflux temperature a certain amount of threo-isomer (V) is
formed as well. The results were interpreted in terms of a certain
degree of reversibility for the condensation reaction [17]:

$$\underset{(IV)}{\overset{\displaystyle Ph \blacktriangleright \overset{\overset{\displaystyle H}{\vdots}}{\underset{\displaystyle R\blacktriangleright \overset{\displaystyle |}{C}-COOR'}{\overset{\displaystyle |}{C}}-\overset{\overset{\displaystyle ZnBr}{|}}{N}-Ph}}{\vphantom{.}} \quad \overset{\displaystyle \longrightarrow}{\longleftarrow} \quad \underset{+}{\underset{\displaystyle PhCH=N-Ph}{\overset{\displaystyle RCH-C\overset{O}{\underset{OR'}{\diagup}}}{\overset{\overset{\displaystyle ZnBr}{|}}{}}}} \quad \overset{\displaystyle \longrightarrow}{\longleftarrow} \quad \underset{(V)}{\overset{\displaystyle Ph\blacktriangleright \overset{\overset{\displaystyle H}{\vdots}}{\underset{\displaystyle R---\overset{\displaystyle |}{C}-COOR'}{\overset{\displaystyle |}{C}}-\overset{\overset{\displaystyle ZnBr}{|}}{N}-Ph}}{\underset{\displaystyle \blacktriangle\,H}{}}}$$
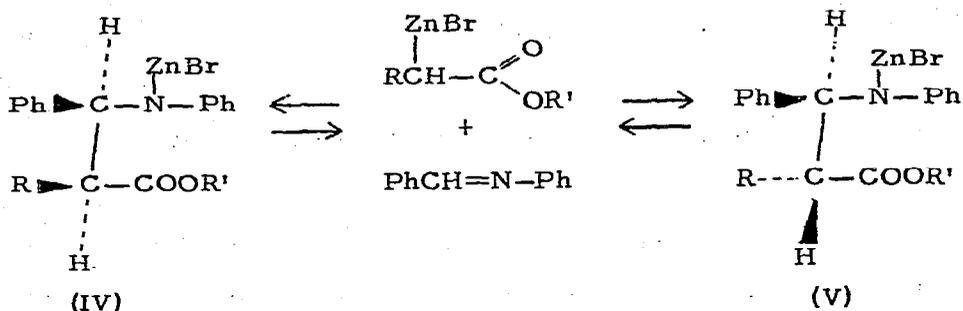
A study of the stereochemistry of addition of Reformatsky reagents to 2-methyl- and 2-ethylcyclohexanone revealed a strong preference for equatorial attack the ratio of trans- to cis-epimeric alcohols being in the order of 4/1 [18]:

$$\text{(cyclohexanone with R, O)} + BrZnCH_2C\overset{O}{\underset{OR'}{\diagup}} \xrightarrow{(H_2O)} \text{(cyclohexane with -R, CH}_2\text{COOR', OH)} + \text{(cyclohexane with -R, OH, CH}_2\text{COOR')}$$
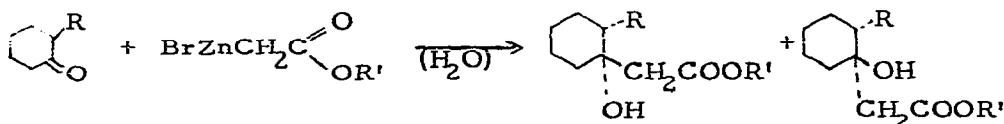
This is the trend generally followed by alkylzinc compounds for this type of addition (AS 69; 223).

Blagoev and coworkers have shown that in DMSO at $45°$ the condensation product of the Reformatski reagent derived from methyl α--bromophenylacetate and benzaldehyde rapidly equilibrates to a mixture of erythro- (35%) and threo- (65%) isomers [19]:

$$\underset{\underset{\displaystyle BrZnO \quad H \quad \underline{erythro-}}{\blacktriangle \qquad \blacktriangle}}{Ph-\overset{\overset{\displaystyle H}{\vdots}}{C}-\overset{\overset{\displaystyle Ph}{\vdots}}{C}-COOMe} \quad \rightleftarrows \quad \underset{\underset{\displaystyle BrZnO \quad Ph \quad \underline{threo-}}{\blacktriangle \qquad \blacktriangle}}{Ph-\overset{\overset{\displaystyle H}{\vdots}}{C}-\overset{\overset{\displaystyle H}{\vdots}}{C}-COOMe}$$
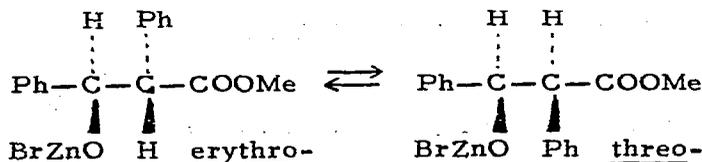
The same authors observed that replacement of the methyl by a terti-

ary butyl group slightly favors the formation of the erythro-isomer

(erythro/threo = 48/52) [20]. Gaudemar et al. have shown that in

DMSO at -5° the condensation of benzaldehyde or acetophenone with

the Reformatsky reagent derived from ethyl or propyl α-bromobutyrate

is kinetically controlled [21].

   The asymmetric synthesis of β-hydroxyesters using achiral

reagents has been realized by carrying out the Reformatsky condensa-

tion in an asymmetric solvent. The use of (-)spartein (a tertiary dia-

mine) has made possible the synthesis of β-hydroxyester with (S) con-

figuration having optical purities as high as 98%. Application of the

preformed reagent in dimethoxymethane increased the optical purity

which depending on the substituent groups was in the order of 35-98%

[22].

   Reformatsky reagents undergo conjugate addition upon interaction

with diethyl alkylidene malonates, 1,4-adducts having been isolated in

yields of 52-60% [23]:
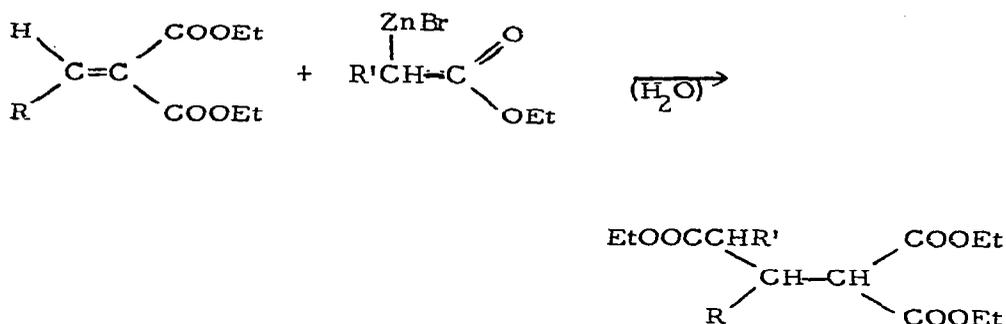

   A similar 1,4-addition takes place with alkylidene cyanoacetates

allowing the preparation in 50-60 yield of α-cyanoglutaric esters [24]:

$$\underset{R}{\overset{H}{>}}C=C\underset{COOEt}{\overset{CN}{<}} \quad + \quad BrZnCH_2C\underset{OEt}{\overset{O}{<}} \quad \xrightarrow{(H_2O)} \quad \underset{\underset{CH_2-COOEt}{|}}{R-CH-CH}\underset{COOEt}{\overset{CN}{<}}$$
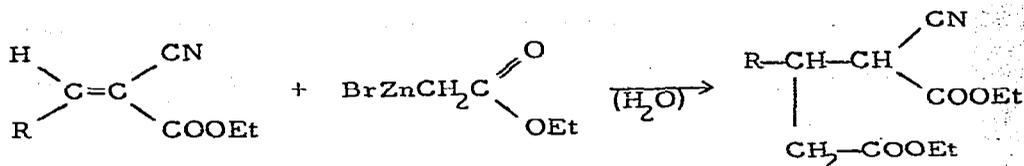
(R = Et, n-Pr, i-Pr)

Reformatsky reagents undergo coupling reactions with carbon halogen bonds. A complete product study of the reaction of the reagent derived from ethyl α-bromobutyrate with bis(chloromethyl)ether has been reported and conditions for obtaining (VI) in 55-65% yield were developed [25]:

$$2 \underset{CH_3}{\overset{CH_3}{>}}C\underset{}{\overset{ZnBr}{—}}C\underset{OEt}{\overset{O}{<}} \quad + \quad (ClCH_2)_2O \quad \xrightarrow{(H_2O)} \quad (EtO\overset{O}{\overset{\|}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-)_2O$$

(VI)
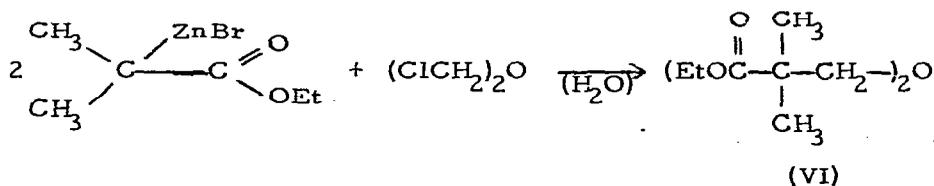
The synthesis of esters of substituted malic acids in yields of 17-60% has been effected by Russian workers via condensation of Reformatsky reagents with α-ketoesters [26]:

$$Ph\overset{O}{\overset{\|}{C}}COOR \quad + \quad BrZnCHR'COOR \quad \xrightarrow{(H_2O)} \quad PhC(OH)(COOR)CHR'COOR$$

(R=Me, Et; R'=H, Me, Et)
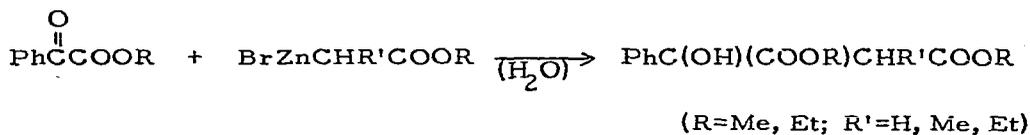
Several papers dealing with synthetic applications of functionally substituted organozinc compounds differing from the traditional Reformatsky reagents have appeared.

Methyl α-bromocrotonate affords an organozinc reagent which undergoes conjugate addition with diethyl alkylidene malonates. A mix-

ture of the products (VII; straight addition) and (VIII; allylic rearrangment) is isolated [27]:

$$R-CH=C \underset{COOEt}{\overset{COOEt}{<}} \quad + \quad BrZnCH_2-CH=CH-COOMe$$

$$\xrightarrow[\text{(H}_2\text{O)}]{} \quad \underset{CH_2-CH=CH-COOMe}{\overset{R-CH-CH(COOEt)_2}{|}} \quad + \quad \underset{CH_2=CH-CH-COOMe}{\overset{R-CH-CH(COOEt)_2}{|}}$$

$$\text{(VII)} \hspace{4cm} \text{(VIII)}$$

$$\text{(R=Et, n-Pr, i-Pr and Ph)}$$
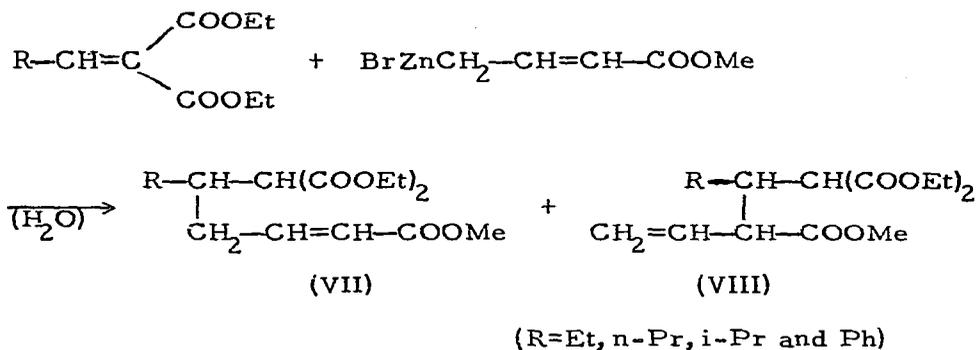
Diethyl dibromomalonate affords an organozinc reagent which upon condensation with aldehydes affords in yields up to 52% not hitherto reported α-bromo-β-hydroxydiesters [28]:

$$R-C \underset{H}{\overset{O}{<}} \quad + \quad BrZnCBr(COOEt)_2 \xrightarrow[\text{(H}_2\text{O)}]{} R-CH(OH)-CBr(COOEt)_2$$

$$\text{(R=Me, Et, n-Pr, CCl}_3 \text{ and n-Hex)}$$
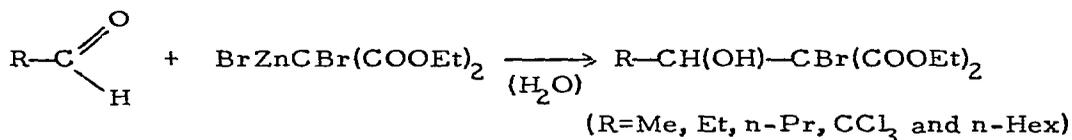
Reaction of the intermediate condensation product with acetyl chloride in dimethoxymethane results in the formation of the methoxymethyl derivatives:

$$R-CH(OZnBr)-CBr(COOEt)_2 \xrightarrow[\text{CH}_2\text{(OMe)}_2]{\text{MeCOCl}} \underset{OCH_2OCH_3}{\overset{R-CH-CBr(COOEt)_2}{|}}$$
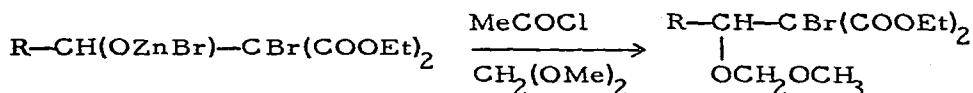
Reaction with acetyl chloride in diethylether affords the corresponding acetates [28]:

$$R-CH-CBr(COOEt)_2 \quad \xrightarrow[\text{Et}_2\text{O}]{\text{MeCOCl}} \quad R-CH-CBr(COOEt)_2$$
$$\quad\ |\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad\ |$$
$$\text{OZnBr}\qquad\qquad\qquad\qquad\qquad\qquad\text{OCOMe}$$
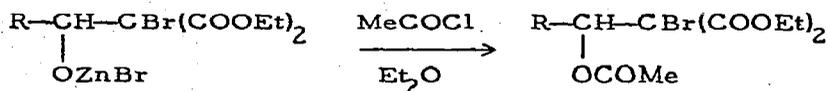
The same organozinc reagent readily reacts with diethyl alkylidene-malonates with formation of an adduct which if the temperature is kept below $-65°$ may be hydrolyzed to the corresponding α-bromotetra-esters (IX; yield 62% for R=Me) [29]:

$$RCH=C\begin{array}{l}{}^{\displaystyle COOEt}\\[-2pt]{}_{\displaystyle COOEt}\end{array} \quad + \quad BrZnCBr(COOEt)_2 \quad \xrightarrow{(H_2O)} \quad RCH\begin{array}{l}{}^{\displaystyle CH(COOEt)_2}\\[-2pt]{}_{\displaystyle CBr(COOEt)_2}\end{array}$$

$$(IX)$$
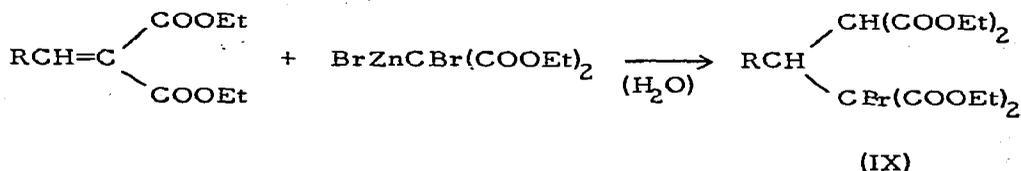
At higher temperatures the adduct eliminates zinc bromide resulting in cyclization with formation of a cyclopropane tetracarboxylic ester (X; yield 59% for R=n-Pr) [29]:

$$\left[\begin{array}{c}\text{ZnBr}\\ |\\ R-CH-C-(COOEt)_2\\ |\\ CBr(COOEt)_2\end{array}\right] \xrightarrow{-\text{ZnBr}_2} \quad R-CH\begin{array}{c}C(COOEt)_2\\ |\\ C(COOEt)_2\end{array}$$

$$(X)$$
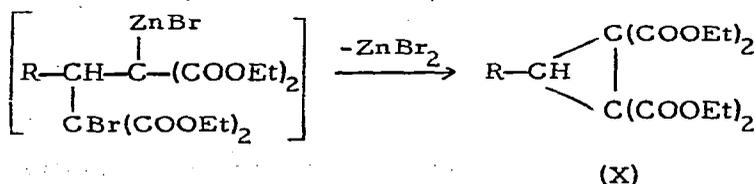
Russian workers have prepared α-substituted β-diketones via the coupling of organozinc reagents derived from α-bromoketones with acyl chlorides [30]:

$$RCH(ZnBr)COCH_2R \quad + \quad R'COCl \quad \longrightarrow \quad R'\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}CH(R)\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}CH_2R$$

(R=Et, n-Pr, n-Bu)
(R'=Me, n-Pr, n-Bu, Ph)

Various synthetic applications of cyanomethylzinc reagents derived from α-bromonitriles (AS 69; 218) have been reported [31]. Addition to benzalacetophenone leads to the formation of γ, δ-unsaturated β-hydroxynitriles (XI) or of δ-ketonitriles (XII) depending on the nature of R and R':

$$
\begin{array}{l}
\mathrm{R'}\!\!\diagdown\!\!\underset{\mathrm{R}\diagup}{\mathrm{C}}\!\!-\!\!\mathrm{CN} \;+\; \mathrm{PhCH{=}CHCPh} \xrightarrow[\mathrm{(H_2O)}]{}
\end{array}
$$

PhCH=CH—$\overset{\overset{\textstyle OH}{|}}{\underset{\underset{\textstyle Ph}{|}}{C}}$—CRR'CN

(XI)
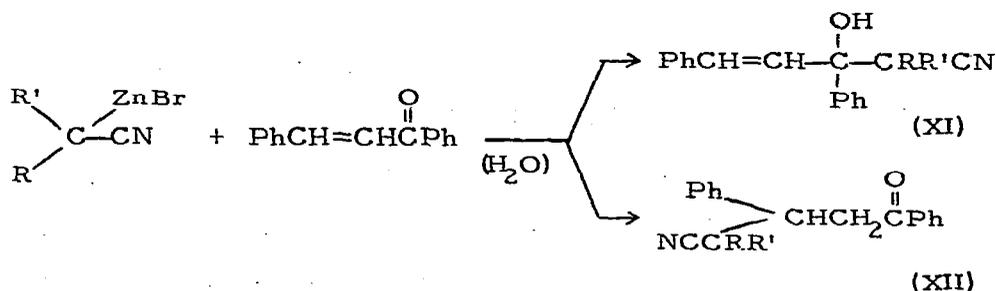
$\mathrm{\underset{NCCRR'}{Ph}\!\!\diagdown}$ CHCH$_2$$\overset{O}{\overset{\|}{C}}$Ph

(XII)

Reaction with crotonaldehyde results in 1,2-addition only:

$$
\mathrm{MeCH{=}CH{-}C}\!\!\diagup\!\!\!^{O}_{\diagdown H} \;+\; \mathrm{R'}\!\!\diagdown\!\!\underset{\mathrm{R}\diagup}{\mathrm{C}}\!\!-\!\!\mathrm{CN} \xrightarrow[\mathrm{(H_2O)}]{} \mathrm{MeCH{=}CH{-}}\overset{\overset{\textstyle OH}{|}}{CH}\mathrm{{-}CRR'CN}
$$

With diethyl alkylidene malonates exclusively 1,4-addition takes place, the corresponding diester nitriles (XIII) having been isolated in yields of 55-70% [31]:

$$
\mathrm{R'}\!\!\diagdown\!\!\underset{\mathrm{R}\diagup}{\mathrm{C}}\!\!-\!\!\mathrm{CN} \;+\; \mathrm{R''CH{=}C}\!\!\diagup\!\!\!^{COOEt}_{\diagdown COOEt} \xrightarrow[\mathrm{(H_2O)}]{}
$$

R''—CH—CH(COOEt)$_2$
|
R—C—R'
|
CN

(XIII)

Preformed organozinc reagents derived from α-bromoamides (AS 67; 237) add across the C=N double bond of Schiff bases with formation in good yield of β-aminoamides [32]:

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$$RCH=NR' \; + \; R'\!\!-\!\!\overset{\overset{\displaystyle ZnBr}{\displaystyle |}}{CH}\!\!-\!\!CONEt_2 \; \xrightarrow[(H_2O)]{} \; \underset{R'NH}{\overset{R}{\diagdown}}CH\!\!-\!\!CH(R'')\!\!-\!\!CONEt_2$$

The reaction proceeds with a high degree of stereoselectivity (e.g. 85/15 ratio of diastereoisomers if R=R'=Ph and R''=Et).

## B. Reactions of alkylzinc and alkenylzinc compounds with carbon- -carbon and carbon-hetero atom unsaturated bonds

The chemical reactivity of alkyl and alkenylzinc compounds towards unsaturated molecules and the mechanistic and stereochemical aspects of such reactions have continued to attract attention in particular of French chemists. This research has produced a number of valuable synthetic procedures.

Jones et al. have compared the stereochemistry of the addition of dimethylzinc and dimethylcadmium towards 2-phenylpropanal, 2- -phenylbutanal and 2-phenyl-3-methylbutanal- with that observed for Grignard reagents. The observed trend in stereoselectivity with a change in metal, the absence of halide dependence on the stereochemistry for zinc and cadmium reactions, and the inertness of Me_2Zn and Me_2Cd prepared from MeLi are considered consistent with a bridged four-centre transition state (XIV) [33].

(XIV)

The same authors have compared the product composition and stereochemistry of the reaction of in situ n-propylzinc and -cadmium reagents

with 4-tert-butylcyclohexanone. The zinc reagent "2n-PrMgBr-ZnBr$_2$"
shows preference for reduction over addition. Whereas both Mg and
Cd reagents give preferentially axial reduction, the Zn reagents in
two instances gave the non-thermodynamic axial alcohol as the major
product [34]:

The addition of tetrabutylammonium halides (Cl > Br > I) has an
accelerating effect (by a factor of 9 for Bu$_4$NCl) on the addition reaction
of di-n-propylzinc and benzaldehyde and little influence on the reduc-
tion reaction causing a pronounced change in the product ratio 1-phenyl-
butanol-1/benzylalcohol (from 1.3 to 15.6 for Bu$_4$NCl). Spectroscopic
results indicate complexation of the salt with the dialkylzinc rather
than with the carbonyl compound [35].

The reaction of the organozinc reagent derived from 1-bromo-
pentene-2 with ketones proceeds with partial allylic rearrangment
resulting in the formation of a mixture of linear and branched alcohols
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 the synthesis of the more stable linear alcohols of the type

EtCH=CHCH$_2$C(OH)RR' (R=R'=Et, i-Pr, n-Bu) in 100% purity [36].

A similar situation applies for the condensation of the organozinc reagent derived from 1-bromopentadiene-2,4 with aldehydes and ketones:

$$
\begin{array}{c}
CH_2=CH-CH=CH_2CH_2ZnBr \\
+ \\
RR'C=O
\end{array}
\xrightarrow{(H_2O)}
\begin{array}{c}
\overset{\displaystyle C(OH)RR'}{\underset{\displaystyle |}{CH_2=CH-CH-CH=CH_2}} \\
+ \\
CH_2=CH-CH=CH-CH_2-C(OH)RR' \\
(XV)
\end{array}
$$

Changing reaction conditions from 3 hrs at 20°/THF to 3 hrs at 20° plus 45 hrs at 60°/THF allows the exclusive synthesis of a variety of linear dienic alcohols of type (XV) [37].

Allylzinc bromide undergoes conjugate addition with alkylidene cyanoacetates [24]:

$$
CH_2=CHCH_2ZnBr + RCH=C\overset{\displaystyle CN}{\underset{\displaystyle COOEt}{\diagup}}
\xrightarrow{(H_2O)}
CH_2=CH-CH_2-\overset{\displaystyle R}{\underset{\displaystyle |}{CH}}-CH\overset{\displaystyle CN}{\underset{\displaystyle COOEt}{\diagup}}
$$

(R=Me, Et, n-Pr, i-Pr, Ph)

Reaction with the ethoxymethylene compound (XVI) yields the bis-allyl substituted product (XVII) in 20% yield [24]:

EtOCH=C ⟨ CN, COOEt ⟩ (XVI)   →(CH₂=CHCH₂ZnBr)→   CH₂=CH—CH₂ \ CH—CH ⟨ CN, COOEt ⟩ / CH₂=CH—CH₂ (XVII)

Both conjugate addition (AS 69; 224) and carbonyl addition take place upon interaction of di-n-butylzinc with methyl α-chloroacrylate in either toluene or THF [38]:

H⟩C=C⟨Cl, COOMe / H   + Bu₂Zn →

Bu—C(H)—C(H)⋯ ⊖ ⊕ZnBu, C=O, OMe   (XVIII)

H⟩C=C⟨Cl / H \ C⟨OZnBu, Bu⟩ / MeO

It was shown that the conjugate addition product (XVIII) undergoes a cyclization reaction with a second molecule of methyl α-chloroacrylate to produce the cyclopropane (XIX) with elimination of n-butylzinc chloride:

(XVIII) + H⟩C=C⟨Cl, COOMe / H   →   CH₂—C⟨Cl, COOMe⟩ / C⟨COOMe⟩ / C₅H₁₁ (XIX) + BuZnCl

n-Butyl(dimethyl malonato)zinc exclusively undergoes conjugate addition [38].

Three-membered ring formation also occurs upon interaction of ethylzinc chloride with methyl α-chloroacrylate. As shown by IR and NMR the product of this reaction is cis-dimethyl 1-propyl-2-chloro--1,2-cyclopropanedicarboxylate (XXI). The following reaction scheme was considered [39]:

(XX)

(XXI)

The reaction of allylzinc reagents with α-alkoxyketones involves allylic rearrangment, e.g. [40]:

$$CH_2=CH-CH(C_2H_5)-C(C_3H_7)(OH)-CH_2OCH_3$$

α-Alkoxyesters afford diallyl-substituted alkoxycarbinols in excellent yield. Pentenylzinc reagent affords a 3/1 mixture of (XXII) and (XXIII) upon reaction with ethyl ethoxyacetate; the formation of (XXIV) is not observed [40].

$$CH_2=CH-CH(C_2H_5) \atop CH_2=CH-CH(C_2H_5)\!\!\!\diagdown\!\!\diagup CH(OH)CH_2OC_2H_5 \qquad\qquad (XXII)$$

$$CH_2=CH-CH(C_2H_5) \atop C_2H_5CH=CH-CH_2\!\!\!\diagdown\!\!\diagup CH(OH)CH_2OC_2H_5 \qquad\qquad (XXIII)$$

$$C_2H_5CH=CH-CH_2 \atop C_2H_5CH=CH-CH_2\!\!\!\diagdown\!\!\diagup CH(OH)CH_2OC_2H_5 \qquad\qquad (XXIV)$$

The formation of diallyl-substituted secondary amines from the reaction of imino ethers with allylzinc bromide probably proceeds via the intermediate formation of a Schiff base and not, as previously suggested, via an isonitrile [41]:

$$PhNH=CHOEt + RM \longrightarrow Ph-\overset{M}{\underset{}{N}}-\overset{OEt}{\underset{}{CH}}-R \underset{-MOR}{\longrightarrow}$$

$$PhN=CHR \overset{RM}{\longrightarrow} Ph-\overset{M}{\underset{}{N}}-CH(R_2) \underset{(H_2O)}{\longrightarrow} PhNHCHR_2$$

The reaction of isonitriles with organozinc compounds offers a route to otherwise difficultly available symmetrically substituted secondary amines of the type $RNHCR'_3$, e.g. [41]:

$$Ph\text{—}N\text{=}C: \quad + \quad 3\,CH_2\text{=}CHCH_2\,ZnBr \quad \xrightarrow[\text{(H}_2\text{O)}]{\text{THF}} \quad PhNHC(CH_2CH\text{=}CH_2)_3$$

<div align="center">(30%)</div>

Such compounds may be obtained in more attractive yields via the

reaction of allylzinc bromide with iminocarbonates [42]:

$$Ph\text{—}N\text{=}C(OEt)_2 \quad + \quad RM \quad \longrightarrow \quad Ph\text{—}\underset{|}{\overset{M}{N}}\text{—}\underset{|}{\overset{OEt}{C}}(R)OEt \quad \xrightarrow[(-MOEt)]{}$$

$$Ph\text{—}N\text{=}C(R)OEt \quad + \quad RM \quad \longrightarrow \quad Ph\text{—}\underset{|}{\overset{M}{N}}\text{—}\underset{|}{\overset{OEt}{C}}R_2 \quad \xrightarrow[(-MOEt)]{}$$

$$PhN\text{=}CR_2 \quad + \quad RM \quad \longrightarrow \quad Ph\text{—}\underset{|}{\overset{M}{N}}\text{—}CR_3 \quad \xrightarrow[\text{(H}_2\text{O)}]{} \quad PhNHCR_3$$

<div align="center">(RM = CH_2=CHCH$_2$ZnBr; yield 61%)</div>

With substituted allylzinc reagents the reaction which involves allylic

rearrangment stops at the iminoether stage [42]:

$$PhN\text{=}C(OEt)_2 \quad + \quad RCH\text{=}CHCH_2\,ZnBr \quad \xrightarrow[\text{(H}_2\text{O)}]{} \quad PhN\text{=}C \overset{\displaystyle OEt}{\underset{\displaystyle CHRCH\text{=}CH_2}{}}$$

<div align="center">(R=Me; 66%)</div>
<div align="center">(R=Et; 40%)</div>

Nivert and Miginiac have shown that the organozinc reagent

derived from propargylbromide with gem-aminoethers or with aldimines

affords a mixture of the acetylenic and allenic amines in which the

former strongly predominate [43]:

$$CH_2\text{=}C\text{=}CHZnBr \qquad\qquad HC\text{≡}CCH_2CH(R)N(C_2H_5)_2$$

<div align="center">+ $\xrightarrow{\text{(H}_2\text{O)}}$ +</div>

$$C_4H_9OCH(R)N(C_2H_5)_2 \qquad\qquad CH_2\text{=}C\text{=}CHCH(R)N(C_2H_5)_2$$

$$CH_2=C=CHZnBr \qquad\qquad HC\equiv CCH_2CH(C_6H_5)NHR$$

$$+ \qquad\qquad\qquad \overrightarrow{(H_2O)} \qquad\qquad +$$

$$C_6H_5CH=NR \qquad\qquad CH_2=C=CHCH(C_6H_5)NHR$$

An independent study of the reaction of allenylzinc bromide with Schiff bases was reported by Moreau and Gaudemar. These authors also obtained mixtures of acetylenic and allenic amines the latter having been obtained in yields up to 54% [44]. L. Miginiac made the interesting observation that whereas the condensation of the organozinc reagent derived from 3-bromobutyne-1 with gem-aminoethers or with aldimines affords nearly exclusively acetylenic amines, the corresponding reactions of the 1-bromo-butyne-2 reagent yield nearly exclusively α-allenic tertiary and secondary amines [43].

Abenhaim et al. have established the highly stereospecific nature of the ring opening of 1-phenyl-1,2-epoxypropane by diallylzinc which occurs with inversion of configuration at the benzylic carbon atom. Whereas the (1 R, 2 R) trans-epoxide reacts exclusively at the benzylic carbon atom, the (1 S, 2 R) cis-isomer reacts to a small extent at the alifatic carbon atom as well [45]:

(1 R, 2 R) trans   3-phenylhexene-4-ol-1(2 R, 2 S)

$$\xrightarrow[\text{(H}_2\text{O)}]{\text{All}_2\text{Zn}}$$

(92%)

(1S, 2R) cis

3-phenylhexene-5-ol-1 (2R, 3R)

(8%)

1-phenyl-2-methylpentene-4-ol-1

(1R, 2R)

The remarkable reactivity of allylzinc reagents is illustrated by their reactions with carbon-carbon unsaturated systems.

Allylzinc bromide adds readily to α-allenic amines with the formation after hydrolysis of α, ϵ-diolefinic amines [43]:

$$CH_2=C=C(CH_3)CHRNR'(C_2H_5) \; + \; CH_2=CHCH_2ZnBr \; \xrightarrow[\text{(H}_2\text{O)}]{\text{THF}}$$

$$CH_2=CHCH_2CH_2CH=C(CH_3)CHRNR'(C_2H_5)$$

Of particular interest is the ready formation of gem-dimetallic and gem--trimetallic reagents from the reaction of allylic organozinc reagents with acetylenic organometallic compounds, e.g. [46]:

$$CH_2=CHCH_2 \underset{Ph}{\overset{}{}}C=C\overset{MgBr}{\underset{Zn.Br}{}}$$

$$\downarrow (H_2O)$$

$$CH_2=CHCH_2 \underset{Ph}{\overset{}{}}C=CH_2 \qquad (22\%)$$

$$PhC \equiv CMgBr \xrightarrow{\quad CH_2=CHCH_2ZnBr \quad}$$

1/1

1/2

$$\underset{CH_2CH=CH_2}{\overset{CH_2CH=CH_2}{Ph-\underset{|}{\overset{|}{C}}-CH_3}} \qquad (65\%)$$

$$\uparrow (H_2O)$$

$$\underset{CH_2CH=CH_2}{\overset{CH_2CH=CH_2}{Ph-\underset{|}{\overset{|}{C}}-\overset{ZnBr}{\underset{ZnBr}{C}}-MgBr}}$$

With vinylic organometallic reagents an exothermal addition takes place at 35°, e.g. [46]:

$$C_3H_7CH=CHMgBr \ + \ CH_2=CHCH_2ZnBr \ \longrightarrow \ \underset{CH_2=CHCH_2}{\overset{C_3H_7}{}}CH-CH\overset{ZnBr}{\underset{MgBr}{}}$$

$$\downarrow (H_2O)$$

$$CH_2=CHCH_2CH(CH_3)C_3H_7$$

$$(58\%)$$

C. Carbenoid reactions of organozinc compounds

The carbenoid reactivity of appropriate organozinc reagents has continued to attract attention and further examples of their application in organic and organometallic synthesis have been published.

The subject of carbenoid reactions of halomethylzinc compounds has been briefly reviewed by Seyferth with emphasis on the author's own contributions in this area [47].

Several papers have dealt with synthetic applications of the conventional Simmons-Smith reagent zinc-copper couple/methylene iodide. Gem-dimethylcycloheptadienes have been prepared via cyclopropanation of 5,5-dimethyl-2-cyclohexanol coupled with homoallylic ring expansion [48]:

The Simmons-Smith reaction of cycloocten-3-ol afforded a stereoselective route to anti-bi-cyclo[6.1.0]nonan-2-ol (XXV) [49]:

(XXV)

The corresponding reaction of cis-cyclononen-3-ol affords a highly stereoselective route (less than 0.05% of syn-epimer formed) to anti--bicyclo [7.1.0] decan-2-ol (XXVI) [50]:

(XXVI)

Le Perchec and Conia obtained bicyclopropylidene via cyclopropanation
of vinylidenecyclopropane [51]:

Templeton and Wie have investigated the effect of 3-oxygen functions
(3α- and 3β-hydroxy, 3α- and 3β-acetoxy, 3-ethylene acetal) of
5,6-unsaturated steroids on the addition of the Simmons-Smith reagent
to the steroidal 5,6-double bond. Of the various 5-cholestene derivatives
studied, only in the presence of the 3α-hydroxy function did reaction
take place with formation of the expected 3α-hydroxy-5,6α-cyclopropano-
-5α-cholestane [52]:

Furukawa et al. have continued their investigation of the gem-di-
iodoalkane/diethylzinc cyclopropanation reagent discovered by these
authors (AS 69; 225).

The relative reactivity of olefins towards the zinc carbenoid reagent generated from diethylzinc and methylene iodide was found to decrease in the order tetramethylethylene > trimethylethylene > cyclo-hexene > hept-1-ene (order of decreasing nucleophilicity). Experiments with alkyl vinylethers (ROCH=CH$_2$) and cis-alkenylethylethers (RCH=CHOC$_2$H$_5$) revealed the importance of steric in addition to electronic effects. The outcome of experiments with substituted styrenes (ρ-value of -1.61±0.05) suggests that methylene transfer by RZnCH$_2$I (XXVII) is a more nucleophilic reaction than that of dichloro-carbene (XXVIII) [53].

(XXVII)   (XXVIII)

The same group has studied the stereoselectivity of the benzaliodide/ /diethylzinc reagent in reactions with olefins. The syn-selectivity shown by the phenylcarbenoid is much higher in ethers (e.g. syn/anti = 17.1 for the reaction with cyclohexene in diethylether) than in hydrocarbons (syn/anti = 6.6 for the same reaction in pentane) indicating the impor-tance of coordination of the solvent to the metal atom [54]:

The zinc carbenoid shows larger syn-selectivity than the corresponding lithium carbenoid [54].

Interestingly the cyclopropanation reaction of olefins by the Et_2Zn/CH_2I_2 reagent is greatly accelerated by oxygen. In experiments where air was passed into the space above the reaction mixture at a rate of 10 ml/min the yields are improved and reaction times are much shorter as compared with experiments performed under a nitrogen atmosphere [55].

The formation of halogenocarbenoids of zinc by the interaction of diethylzinc with trihalogenomethanes offers a novel synthetic route to halogenocyclopropane derivatives:

CHF_2I was the most useful for the preparation of the fluorocyclopropane, $CHCl_2I$ for the chlorocyclopropane and $CHBr_2I$ for the bromocyclopropane derivative. A dihalogenomethylzinc derivative is postulated as an intermediate. This type of reaction displays syn-selective behaviour the endo-isomers of 7-fluoro-, 7-chloro- and 7-bromonorcarane predominating over their exo-isomers [56].

Russian authors in their investigation of the interaction of diethylzinc with polychloromethanes observed the formation of ethyl chloride (41%) and 1-chloropropene (42%) as well as dichloronorcarane, if the reaction with carbon tetrachloride was carried out in the presence of cyclohexene. These reactions were believed to proceed via the intermediate formation of $EtZnCCl_3$ carbenoid. Insertion of dichlorocarbene (via $PrHgCCl_3$ or $PhHgCCl_3$) into the Zn—C bond of Et_2Zn affords intermediate dichloropropylzinc derivatives which yield 1-chloropropene by elimination and isomerization of ethylchlorocarbene [57]:

$$Et_2Zn \xrightarrow[-PhHgCl]{PhHgCl_3} \left[EtZnCCl_2Et \right] \xrightarrow{-EtZnCl} \left[: CClEt \right] \longrightarrow ClCH=CHMe$$

Seyferth and Andrews have published the details of their synthesis of halomethyl derivatives of tin, lead and mercury via the reaction of iodomethylzinc iodide or bromomethylzinc bromide in THF with the appropriate metal or organometallic halide, e.g. [58]:

$$CH_2I_2 + Zn\!-\!Cu \xrightarrow{THF} \left[ICH_2ZnI \right] \xrightarrow{Me_3SnCl} Me_3SnCH_2I + ZnClI$$

These reactions are pictured as involving nucleophilic attack by the XCH_2ZnX reagent at the electrophilic heavy metal center. The procedure works best for CH_2I-transfer. The corresponding bromomethyl and chloromethyltin compounds are best prepared by the reaction of the iodomethyl derivative with silver bromide or silver chloride in aceto-nitrile. In the same paper the possibility that interaction of the Simmons-Smith reagent with the silicon-hydrogen bond in organosilanes may involve a two-step alkylation-reduction or reduction-alkylation sequence (AS 65; 46) was eliminated. The exclusive formation of Et_3SiCH_2D and $n\!-\!Bu_3SiCH_3$ from the reaction of a mixture of Et_3SiD and $n\!-\!Bu_3SiH$ with an excess of ICH_2ZnI shows that the direct insertion process is operative [58].

Furukawa et al. have investigated the reaction of organosilicon and organotin hydrides with the $Et_2Zn/RCHI_2$ reagent. The Si—H bond in a variety of triorganosilanes reacts with insertion of a methylene or ethylidene group (cf. AS 65; 46):

$$R^1R^2R^3SiH \xrightarrow{Et_2Zn/RCHI_2} R^1R^2R^3SiCH_2R$$

$$(R = H \text{ or } Me)$$

However, in the reaction of triethyltin hydride reduction of the organic iodide by the organotin hydride predominates over the insertion of the methylene group into the Sn—H bond. Hammet correlations of relative reactivities of substituted aryldimethylsilanes towards the zinc carbenoid yielded a ρ-value of -1.11 ± 0.03 and -1.19 ± 0.05 for methylene and ethylene insertion, respectively, as compared with a ρ-value of -1.31 for the corresponding methylene insertion via bis(bromomethyl)-mercury (AS 69; 259) suggesting a similar transition state (XXIX) for both reactions [59]:

$$Z = XZn, \quad R = H, \quad Y = I$$
$$Z = XZn, \quad R = Me, \quad Y = I$$
$$Z = HgCH_2Br, \quad R = H, \quad Y = Br$$

(XXIX)

# III. ORGANOZINC COMPOUNDS AS POLYMERIZATION CATALYSTS

Several papers providing details on the catalytic properties of organozinc compounds in polymerization reactions have appeared. Abstracts of patent applications and patents describing a variety of 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.

Kuntz has presented an excellent survey of the mechanism of epoxide polymerizations with emphasis on coordinative polymerizations such as brought about by zinc-containing initiator systems [60]. The catalyst system di-isobutylaluminium acetylacetonate/diethylzinc/water

was found to be particularly effective in bringing about the copolymeri-
zation of propylene oxide, epichlorohydrin and allylglycidylether [61].
The maximum conversion to polymer is observed when the amount of
water present is less than that required to react with all the metal-
-carbon bonds present in the catalyst components. A kinetic study has
revealed that the initial polymerization rate was at a maximum for the
system $R_2Al\,acac/0.5\,H_2O/R_2Zn$. It was speculated that the active cata-
lyst, which is of the living type, requires both Al—O—Al and R—Al
groups and that the R_2Zn component is coordinated to the Al—O—Al
compound as shown in (XXX) [60, 61]:

$$
\begin{array}{c}
R\diagdown \underset{|}{Zn}\diagup R \\
\text{Me}-O \diagdown \; O \; \diagup O-\text{Me} \\
\text{Me}-O \diagup Al \diagdown_R \quad _R \diagup Al \diagdown O=\text{Me}
\end{array}
$$

(XXX)

The zinc atom may play a major role in epoxide monomer coordination
and aluminium a major role in polymer chain growth [60]:

$$
\begin{array}{ccc}
\underset{|}{CH_2Cl} & & \underset{|}{CH_3} \\
CH{-}CH_2 \quad \underset{|}{CH_3} & & CH{-}CH_2 \quad \underset{|}{CH_2Cl}\;\underset{|}{CH_3} \\
\diagdown O \diagup \quad \diagup OCHCH_2OR & \xrightarrow{\;1\;} & \diagdown O \diagup \quad \diagup OCHCH_2OCHCH_2OR \\
Zn \quad Al & & Zn \quad Al \\
O & & O
\end{array}
$$

Recent papers from the group of Furukawa at Kyoto University have clarified several aspects of epoxide polymerizations initiated by dialkylzinc catalyst systems. The catalytic reproducibility of the Et_2Zn/H_2O system for the polymerization of propylene oxide is improved by the removal of free Et_2Zn; catalyst activity requires the presence of both Zn—O and Zn—Et bonds in the active catalyst species [62]. The kinetics of the polymerization of propylene oxide using the initiator system diethylzinc/water (1/2) has been discussed [63]. Asymmetric selection polymerization of epoxides (formation of an optically active polymer from a racemic monomer mixture) earlier realized by Tsuruta et al. by using dialkylzinc compounds with L-α-amino acids or optically active alcohols as cocatalysts (AS 69; 227) has been brought about by Furukawa et al. by using an optically active dialkylzinc compound: the polymerization of DL-propylene oxide with (+)-bis(2-methyl-butyl)zinc/water catalyst afforded optically active poly-propylene oxide leaving the antipode monomer [64]. Addition of diethylzinc following deactivation of the asymmetric catalyst by the further addition of water resulted in restoration of catalyst activity, but the catalyst was non--stereoselective. If, however, the optically active dialkylzinc was added to the deactivated catalyst, an active catalyst with asymmetric selectivity was regenerated [64]. The asymmetric selection polymerization of styrene oxide has been effected with the catalyst system diethylzinc/ /(-)-menthol [65].

Sakata et al. have demonstrated the effectiveness of diethylzinc/

α, β-unsaturated ketone catalyst systems for the polymerization of

propylene oxide [66]. Methylisopropenylketone; acrylophenone and β, β-

-dimethylacrylophenone were suitable, but carbonyl compounds other

than ketones (e.g. 2-furylacroleine or methyl acrylate) were ineffective.

Conjugate addition of Et_2Zn to α, β-unsaturated ketones (AS 69; 224)

gives a catalyst with better activity and stability at high temperature [66].

Inoue and Tsuruta at Tokyo University have continued their

fruitful studies dealing with the application of organozinc compounds in

the area of polymerization catalysis. Of particular interest is their

investigation of the stereochemistry of the alternate copolymerization

of carbon dioxide with cis-1,2-epoxycyclohexane (EPCH) using a

Et_2Zn/H_2O (1/1) catalyst system [67]. The configuration of the EPCH

unit in the polycarbonate copolymer (cis or trans) was determined

following alkaline hydrolysis or $LiAlH_4$-reduction of the copolymer. In

both cases the 1,2-cyclohexanediol formed was found to be exclusively

trans showing that the configuration of the EPCH carbon atom involved

in the ring opening is specifically inverted during the copolymerization

[67]:

Hydrolysis of poly-(propylene carbonate) obtained by alternating co-

polymerization of R-(+)-propylene oxide with carbon dioxide using a

Et_2Zn/H_2O catalyst, followed by treatment with p-nitrobenzyl chloride,

resulted in transformation of the epoxide unit of the copolymer into

propylene glycol bis-p-nitrobenzoate. Determination of the optical

activity of this ester revealed the inversion of the configuration of the asymmetric carbon atom of the epoxide upon copolymerization. Therefore, the organozinc-catalyzed ring opening takes place predominantly at the methylene-oxygen linkage indicating an anionic mechanism [68].

Kawakami and Tsuruta observed a low catalytic activity for n--butyl(dimethylmalonato)zinc in the polymerization of methyl acrylate or methyl methacrylate provided the polymerization was carried out in dimethylsulfoxide or hexamethylphosphoric triamide (HMPT) [3]. Methyl α-chloroacrylate can be polymerized or copolymerized with styrene in toluene, THF or HMPT solution using n-Bu$_2$Zn or n-butyl-(dimethylmalonato)zinc as a catalyst. The results of the copolymerization experiments as well as kinetic studies indicate a radical-type polymerization in toluene or THF, but in HMPT an anionic mechanism applies [38].

The use of diethylzinc as a third cocatalyst in a Ziegler-Natta type catalyst system allowed the block copolymerization of ethylene with methyl methacrylate. Under certain conditions no homopolymerization takes place and products with controlled composition could be obtained [69].

The valence state of titanium in the Et$_2$Zn/TiCl$_3$ catalyst used to polymerize propylene to isotactic polymer has been investigated. A direct relationship between the Ti^{2+} content and the catalyst activity or the molecular weight or isotacticities of the polymers was not observed [70].

IV. STRUCTURAL, SPECTROSCOPIC AND PHYSICAL STUDIES

A. Structural studies

An X-ray crystal structure determination of the anionic zinc-

-borane complex methyltriphenylphosphonium bis(dodeca hydro-<u>nido</u>-
-decarborato)zincate $[Ph_3MeP]_2[Zn(B_{10}H_{12})_2]$ has been reported [71].
The structure can be considered to comprise two bidentate $B_{10}H_{12}^{2-}$
ligands co-ordinated tetrahedrally to zinc (Fig. 1).

Fig. 1. Structure of $[Ph_3MeP]_2[Zn(B_{10}H_{12})_2]$ showing the positions of the
zinc and boron atoms only [from N. N. Greenwood et al., J. Chem. Soc.
(A), 1971, 809].

B. Spectroscopic studies

    The IR and Raman spectra of the isotopic analogs of lithium tetra-
methylzincate $^7Li_2Zn(CH_3)_4$, $^6Li_2Zn(CH_3)_4$ and $^7Li_2Zn(CD_3)_4$ have been
reported. The spectra indicate T_d symmetry around the zinc atom. A
band at 520 cm^{-1} in the IR spectrum of $^7Li_2Zn(CD_3)_4$ is assigned to the
Zn—C stretching mode [72].

A PMR study of the Schlenk equilibrium for methyl- and ethylzinc

iodide in THF solution has been reported by Evans et al. [73]. At -70°

alkyl exchange between alkylzinc iodide and dialkylzinc is slow on the

PMR time scale. For solutions in which the Zn/I ratio was 1.00/1.05

(corresponding to "alkylzinc iodide" with a small amount of zinc iodide)

only one line was observed at -90° confirming that the Schlenk equi-

librium lies well to the right ($K \geqslant 500$ at -90°):

$$R_2 Zn \;+\; ZnI_2 \;\rightleftharpoons\; 2\,R\,ZnI \qquad (R = Me, Et)$$

Oliver et al. have studied the effects of solvent on the rate and

mechanism of exchange of methyl groups in the system dimethylzinc-

trimethylindium [74]. Activation energies and kinetic parameters are

reported. Evidence is presented for changes in the mechanism of the

reaction in going from a non-coordinating solvent (dichloromethane,

$E_a < 5$ kcal/mole) to a "weakly" coordinating solvent (diethylether,

$E_a^{\neq} = 9.1$ kcal/mole; $\Delta S^{\neq} = -14$ eu) to a strongly coordinating solvent

(triethylamine, $E_a^{\neq} = 16.3$ kcal/mole; $\Delta S^{\neq} = +2$ eu).

A detailed discussion of the 28.87 MHz and 80.53 MHz ^{11}B-NMR

spectra of the anionic zinc complex of the dodecahydro-nido-deca-

borate(2-) ion $\left[Me_4N\right]_2 \left[Zn(B_{10}H_{12})_2\right]$ has been presented by Greenwood and

Travers [7] and the results were correlated with the known structure

[71] in the solid state.

t-Butoxy radicals generated by photolysis of di-t-butyl peroxide

in the presence of diethylzinc induce an homolytic bimolecular substitu-

tion at the metal centre. If the reaction is carried out in an E.S.R.

cavity the E.S.R. spectrum of the ethyl radical can be observed [75]:

$$t\text{-BuO} \cdot \;+\; Et_2 Zn \;\longrightarrow\; EtZnO\text{-}t\text{-Bu} \;+\; Et \cdot$$
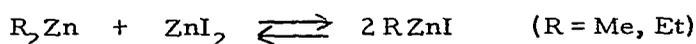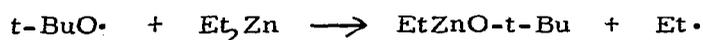
C. Other physical studies

Complex formation of $(CH_3)_2Zn$, $(C_2H_5)_2Zn$ and $(iso-C_3H_7)_2Zn$ with 2,2'-bipyridine, ethylene diamine and N,N,N',N'-tetramethyl-ethylene diamine has been studied by an oscillometric method. The stoechiometry and dissociation constant of the complexes were in agreement with earlier results (AS 67; 235) [76].

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