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The Less Familiar Reactions of Organocadmium Reagents

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I. Introduction

Although the formation of organocadmium compounds (R_2Cd or RCdX) was suggested several times from 1853 to 1891,[1-4] the first purified reagents—dimethyl- and diethylcadmium—were reported by Krause in 1917.[5] Recognition of their utility as reagents in synthesis, however, stems from the pioneering work initiated much later by Gilman and Nelson.[6] Their synthetic use to the present time has been restricted almost exclusively to the preparation of ketones from acid chlorides and anhydrides, a subject which was reviewed in 1946[7] and again in 1954.[8]

Apparently, most organic chemists still assume that organocadmium reagents are peculiarly unreactive toward aldehydes and ketones, the latter being the end products of their reactions with acid chlorides and anhydrides. This misconception has been restated in well-recognized textbooks in organic chemistry, published in the U.S.A. as recently as 1973, 1975, and 1976. In a book on organozinc and organocadmium compounds published in 1967,[9] most of the discussion of the latter dealt with the reactions with acid chlorides. Only in the most recent, extensive review by Nützel of organocadmium compounds[10] is there a presentation of some of the less familiar reactions, with aldehydes, ketones, and organic halides.

The simple generalization, however, that organocadmium reagents react only with acid chlorides, anhydrides, and 1,2-dicarbonyl compounds must of necessity be modified since the important discovery by Kollonitsch[11-13] that the reagents differ markedly in their reactivity with organic substrates, depending on the presence or absence of magnesium or lithium salts. Thus, in situ reagents are reactive toward simple aldehydes and ketones, whereas purified reagents (i.e., salt-free) are much more selective. Nevertheless, even in situ cadmium reagents are considerably lower in their reactivity than the corresponding magnesium or lithium compounds and consequently are promising selective reagents for transforming aldehyde, ketone, acid chloride, and acid anhydride functions without affecting ester, nitrile, amide, nitro, and other functional groups present in the same molecule. Perhaps of greatest synthetic utility is the selective displacement by organocadmium reagents of halides (or other suitable leaving groups) in substrates containing other functionalities, which would be decomposed by the more reactive lithium or magnesium compounds.

What follows is a survey of some of these less familiar reactions of organocadmium reagents—simple additions, displacements, reductions, and rearrangements.

An effort has been made to survey the literature through 1975, but without including the reactions with acid chlorides and anhydrides which have been covered in earlier reviews. (In addition to *Organometallic Chemistry Reviews, B* (1977–1973) and *Journal of Organometallic Chemistry*, (1973–), see, for example, ref 14, 15, and 16.)

It is noteworthy that organocadmium compounds are not included in an extensive chapter on the literature of the main-group organometallics published in 1975.[17]

II. The Organocadmium Reagent

A. Methods of Preparation

Of the many possible routes to organometallic compounds described by Jones and Gilman,[18] only a few have been used in preparing cadmium compounds. Further details on synthesis of organocadmium reagents can be found in the extensive treatise by Nützel.[10]

1. Exchange between an Organometallic Reagent and a Cadmium Salt

Although not chronologically the first method attempted for preparation of organocadmium reagents, the interaction of an organometallic reagent and a cadmium salt has become the standard route to their synthesis. It was first reported in 1917 by Krause,[5] who prepared dimethyl- and diethylcadmium by distillation of the reaction mixture from the alkylmagnesium halide and cadmium bromide. Some of the properties of these purified reagents were described many years later in a book by Krause and von Grosse.[19] Success of the method depends upon the generalization[18] that the equilibrium involving two organome-

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tallics lies on the side of the less reactive partner. Limitations and variations in the method as a general route to organometallics were noted in the ensuing years. It was found, for example, that alkyl bromides were superior to chlorides or iodides and that dibutyl ether was inferior to diethyl ether as solvent.[20] Cason recommended replacing solvent ether with benzene after formation of the organocadmium reagent,[7] a technique which became standard practice in many synthetic procedures.

Alkyl and aryl[21] lithium reagents also exchange readily with cadmium salts, but they have not been as widely used. Highly purified dimethylcadmium has been prepared from trimethylaluminum and cadmium acetate.[22]

$$2(CH_3)_3Al + 3Cd(OAc)_2 \rightarrow 3(CH_3)_2Cd + 2Al(OAc)_3 \quad (1)$$

Exchange between aluminum alkyls and cadmium halides has been patented as a synthetic method.[23]

Although vinyl Grignard and lithium reagents generally fail to react,[24] the acetylenic Grignard reagent from butenyne underwent exchange with cadmium chloride to afford the cadmium reagent.[25]

$$CH_2{=}CHC{\equiv}CMgBr + CdCl_2 \rightarrow CH_2{=}CHC{\equiv}CCdCl \quad (2)$$

Allylic cadmium reagents cannot be prepared by this method and, in fact, were reported from a different route for the first time only in 1967.[26] Indirect evidence for the formation of crotyl (or methallyl) cadmium reagent was provided by Agami and Prevost,[27] who allowed "crotylzinc" reagent to interact with cadmium chloride in various solvents and then hydrolyzed the reaction mixture. On the basis of the composition of the butenes (from gas–liquid chromatography), they estimated that the following equilibrium lay 64% on the side of the organocadmium compound.

$$(C_4H_7)_2Zn + CdCl_2 \rightleftharpoons ZnCl_2 + (C_4H_7)_2Cd \quad (3)$$

C_4H_7 = crotyl or methallyl

Difunctional organocadmium reagents from $X(CH_2)_nX$ have been generated by way of the Grignard reagents, n being 4, 5, 6, and 10. The success of the synthesis, as judged by conversion to diketones with acid chlorides, improves as n becomes larger.[28] The organocadmium reagent generated from $X(CH_2)_6X$ with 2 equiv of CdX_2 affords final products (from acid chloride, aldehyde, or ketone) in considerably lower yield.[29]

A methylene insertion into $CdCl_2$ with diazomethane leads to bis(chloromethyl)cadmium, but the yield is only 11%.[30]

$$2CH_2N_2 + CdCl_2 \rightarrow (ClCH_2)_2Cd \quad (4)$$

2. Reaction of an Organic Halide with Cadmium Metal

Before 1900 at least four reports of the attempted preparation of organocadmium reagents from methyl or ethyl iodide and metallic cadmium appeared, the first in 1853.[1-4] In every case evidence for the organometallic compound was fragmentary, the isolation of CdI_2 being taken as an indication that the reaction had proceeded.

With the advent of polar, aprotic solvents in recent years, some limited success has been achieved in the direct synthesis of organocadmium reagents from the metal. The method has been shown to work with alkyl iodides (but not bromides),[31,32] and cadmium cuttings, with hexamethylphosphoramide,[32] dimethyl sulfoxide,[31] or dimethylformamide[31] as solvent. The simple dialkylcadmium compounds thus formed are identical in reactivity with those prepared by Krause.[5] Cadmium metal has been used in place of zinc in a "Reformatsky" reaction, where the solvent was either dimethyl sulfoxide or hexamethylphosphoramide.[33] No such reaction with cadmium has been achieved with the more common solvents (ether, etc.).

$$BrCH_2CO_2C(CH_3)_3 + Cd^0 \xrightarrow[\text{or HMPT}]{Me_2SO} \xrightarrow{n\text{-}C_3H_7CHO} n\text{-}C_3H_7CH(OH)CH_2CO_2C(CH_3)_3 \quad (5)$$

45%, 65%

Highly active cadmium in the form of a slurry, prepared by cocondensation of the metal vapor and solvent at 77 K, reacts with ethyl iodide during several hours' reflux. Evidence for formation of ethylcadmium reagent was based on GLC analysis of ethane after treatment of the reaction mixture with 10% HCl.[34]

Although the best conversions were accomplished with diglyme (83%) and dioxane (74%), it is noteworthy that organometallic formation took place even in hexane (61%) and toluene (55%). Attempts to obtain purified diethylcadmium, however, failed.

Recently the formation of RCdX, complexed with neutral bidentate ligands, has been carried out in an electrolytic cell, with cadmium as the anode and platinum as the cathode.[35] In a typical experiment, electrolysis is conducted on degassed solutions of alkyl (or aryl) halide and tetraethylammonium perchlorate in dry acetone. Yields, based on loss of cadmium at the anode, are of the order of 90%. The fact that acetone can be used as solvent is probably an indication of the strong stabilization of the cadmium compound by the ligands (e.g., 2,2′-bipyridyl, 1,10-phenanthroline, and dioxane). Thus, although of considerable interest, the method is not of promising value for the usual applications to organic synthesis.

There is even some evidence that aryl iodides will undergo reaction with cadmium metal in suitable solvents. It was reported that pentafluoroiodobenzene and cadmium turnings in dimethylformamide, dimethyl sulfoxide, or hexamethylphosphoramide afforded brown solutions, whose ^{19}F NMR spectra indicated the presence of both Ar_2Cd and ArCdI.[36]

3. Reaction of an Organometallic Compound with Cadmium Metal

In a patent in 1963 the preparation of divinylcadmium, a liquid, was described as proceeding from divinylmercury and cadmium metal.[37] That result was later disputed, however, when divinylcadmium, a crystalline solid, was obtained by an alternate route.[38] There is apparently only one documented example of the formation of an organocadmium compound from cadmium metal and another organometallic reagent, that being the reaction of bis(perfluorophenyl)thallium bromide with the metal in the absence of a solvent in a sealed tube at 160 °C for 7 days. The yield of bis(perfluorophenyl)cadmium is reported to be 53%.[39]

$$(C_6F_5)_2TlBr + Cd^0 \rightarrow (C_6F_5)_2Cd \quad (6)$$

4. Metalation

The formation of bis(phenylethynyl) cadmium by way of a metalation reaction has been reported.[40] In this procedure halide-free diphenylcadmium and phenylacetylene, both in ether, were placed in a sealed, evacuated vessel for 8 h at room temperature.

$$C_6H_5C{\equiv}CH + (C_6H_5)_2Cd \rightarrow (C_6H_5C{\equiv}C)_2Cd \quad (7)$$

By contrast it was reported from another laboratory that diethylcadmium (unspecified nature) failed to react appreciably with phenylacetylene in ether at 20 °C under argon.[41] Solvent had a profound effect on the rate of metalation. The half-life for phenylacetylene (as determined by evolution of ethane) varied from 21 h in dimethoxyethane to less than 5 s in tetramethylethylenediamine.

$$2C_6H_5C{\equiv}CH + (C_2H_5)_2Cd \rightarrow 2(C_6H_5C{\equiv}C)_2Cd + 2C_2H_6 \quad (8)$$

In spite of this low reactivity, a later report appeared on the use of the cadmium reagent, generated from phenylacetylene

by way of the ethylcadmium reagent, as a general route to ketones.[42,43] The solvent was ether–benzene, but there was no indication of other conditions required for effecting the metalation.

$$C_2H_5MgBr \xrightarrow{CdCl_2} \xrightarrow{C_6H_5C{\equiv}CH} \xrightarrow{RCOCl} C_6H_5C{\equiv}CCOR \quad (9)$$

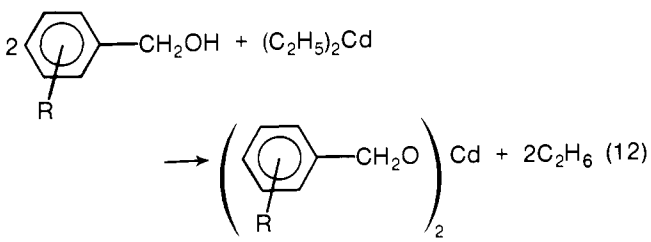
Metalation of tris(pentafluorophenyl)germane with diethylcadmium (unspecified) required heating in toluene at 100 °C for 2 h.[44]

$$(C_6F_5)_3GeH + (C_2H_5)_2Cd \rightarrow [(C_6F_5)_3Ge]_2Cd \quad (10)$$

The solvated unsymmetrical germylcadmium compound was described as arising from metalation of triphenylgermane and diethylcadmium.[45]

$$(C_6H_5)_3GeH + (C_2H_5)_2Cd \rightarrow (C_6H_5)_3GeCdC_2H_5(solvated) \quad (11)$$

The slow abstraction of relatively acidic hydrogens by cadmium reagents, which distinguishes them from Mg and Li reagents,[46] is noteworthy and warrants further investigation. One study has been done with variously substituted benzyl alcohols.



The half-lives, measured by evolution of ethane, at 35 °C for abstraction of hydrogen by halide-free diethylcadmium varied from 80 min (*p*-CF_3) to 36 min (*p*-OCH_3).[47] These results have been correlated with kinetics, isotope effect, and the Hammett relationship.[48]

tert-Butyl alcohol only slowly decomposes dimethylcadmium; disappearance of the reagent (as followed by proton NMR) requires 1.5 h in benzene and even longer in ether.[49] The rate of the second-order proton abstraction from isoamyl alcohol by purified dimethylcadmium is enhanced by the addition of metallic salts ($ZnCl_2$, $AlCl_3$, $MgBr_2$). This behavior is the opposite of that observed with Grignard reagents.[46]

5. Redistribution

The preparation of allylic cadmium reagents has been accomplished by the very rapid redistribution between allylic boron compounds and dimethylcadmium.[26]

$$2(CH_2{=}CHCH_2)_3B + 3(CH_3)_2Cd \xrightarrow{-10\ °C} 3(CH_2{=}CHCH_2)_2Cd + 2(CH_3)_3B \quad (13)$$

Diallyl-, dimethallyl-, and dicrotylcadmium were obtained in the form of solids, the residual trimethylboron by-product (a gas) being removed in vacuo. This is the method of choice for preparation of allyl compounds, for solutions or mixtures from allylic Grignard or lithium compounds and cadmium salts are unstable. The allylic reagents are unique among organocadmium compounds, inasmuch as they are obtained halide-free without any purification step such as distillation or precipitation of metal halide with dioxane.

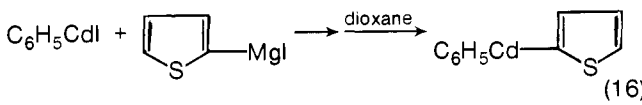
Divinylcadmium has been prepared by the redistribution between divinylmercury and dimethylcadmium, an exchange which is much slower than that for allylic compounds. The two components were heated at 60 °C in a sealed container for 5 days. After the dimethylmercury had been removed in vacuo, the residual divinylcadmium was purified by sublimation.[38]

$$(CH_2{=}CH)_2Hg + (CH_3)_2Cd \rightarrow (CH_2{=}CH_2)_2Cd + (CH_3)_2Hg \quad (14)$$

It has been reported that unsymmetrical cadmium reagents RR′Cd can be obtained by a controlled redistribution reaction. *n*-Butylethylcadmium, for example, was described as arising from two sources.[50]

$$\left.\begin{array}{l} n\text{-}C_4H_9CdI + C_2H_5MgCl \\ n\text{-}C_4H_9MgBr + C_2H_5CdI \end{array}\right\} \rightarrow n\text{-}C_4H_9CdC_2H_5 \quad (15)$$

It was reported that 2-thienylphenylcadmium, in the form of a hemidioxanate, was obtained from equimolar amounts of phenylcadmium iodide and thienylmagnesium iodide; the magnesium iodide was precipitated by dioxane.[51]



B. Nature of the Reagent

The nature of the cadmium reagent depends on its method of preparation. The most common procedure is to prepare a cadmium reagent by addition of a cadmium salt (usually the chloride or bromide) to a solution of a Grignard or lithium reagent in ether or other suitable solvent.[7,8] The resulting in situ reagent, used directly, contains 1 or 2 molar equiv of magnesium halide, depending on the relative amounts of organometallic and cadmium salt. These alternatives are illustrated below for preparations from a Grignard reagent.

$$2RMgX + CdX_2 \rightarrow \underset{\text{"dialkylcadmium"}}{R_2Cd} + 2MgX_2 \quad (17a)$$

$$RMgX + CdX_2 \rightarrow \underset{\text{"alkylcadmium halide"}}{RCdX} + MgX_2 \quad (17b)$$

"Purified" cadmium reagents, free of halide, can be obtained by direct distillation at reduced pressure if the compound is sufficiently volatile. Dimethylcadmium, diethylcadmium,[5] and di-*n*-butylcadmium[52] have been isolated in this way, for example. An alternative method of removing inorganic halides is accomplished by precipitation of the salts with dioxane. For example, di-*p*-tolylcadmium[53] and dicyclohexylcadmium[54] were isolated as solid dioxanates by treatment of an ethereal solution with dioxane. Diphenylcadmium was purified by sublimation following a similar treatment with dioxane.[55] Another route to halide-free reagents depends on the method of Thiele[26] developed for allylic cadmium reagents, in which a redistribution is carried out between an allylic boron compound and dimethylcadmium.

A careful distinction should be made between in situ and "purified" organocadmium reagents in any assessment of their behavior. It was first pointed out by Kollonitsch[11-13] that their properties may be markedly different, and this situation has been confirmed by many other workers.

Relatively few investigations into the composition and structure of organocadmium reagents have been carried out. The use of spectroscopy to deduce structures is complicated by the many components in equilibrium in the in situ reagents, and information on purified compounds may be of limited use for conclusions about the former.

A characteristic infrared band at about 540 cm^{-1} has been noted[56,57] for the Cd–C bond in dimethylcadmium, and infrared spectroscopy has been the basis for some conclusions about the structure[58] and position of equilibrium[59] of in situ reagents. From the rotational spectrum of gaseous dimethylcadmium, the Cd–C bond distance was calculated to be 2.112 Å.[60] The general consensus from vibrational infrared[61] and Raman[61,62] and

pure-rotational Raman spectra is that dimethylcadmium assumes a quasi-linear structure, with free rotation about the Cd–C bonds.[63]

The proton NMR chemical shift in dimethylcadmium[64,65] is intermediate between those of dimethylzinc (higher field) and dimethylmercury, in line with the relative electronegativities of the three metals. Shifts of a few other simple cadmium reagents have been included in a review.[65] In the vinyl compounds, the internal proton NMR chemical shifts decrease as the metal is changed from Zn to Cd to Hg (increasing atomic number and electronegativity). At the same time the various coupling constants decrease.[66] The ^{13}C coupling with Cd in organocadmium compounds has been reviewed.[67] From the coupling constant in dimethylcadmium it was estimated that the carbon possesses 24% s character.[68] The use of ^{113}Cd FT NMR spectroscopy for studying redistribution reactions is discussed in part VIII.

Garrett and co-workers[69] suggested that the chief component formed by mixing purified diethylcadmium and cadmium bromide in THF is $(C_2H_5)_2Cd{\cdot}CdBr_2$, a conclusion based on molecular weight determination and exchange experiments with radioactive ^{115}Cd. More recently Sanders and Ashby[52] have made an extensive study of various in situ reagents in ether derived from n-C_4H_9MgX and CdX'_2 in various proportions (X, X' = Cl, I). Their conclusions were based on elemental analysis for Mg, Cd, and X and on infrared spectra of both soluble and insoluble reaction products. When the reagent is prepared in a Grignard:CdX_2 ratio of 2:1, it seems to consist only of $R_2Cd + MgX_2$. In a 1:1 ratio the reaction seems to afford MgX_2 and an equilibrium mixture of R_2Cd and CdX_2. Cooling the solution from the 1:1 reaction mixture caused precipitation of solids, whose analyses were consistent with the structure $RCdX{\cdot}MgX_2$. At least weak association between cadmium compound and Cd or Mg salt was noted in all cases. From these studies it might be generalized that "dialkylcadmium", prepared in a 2:1 (Grignard:CdX_2) ratio, can be depicted in solution as $R_2Cd + MgX_2 \rightleftharpoons R_2Cd{\cdot}MgX_2$. "Alkylcadmium halide", from a 1:1 ratio, is more complicated. The following additional equilibria are probably involved, with R_2Cd being the dominant organocadmium component.

$$2RCdX + 2MgX_2 \rightleftharpoons R_2Cd + CdX_2 + 2MgX_2 \quad (18a)$$

$$RCdX + MgX_2 \rightleftharpoons RCdX{\cdot}MgX_2 \quad (18b)$$

$$RCdX + CdX_2 \rightleftharpoons RCdX{\cdot}CdX_2 \quad (18c)$$

$$2RCdX \rightleftharpoons R_2Cd + CdX_2 \quad (18d)$$

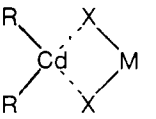
Heretofore reagents depicted as "RCdX" have been isolated as dioxanates.[70]

III. Reactions with Aldehydes and Ketones

A. The Reagent: In Situ vs. Purified

Contrary to widespread belief[75-77] organocadmium reagents, prepared in ether or benzene solvent, add rapidly and efficiently to simple carbonyl compounds—aldehydes and ketones—under mild conditions, provided the in situ reagent is employed. The misconception that cadmium reagents are inert toward simple carbonyls has been restated as recently as 1976 in prominent organic chemistry textbooks in the U.S.A. This misconception stems primarily from two review articles by Cason[7] and Shirley,[8] who discussed the use of cadmium reagents for the synthesis of ketones from acid chlorides and anhydrides; and from an earlier paper by Gilman and Nelson[6] in which it was reported that benzaldehyde and ethylcadmium reagent were converted to the adduct in only 32% yield, even though the reactants were stored in a sealed tube at room temperature for 5 months. The ethylcadmium reagent in Gilman and Nelson's experiment had been distilled, according to the procedure of Krause,[5] and so was free of halide salts. More than 20 years later, Kollonitsch was the first[11,12] to report that organocadmium compounds reacted readily with benzaldehyde (86% yield in 2 h) and other simple carbonyls, provided the in situ or reconstituted reagents were used. He corroborated the unreactivity of purified reagents toward a variety of substrates; and, significantly, he observed that in situ cadmium reagents prepared from organolithium compounds were less effective than those from Grignard reagents. The generality of this behavior—facile additions of in situ organocadmium reagents to aldehydes and ketones—has been confirmed in several publications, notably those originating from the research group at Orsay.[57,78-99]

The metal halide present in an in situ or reconstituted cadmium reagent may function in one of several ways to "activate" the reagent; two possibilities are that it forms a complex with R_2Cd (represented by **1**) or coordinates with the carbonyl group as in **2**, thus enhancing the nucleophilicity of R_2Cd in the first case



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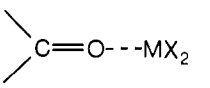


2

and making the carbonyl group more electrophilic in the latter case. Infrared evidence has been presented for structures of type **1**, where the metal halide is magnesium bromide.[58] Magnesium halides promote addition reactions far more effectively than do zinc, cadmium, lithium[85] or aluminum salts.[82] The nature of the halide plays a noticeable but less pronounced role. Among magnesium salts, iodides are most effective[100,101] and chlorides least effective (fluorides have not been investigated). That is, an in situ organocadmium reagent prepared from:

$$2RX + 2Mg \rightarrow 2RMgX \xrightarrow{CdX_2} R_2Cd + 2MgX_2 \quad (19)$$

is most effective when X = I throughout. Comparable reconstituted reagents can be prepared by the addition of 2 molar equiv of MgI_2 to purified R_2Cd.

In the special case of ethoxymethylcadmium reagent, $(C_2H_5OCH_2)_2Cd$, its preparation by way of the corresponding Grignard reagent is satisfactory only with cadmium iodide, for both cadmium chloride and bromide were found to have reacted incompletely even after 48 h.[81]

B. Allylic Reagents

It is remarkable that allylic cadmium reagents, prepared *free of metal halide* by way of organoboron compounds,[26] are highly reactive toward aldehydes and ketones[102-104] as evident in the following syntheses of secondary and tertiary alcohols.[102]

$$2(CH_2{=}CHCH_2)_3B + 3(CH_3)_2Cd \rightarrow 3(CH_2{=}CHCH_2)_2Cd + (CH_3)_3B \quad (20)$$

$$(CH_2{=}CHCH_2)_2Cd + RR'CO \rightarrow RR'C(OH)CH_2CH{=}CH_2 \quad (21)$$

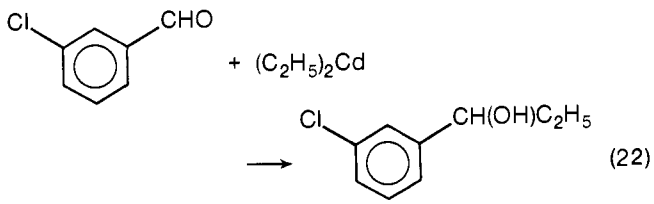
R = H, R' = Pr (74%) R = Me, R' = Et (85%)

R = H, R' = Ph (80%) R = R' = Et (89%)

Reactions must be carried out under unusually mild conditions (below 10 °C), presumably because of the instability of the allylic cadmium compound. Yields are, in fact, superior to those from the comparable Grignard reagent, which is known to undergo extensive coupling as a side reaction.

C. Scope

Electron-withdrawing substituents in benzaldehydes activate the carbonyl group toward addition. *m*-Chlorobenzaldehyde is converted to the alcohol in 83% yield with *purified* ethylcadmium reagent, under conditions where benzaldehyde reacts to the



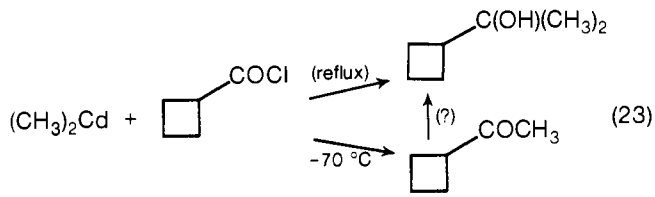
(22)

extent of only 20%. *p*-Chlorobenzaldehyde is likewise readily attacked, whereas *p*-tolualdehyde, containing an electron-rich group, is even less reactive than benzaldehyde.[83]

As expected, α-chlorine substituents in aliphatic aldehydes or ketones enhance the tendency for addition as well. Thus, α,α- or α,α′-dichloro ketones underwent addition with in situ "R_2Cd" (R unspecified) to the extent of 30–50%, whereas the conversion with dichloroacetaldehyde was 35–65% and that with chloral was 45–70%.[78] It was reported that one chlorine substituent was not sufficient to activate an aldehyde or ketone carbonyl toward addition, but results from such experiments were not described. This is unexpected in view of the general addition to both aliphatic aldehydes and ketones.

If the addition of cadmium reagents to carbonyls is nucleophilic in nature, then one would expect ketones to be less readily attacked than aldehydes. To the limited extent that comparable information is available, this generalization seems to hold. Thus, for example, the tertiary alcohol from methyl ethyl ketone and excess *n*-butyl reagent is formed in 45% yield under conditions where benzaldehyde reacts with an equivalent of the ethyl reagent to the extent of 85%.[86]

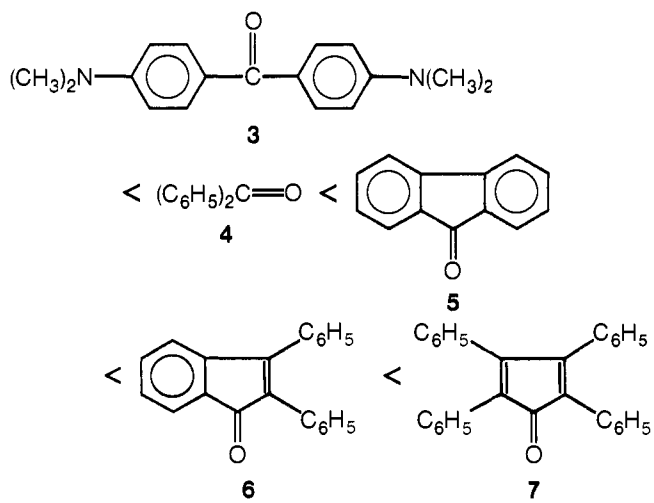
Apparently methyl cyclobutyl ketone is unusually reactive toward the in situ methylcadmium reagent. The acid chloride of cyclobutanecarboxylic acid, under the "usual" reaction conditions (excess of cadmium reagent to which the chloride is added at reflux temperature), affords exclusively the tertiary alcohol, presumably by way of the ketone. When the acid chloride is



(23)

added at −70 °C to a limited amount of cadmium reagent, the ketone is formed in 66% yield.[75,105]

Aromatic ketones, as expected, are less reactive than aliphatic compounds. Michler's ketone (**3**) is presumably inert to cadmium reagents in general, inasmuch as these reagents give no color test.[71] Benzophenone reacts to the extent of about 40%[91] with in situ ethylcadmium reagent, which, however, adds in 86, 91, and 100% yields to the aromatic ketones **5**, **6**, and **7**,



3

4

5

6 **7**

TABLE I. Solvent Effect in the Reaction of Purified Diethylcadmium with Benzaldehyde

$$C_6H_5CHO + (C_2H_5)_2Cd \xrightarrow{63\ °C} C_6H_5CH(OH)C_2H_5$$

solvent	time, h	yield, %
hexane	15	20
hexane:TMED (3:1)	6	63
hexane:HMPT (1:1)	15	80

respectively.[90] Ketone **7**, in fact, undergoes addition in about 85% yield with purified halide-free ethyl reagent whereas **5** is inert under the same conditions.[90,106]

Formate esters, like "aldehydes" in general, react with in situ but not purified reagents. The yield of diphenylcarbinol from ethyl formate and the phenylcadmium reagent (present in excess) is 45%.[86]

$$HCO_2C_2H_5 + 3Ph_2Cd \rightarrow Ph_2CHOH \qquad (24)$$

The dramatic change in the reactivity of cadmium reagents in polar, aprotic solvents has been noted. Purified reagents (halide-free) are greatly activated by use of the solvents tetramethylethylenediamine (TMED) or hexamethylphosphortriamide (HMPT).[83] A comparison of the yields of alcohol in the familiar addition of purified diethylcadmium to benzaldehyde, shown in Table I, points out the efficacy of these solvents in promoting the reaction.

A "Reformatsky" reagent from cadmium metal (as well as aluminum) has been reported. The bromo ester is allowed to react with cadmium metal in dimethyl sulfoxide or HMPT; then the mixture is treated with butyraldehyde. In the limited number of examples reported,[33] the *tert*-butyl ester appears to be superior. No β-hydroxy ester was isolated from ethyl bromoacetate under similar conditions.

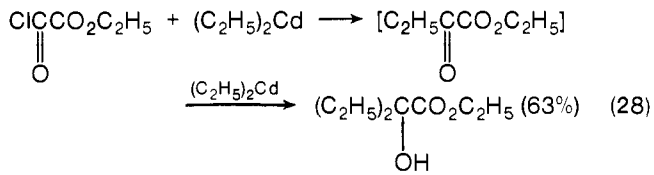
$$BrCH_2CO_2CH(CH_3)_2 + Cd \xrightarrow{Me_2SO}\ \xrightarrow{C_3H_9CHO}\ \xrightarrow{H^+} C_3H_9CH(OH)CH_2CO_2CH(CH_3)_2 \quad (25)$$
23%

$$BrCH_2CO_2C(CH_3)_3 + Cd \xrightarrow{Me_2SO}\ \xrightarrow{C_3H_9CHO}\ \xrightarrow{H^+} C_3H_9CH(OH)CH_2CO_2C(CH_3)_3 \quad (26)$$
65%

$$BrCH_2CO_2C(CH_3)_3 + Cd \xrightarrow{HMPT}\ \xrightarrow{C_3H_9CHO}\ \xrightarrow{H^+} C_3H_9CH(OH)CH_2CO_2C(CH_3)_3 \quad (27)$$
45%

The solvent must play a vital role in oxidation–reduction between halo ester and metal, for Nieuwland and Daly had reported failures in 1931 in similar attempts to generate cadmium enolates from α-chloro esters and cadmium powder in benzene, toluene, or without solvent.[107]

The fact that organocadmium reagents will add to "activated" carbonyl compounds—those in α-diketones, α-keto esters, etc.—was probably first realized by Gilman and Nelson,[6] who observed that ethyl chlorooxalate formed not the expected ethyl α-ketobutyrate with ethylcadmium reagent, but the hydroxy ester which presumably came from addition of cadmium reagent to the intermediate keto ester.



(28)

It was later shown that α-keto esters do indeed undergo addition readily.[98,108] An example is the reaction of ethyl 2-oxohexanoate with in situ *n*-butylcadmium reagent at 0 °C.[108]

Table II. Stereochemistry of Addition of Methyl Organometallics to 4-*tert*-Butylcyclohexanone

organometallic (ether)	% *Z*	% *E*	*Z*:*E*
CH_3MgBr	68	32	2.2
CH_3MgI	62	38	1.6
$2CH_3MgBr + CdCl_2$	50	50	1.0
$2CH_3MgI + CdCl_2$	42	5z	0.74

$$n\text{-}C_4H_9COCO_2C_2H_5 + (C_4H_9)_2Cd \rightarrow (C_4H_9)_2C(OH)CO_2C_2H_5\ (80\%) \quad (29)$$

Even when the reaction of ethoxalyl chloride was carried out by slow, inverse addition, the keto ester was a minor product.[108] A few examples of other compounds which undergo selective addition at an activated carbonyl (underlined) are represented below.

$CH_3COCOCH_3$[86,109] $C_2H_5OCOCOCO_2C_2H_5$[97,110]

C_6H_5COCHO[111]

$C_6H_5COCOC_6H_5$[112] $CH_3COCO_2C_2H_5$[98]

D. Stereochemistry of Additions to Aldehydes and Ketones

The limited stereochemical studies of additions to simple carbonyls have been carried out with a view to comparing the selectivity of various organometallic reagents, notably the magnesium, lithium, aluminum, cadmium, and zinc compounds. This subject was thoroughly reviewed in 1975,[113] and so only the highlights will be mentioned here. Only a few studies of the stereochemistry of addition of organocadmium reagents to carbonyl compounds have been published, in sharp contrast to the extensive, detailed studies of similar reactions with magnesium and aluminum compounds.[113]

Even with the limited information, however, some striking peculiarities of the cadmium (and zinc) reagents are noteworthy. In the reaction of the methyl reagent with 4-*tert*-butylcyclohexanone, there is relatively more axial attack, to give the nonthermodynamic diastereomeric alcohol, with cadmium (and zinc) than there is with the magnesium or lithium reagents.[100] Thus, for example, the *Z* and *E* alcohols, arising, respectively, from equatorial and axial attack of the organometallic reagent, form in substantially different amounts (normalized %) with a change in the metal from magnesium to cadmium (see Table II). Under these conditions the ketone is effectively consumed (≥95%).

The only other instance of enhanced axial attack in 4-*tert*-butylcyclohexanone is that when trialkylaluminum reagents are used in excess.[113] Originally this behavior was rationalized as arising from "tighter" transition states for cadmium (and zinc), as compared to those for magnesium,[100] where the transition state models were based on earlier suggestions.[114,115] Ashby and Laemmle have offered support for their theory of steric compression as an explanation for this behavior, as it has been used to explain the enhanced axial attack by excess alkylaluminum reagents.[113]

The in situ propylcadmium reagent is less reactive and more stereoselective than the methyl reagent;[89,116] that is, there is less axial attack in 4-*tert*-butylcyclohexanone with the propyl reagent.

The halide-free allylcadmium reagent, on the other hand,

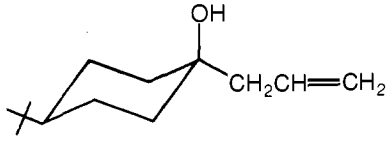


TABLE III. Stereoselective Addition of In Situ "Crotyl" Organometallic Reagents to Achiral Aldehydes (RCHO)

metal temp. (°C)	% "threo" (normalized) R = C_2H_5	*n*-C_3H_7	$(CH_3)_2CH$	$(CH_3)_3C$
Mg (+35)	52	51	58	75
Zn (+35)	45	46	70	84
Cd (−20)	50	51	80	86

exhibits even a higher preference for equatorial attack, the *Z* alcohol constituting 78% of the mixture of diastereomers.[104]

Acyclic carbonyl compounds have been examined in only two laboratories. In one case,[101] a marked change in stereoselectivity in the addition to α-substituted phenylacetaldehydes by methylcadmium (and zinc) as compared to the magnesium reagents was observed. The erythro isomer is the favored alcohol product when R = methyl or ethyl, but the threo isomer predominates when R = isopropyl. This changeover in stereoselectivity would not be predicted from the models of Cram,[117] Karabatsos,[118] or Felkin.[119]

$$C_6H_5\underset{\displaystyle R}{\underset{|}{C}}HCHO + CH_3M- \longrightarrow C_6H_5\underset{\displaystyle R}{\underset{|}{C}}HCH(CH_3)OH \quad (30)$$

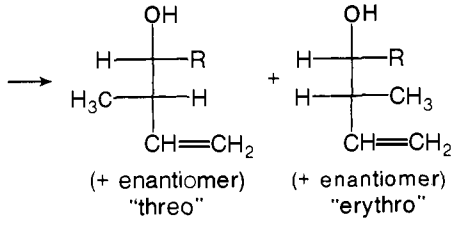
While in the cases where erythro is favored, the cadmium reagent is less stereoselective than the magnesium compound, the cadmium is *more stereoselective* (greater fraction of threo) when R = isopropyl.

The reaction of "crotyl" cadmium reagent with achiral aldehydes (or ketones) could lead to a complex mixture of products arising from a combination of allylic rearrangement and stereoselective addition.

$$RC(=O)R' + \text{"}CH_3CH{=}CHCH_2CdX\text{"} \rightarrow RR'C(OH)CH_2CH{=}CHCH_3 \text{ (racemic mixture)} + RR'C(OH)CH(CH_3)CH{=}CH_2 \text{ (two racemic mixtures)} \quad (31)$$

Remarkably, the "crotyl" reagent, prepared in situ from crotyl bromide by way of the Grignard reagent, affords exclusively the methyallyl adducts.[103,120] Addition to aldehydes thus constitutes an interesting situation where two chiral centers are generated simultaneously. Four cases were examined (R = ethyl, *n*-propyl, isopropyl, *tert*-butyl); in the first two, no stereoselectivity was observed. In the latter two, the "threo" isomer predominated. Qualitatively similar results were observed for the Mg and Zn compounds; all three sets of results are presented in Table III.

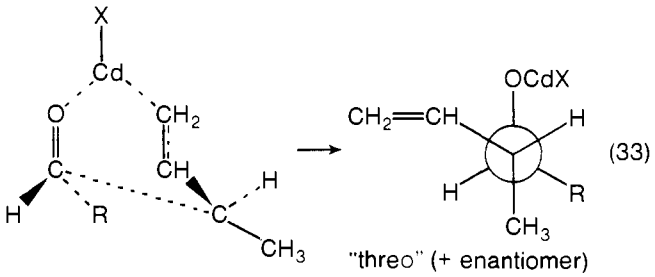
$$RCHO + CH_3CH{=}CHCH_2CdX \rightarrow$$



(32)

If one assumes the crotyl reagent adds in a concerted, allylic rearrangement (an S_E' process), two contrasting transition states **8** and **9** can be drawn as shown (alternative arrangements, leading to other conformers, are, of course, possible).

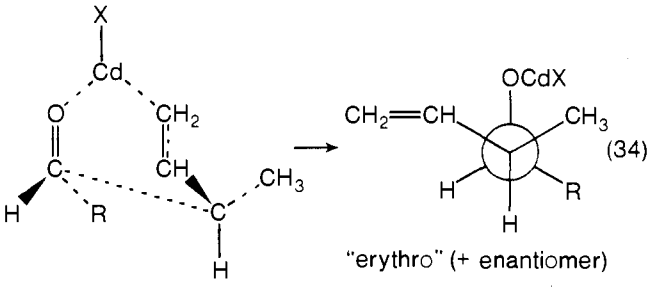
Transition state **8** is favorable in that it lacks the gauche interaction between the methyl and the incipient hydroxyl group.



8 (+ enantiomer)

"threo" (+ enantiomer)

(33)



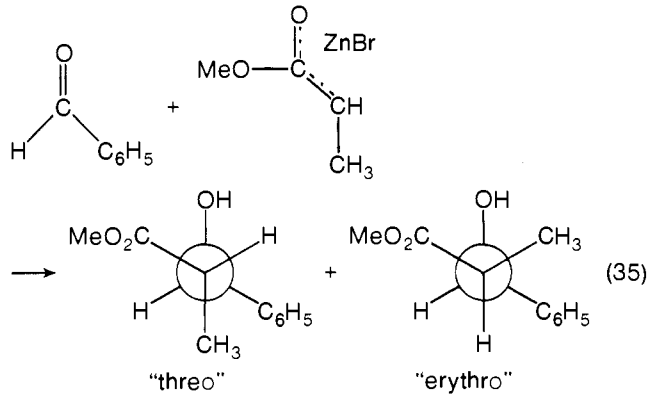
9 (+ enantiomer)

"erythro" (+ enantiomer)

(34)

The results are consistent with this picture, for the stereoselectivity increases as the size of "R" increases. It is of interest that this interpretation holds only if one considers methyl "large" and vinyl "medium" at the organometallic site.

Precedent for this kind of stereoselectivity can be found in the addition of the Reformatsky reagent from methyl α-bromopropionate to benzaldehyde,[121] in which the "threo":"erythro" ratio of products is 63:37. In transition states leading to these β-hydroxy esters, the carbomethoxy carbonyl takes the place of the vinyl group in **8** and **9**.



"threo" "erythro"

(35)

E. Side Reactions

It was noted by Tatibouët and Freon[78] in 1963 that when they repeated Kollonitsch's reaction between the in situ ethylcadmium reagent and benzaldehyde, they obtained not only the reported ethylphenylcarbinol, but benzyl alcohol as well, the latter a reduction product.

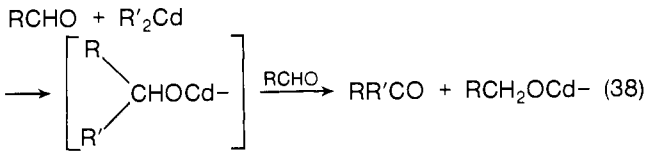
$$C_6H_5CHO + (C_2H_5)_2Cd \rightarrow C_6H_5CH(OH)C_2H_5 + C_6H_5CH_2OH \quad (36)$$

The possible formation of reduction products accompanying additions to aldehydes was subsequently investigated by Soussan in the same laboratory.

$$RCHO + R'_2Cd \longrightarrow RCH(OH)R' + RCH_2OH + R\overset{O}{\overset{\|}{C}}R' \quad (37)$$

R, R' = CH_3, n-C_3H_7, C_6H_5

Products from the reactions of acetaldehyde, butyraldehyde, and benzaldehyde with in situ methyl-, n-propyl-, and phenylcadmium reagents were analyzed by gas chromatography. In every case, both reduction and oxidation products were found, in approximately equal amounts. This suggests that they arise by the Meerwein–Pondorff–Verley (M–P–V) reduction (Oppenauer oxidation) route.



(38)

In some instances the tertiary alcohol, resulting from further addition of cadmium reagent to the ketone, was also detected in trace amounts. An example is the reaction of butyraldehyde with the methylcadmium reagent.

$$n\text{-}C_3H_7CHO + (CH_3)_2Cd \rightarrow n\text{-}C_3H_7CH(OH)CH_3 + n\text{-}C_3H_7CH_2OH + n\text{-}C_3H_7COCH_3 + n\text{-}C_3H_7C(OH)(CH_3)_2 \quad (39)$$

In a more detailed examination of the reaction of butyraldehyde with the n-propylcadmium reagent, it was shown that the amount of oxidation–reduction products increased with an excess of the cadmium reagent.

A similar array of products was reported by Soussan from the 1,6-bis-cadmium reagent and butyraldehyde.[79] Solvent and other reaction conditions were not specified, but it was noted that the relative amounts of the products changed with variation in the ratio of aldehyde:cadmium reagent.

$$n\text{-}C_3H_7CHO + XCd(CH_2)_6CdX \rightarrow CH_3(CH_2)_5CH(OH)C_3H_7\text{-}n \quad (40)$$

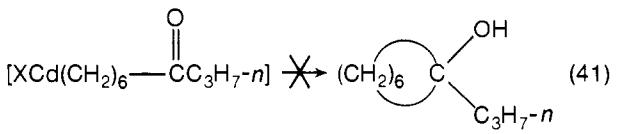
$CH_3(CH_2)_5COC_3H_7$-n

n-$C_3H_7CH(OH)(CH_2)_6CH(OH)C_3H_7$-$n$

n-$C_3H_7CO(CH_2)_6CH(OH)C_3H_7$-$n$

n-$C_3H_7CO(CH_2)_6COC_3H_7$-n

1-Butanol, the M–P–V reduction product of butyraldehyde, was reported to be formed as well. It is of interest that there was no tendency for cyclization, for example, to form 1-n-propylcycloheptanol.



(41)

An even more complex sequence of reactions has been noted when the "addition" reaction of benzaldehyde and ethylcadmium reagent is carried out in ether in the presence of a variety of metal halides ($MgCl_2$, $MgBr_2$, MgI_2, $ZnBr_2$, LiBr, $AlCl_3$).

Not only were the oxidation–reduction products noted earlier found, but benzyl benzoate (Tischenko reaction), ethylphenylcarbinyl benzoate (Cannizzaro ?), and benzalpropiophenone and ethylidenepropiophenone (aldol condensation) were detected in minimal amounts.[82] The side reactions (in particular the M–P–V reduction, Oppenauer oxidation) are enhanced as the amount of added metal halide is decreased; that is, the side reactions predominate as the reagent approaches the "purified" state, when simple addition is very slow. The addition of $CdBr_2$ was reported to have no effect, but in this case the solvent was DMF.

Reduction accompanies addition of the in situ benzylcadmium reagent to the "activated" ketone benzil.[112] It is not clear what is serving as reducing agent. One possibility—that the benzyl reagent is oxidized to the alkoxide, which, in turn, takes part in a M–P–V process—appears ruled out. The composition of

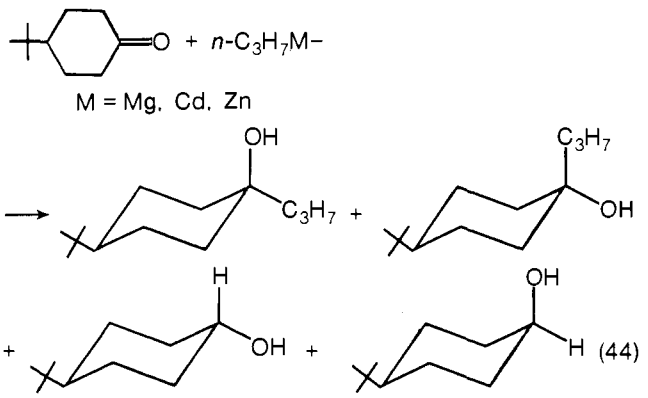
products, analyzed by column chromatography and NMR, does not change when oxygen is excluded. Furthermore, no trace of benzaldehyde could be detected.

$$C_6H_5COCOC_6H_5 + (C_6H_5CH_2)_2Cd \longrightarrow C_6H_5C(OH)(CH_2C_6H_5)COC_6H_5 + C_6H_5CH(OH)COC_6H_5 \quad (42)$$

A somewhat analogous situation has been noted in the formation of the cis enediol dibenzoate from benzoyl chloride and ethylcadmium reagent under Barbier (one-step) conditions.[122]

$$C_6H_5COCl + (C_2H_5)_2Cd \longrightarrow \underset{C_6H_5COO}{\overset{C_6H_5}{}}C{=}C\underset{OOCC_6H_5}{\overset{C_6H_5}{}} \quad (43)$$

A case in which the alkylcadmium reagent serves as the reducing agent has been noted where *n*-propylcadmium reacts with 4-*tert*-butylcyclohexanone.[89,116] Addition, however, predominates over reduction.[89,116] In a comparison of various or-



(44)

ganometallics, it has been found in two different laboratories[89,116] that the ratio of addition:reduction decreases in the order Cd, Mg, Zn. Stereoselectivity in the reduction decreases in the order Mg, Cd, Zn. In one instance, in fact, the propylzinc reagent (from propylmagnesium bromide and $ZnBr_2$) affords mainly the nonthermodynamic axial alcohol.[116]

IV. Reactions with Other Unsaturated Functional Groups

A. Esters and Lactones

There are very few instances recorded in which an ester reacts by addition of an organocadmium reagent at the carbonyl group. (It has already been pointed out that propiolactone is attacked at the β carbon.[123]) Halide-free allylic cadmium reagents seem to be exceptional, for they add to ethyl acetate to afford the tertiary alcohol.[104,124]

$$CH_3CO_2C_2H_5 + (CH_2{=}CHCH_2)_2Cd \longrightarrow CH_3C(OH)(CH_2CH{=}CH_2)_2 \quad (45)$$

Reaction with other in situ organocadmium compounds is limited to "activated" esters[6,85,86,88] such as diethyl oxalate.

$$(CO_2C_2H_5)_2 + (C_2H_5)_2Cd \longrightarrow (C_2H_5)_2C(OH)CO_2C_2H_5 \quad (46)$$

Even in these cases, addition occurs at only one ester function. The reaction fails with halide-free reagents.[88] The fact that ethyl formate undergoes addition is consistent with the tendency for aldehydes to react readily.[86]

$$HCO_2C_2H_5 + (C_6H_5)_2Cd \longrightarrow (C_6H_5)_2CHOH \quad (47)$$
(in situ)

The more common situation is that an ester or lactone function survives while other groups undergo addition or displacement with the cadmium reagent. Some representative examples are the following.

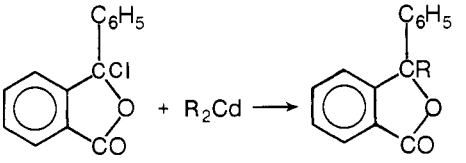
$$CH_3CH(OAc)CH_2COCl + (CH_3)_2Cd \longrightarrow CH_3CH(OAc)CH_2COCH_3 \text{ (ref 125)} \quad (48)$$

$$\underset{CO_2C_2H_5}{\overset{COCl}{}}(CH_2)_n + R_2Cd \longrightarrow \underset{CO_2C_2H_5}{\overset{COR}{}}(CH_2)_n \quad (n \geq 2) \text{ (ref 7, 8, 96)} \quad (49)$$

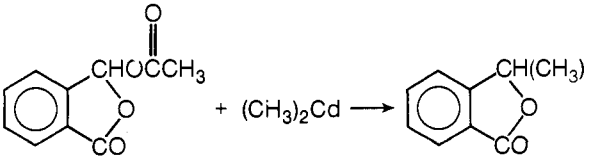
$$CH_3COCO_2C_2H_5 + R_2Cd \longrightarrow CH_3CR(OH)CO_2C_2H_5 \text{ (ref 98)} \quad (50)$$

$$\underset{CO_2C_2H_5}{\overset{CO_2C_2H_5}{}}CO + R_2Cd \longrightarrow \underset{CO_2C_2H_5}{\overset{CO_2C_2H_5}{}}RC(OH) \text{ (ref 97, 110)} \quad (51)$$

$$CH_3OCH(Cl)CO_2CH_3 + (C_6H_5)_2Cd \longrightarrow CH_3OCH(C_6H_5)CO_2CH_3 \text{ (ref 126)} \quad (52)$$

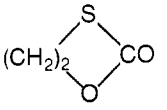


(ref 127, 128) (53)



(ref 129) (54)

Recent interest in the use of diethylcadmium as a catalyst for the polymerization of ethylene monothiocarbonate



suggests that thio esters (or lactones) are more susceptible to attack by cadmium reagents than the oxygen analogs.[130]

B. Amides, Lactams, and Nitriles

The generalization made in 1963[78] that amides and nitriles are unreactive toward organocadmium compounds has not been disputed. The only exception is the case of dimethylformamide, which was reported to be converted in 40% yield to benzaldehyde with an excess of the in situ phenylcadmium reagent.[86]

$$(C_6H_5)_2Cd + HCON(CH_3)_2 \longrightarrow \left[C_6H_5CH\begin{matrix}N(CH_3)_2\\OCdC_6H_5\end{matrix}\right] \xrightarrow{H_2O} C_6H_5CHO \quad (55)$$

Inasmuch as the reaction did not proceed further, even though benzaldehyde is known to react under such conditions, it is reasonable to assume that the initial adduct persists until the hydrolysis step.

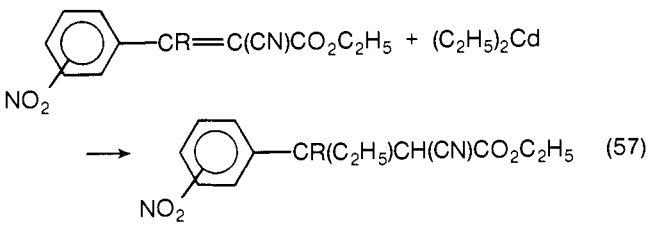
Presumably lactams, unless highly strained, would likewise be inert toward cadmium reagents. There are apparently no examples of ring openings of β-lactams.

An example of the inertness of the nitrile group is provided in the case of 3-trichlorosilylpropanenitrile, which undergoes displacement at silicon in 90% yield.[131]

$$Cl_3Si(CH_2)_2CN + (CH_3)_2Cd \rightarrow CH_3Si(Cl_2)(CH_2)_2CN \quad (56)$$

C. Nitro Compounds

Nitroethylenes react with organocadmium compounds in the conjugate manner exclusively,[86,88,132] the nitro group remaining intact. Likewise, cadmium reagents add in the conjugate manner to ethyl nitrocinnamates without affecting the nitro function.[133]



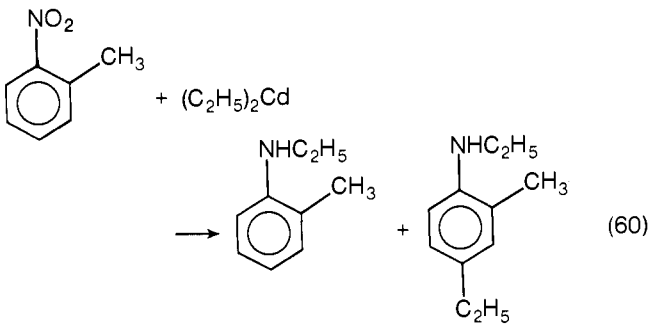
Although α-nitro ketones may lead to a complex mixture with cadmium reagents, in all of the products the nitro group is still present. An example is the addition of the ethylcadmium reagent to nitroacetone.[94]

$$CH_3COCH_2NO_2 + (C_2H_5)_2Cd \rightarrow \underset{40-60\%}{CH_3(C_2H_5)C(OH)CH_2NO_2} + CH_3COC_2H_5 + CH_3NO_2 \quad (58)$$

Nitromethane undergoes metalation rather than addition with purified dimethylcadmium; the bis(nitromethyl)cadmium detonated in the glove box.[134]

$$2CH_3NO_2 + (CH_3)_2Cd \rightarrow (O_2NCH_2)_2Cd + 2CH_4 \quad (59)$$

All the above reactions were carried out under fairly mild conditions (diethyl ether as solvent, gentle reflux) with no effect on the nitro group. In one study, aromatic nitro groups were reduced with a cadmium reagent when the latter was present in excess and the reactions were carried out in dibutyl ether at reflux for 12 h.[135] Under these conditions the nitro group was converted to a secondary amine, the *N*-alkyl group originating from the alkylcadmium reagent. Furthermore, alkylation occurred in some instances in the aromatic ring. Besides the example shown, similar results were recorded for nitrobenzene, nitromesitylene, and *m*- and *p*-nitrotoluene.



Because the reaction conditions for these reductive alkylations are extreme, it is reasonable to assume that nitro groups in general will survive treatment of a multifunctional compound with cadmium reagent under more usual conditions.

D. Miscellaneous Nitrogen Compounds

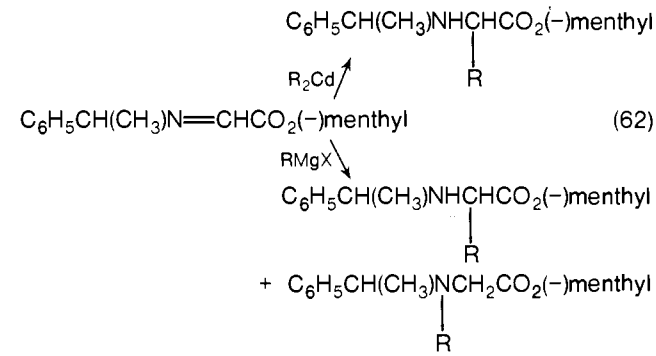
1. Imines

Benzalanilines undergo 1,2-addition at the imine bond with in situ ethylcadmium reagent in high yield (over 90%), whereas the purified reagent is ineffective.[136] The corresponding Grignard reagent adds similarly, but in situ ethylzinc reagent provides the adducts in only 40–60% yield. When $MgBr_2$ is added to the purified cadmium reagent, its effectiveness is restored.[137]

$$ArCH{=}NAr' + (C_2H_5)_2Cd \rightarrow ArCH(C_2H_5)NHAr' \quad (61)$$

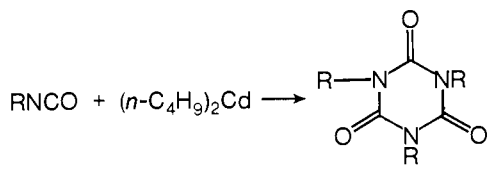
A study was made of the effect of substituents (*p*-OMe, *p*-Me, *p*-Cl, *m*-Cl) in both rings on the rate of addition,[138,139] which appears to have little or no nucleophilic character, for the Hammett ρ values, although small (0.4–1.4), are negative. Thus, electron-withdrawing substituents slightly impede the addition. On the other hand, a Hammett plot for the addition with diethylmagnesium had a positive slope.[140] It was suggested that in the case of Grignard addition, coordination of Mg with the nitrogen is important.

In an asymmetric synthesis of amino acids, by addition of organometallics to iminoglyoxylates, Fiaud and Kagan found in situ cadmium reagents to be superior to the Grignard reagents. While the cadmium route led regiospecifically to the secondary amine, the Grignard reagents were often unselective or else afforded exclusively the tertiary amine.[141]



2. Isocyanates

In contrast to the case with Grignard reagents, isocyanates do not undergo simple addition with in situ alkylcadmium reagents but rather trimerize.[142]



$$R = C_2H_5,\ n\text{-}C_4H_9,\ C_6H_5,\ C_{10}H_7$$

Phenyl isocyanate underwent trimerization with the purified *n*-butyl reagent and with in situ ethyl and *n*-propyl reagents as well. Arylcadmium reagents lead to a complex mixture of products.

3. Thiocyanogen

Reaction of cadmium reagents (apparently halide-free) with $(SCN)_2$ in benzene led to the formation of alkylcadmium thiocyanates, whose decomposition points and vibrational spectra were taken as evidence that they were coordination polymers.[143]

$$RR'Cd + (SCN)_2 \rightarrow RCdSCN + R'SCN \quad (64)$$

R = methyl, ethyl, ethoxy; R′ = methyl, ethyl

4. Nitric Oxide

Nesmeyanov and Markarova reported formation of "$C_6H_5N{=}NNO_3$" from the interaction of purified diphenylcadmium with NO.[144] More recently, Abraham and co-workers have isolated in high yield the methyl analog of cupferron from dimethylcadmium and nitric oxide in benzene at room temperature.[145]

$$(CH_3)_2Cd + 2NO \rightarrow Cd[ONCH_3]_2 \quad (65)$$
$$\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\quad NO$$

TABLE IV. Conjugate Addition of In Situ Cadmium Reagents to Unsaturated Compounds

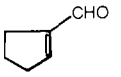
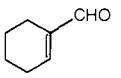
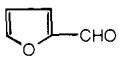
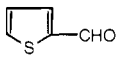
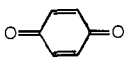
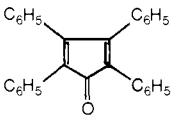
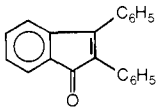
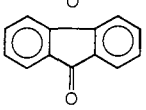
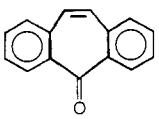
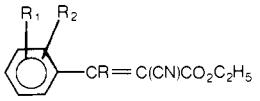
	unsatd compd	Cd reagent (R =)	1,2-addition	1,4-addition	ref
		I. Aldehydes			
1.	$CH_2{=}CHCHO$	C_2H_5	10	0(25)[a]	149,150
2.	$CH_2{=}CHCHO$	C_6H_5	45	0(33)[a]	149, 150
3.	$CH_3CH{=}CHCHO$	CH_3	14	<1	150
		C_2H_5	58	2	150
		n-C_4H_9	40	2	150
4.	$C_6H_5CH{=}CHCHO$	CH_3	72	6	150
5.		CH_3	3	22	150
		C_2H_5	51	49	150
		n-C_4H_9	59	41	150
6.		CH_3	30	5 (starting material recovered, 43%)	150
		C_2H_5	56	16	150
7.		CH_3	82	0	150
		C_2H_5	86	0	150
		C_6H_5	73	0	150
8.		CH_3	78	0	150
		C_2H_5	84	0	150
		C_6H_5	84	0	150
		II. Ketones			
9.	$CH_2{=}CHCOCH_3$	CH_3	trace	5	106
10.	$CH_2{=}CHCOCH_3$	C_2H_5	≃1	3, 7 (10)[a]	106, 149
11.	$CH_3CH{=}CHCOCH_3$	CH_3	trace	5 (83, 89)[a]	106, 149
12.	$CH_3CH{=}CHCOCH_3$	C_2H_5	<1	6 (44, 50)[a]	106, 149
13.	$CH_3CH{=}CHCOCH_3$	$isoC_4H_9$	<1	4 (44)[a]	149
14.	$(CH_3)_2C{=}CHCOCH_3$[b]	C_2H_5	40	0	106
15.	$(CH_3)_2C{=}C(CH_3)COCH_3$[b]	C_2H_5	10	0	106
16.	$CH_3CH{=}C(COCH_3)_2$	C_2H_5	0	95	106
17.	$C_6H_5CH{=}CHCOC_6H_5$	C_6H_5	0	100	151
18.	$C_6H_5(COCH_3){=}C(C_6H_5)COCH_3$	C_2H_5	0	52	106
19.		C_2H_5	<1	5 (70)[a]	106, 149
		C_2H_5 (excess)	<1	20	106, 149
20.		C_2H_5	0	25 (hydroquinone, 25%)	92, 106
21.		C_6H_5		2,6-diphenyl (10%) 2,5-diphenyl (20%) 2,3,5,6-tetraphenyl (20%) hydroquinone (50%)	93
22.		C_2H_5	100	0	106
		C_2H_5 (purified)	82–85	0	106
		n-C_4H_9	100	0	106
		C_6H_5	100	0	106
23.		C_2H_5	91		106
		n-C_4H_9	93		106
		C_6H_5	93		106
24.		C_2H_5	86	0	106
		C_2H_5 (purified)	0–1	0	106
		n-C_4H_9	90	0	106
		C_6H_5	69	0	106
25.		C_2H_5	0	0 (starting material recovered, 90%)	106
		III. Esters, Nitriles, Keto Esters, etc.			
26.	$CH_3CH{=}C(CO_2C_2H_5)_2$	α-$C_{10}H_7$	0	60[c]	153
27.	$CH_3CH_2CH{=}C(CO_2C_2H_5)_2$	α-$C_{10}H_7$	0	65[c]	153
28.	$(CH_3)_2C{=}C(CO_2C_2H_5)_2$	n-C_4H_9	0	28 (diethyl isopropylmalonate, 34%)	156
29.	$(CH_3)_2CHCH{=}C(CO_2C_2H_5)_2$	α-$C_{10}H_7$	0	77[c]	153
30.	$CH_3CH{=}C(COCH_3)CO_2C_2H_5$	C_2H_5	0	85	106
31.	$(CH_3)_2CHCH{=}C(CO_2C_2H_5)$ | $CO(CH_2)_2CO_2C_2H_5$	α-$C_{10}H_7$	0	33	154
32.	$(CH_3)_2C{=}C(CN)_2$	n-C_4H_9	0	5 (isopropyl malononitrile, 39%)	156

TABLE V. (Cont)

	unsatd compd	Cd reagent (R =)	1,2-addition	1,4-addition	ref
33.	$(CH_3)_2C{=}C(CN)CO_2C_2H_5$	n-C_4H_9	0	15 (saturated cyano ester, 23%)	156
		C_6H_5	0	12	156
		$C_6H_5CH_2$	0	92	156
34.	$C_2H_5C(CH_3){=}C(CN)CO_2C_2H_5$	n-C_3H_7	0	12 (saturated cyano ester, 59%)	155
		C_6H_5	0	26	155
		$C_6H_5CH_2$	0	93	155
35.		C_2H_5	0	8 (various adducts obtained; no yields recorded)	133
36.	$CH_3CH{=}CHNO_2$	C_2H_5	0	60	132
		n-C_4H_9	0	55	132
		C_6H_5	0	55	132
37.	$C_2H_5CH{=}CHNO_2$	C_2H_5	0	55	132
		n-C_4H_9	0	60	132
		C_6H_5	0	50	132
38.	$(CH_3)_2CHCH{=}CHNO_2$	C_2H_5	0	55	132
		n-C_4H_9	0	60	132
		C_6H_5	0	50	132
39.	$C_6H_5CH{=}CHNO_2$	C_2H_5	0	76	132
		n-C_4H_9	0	70	86, 132
		C_6H_5	0	50	132

[a] Yield of condensation products from subsequent conjugate addition. [b] Forcing conditions (excess Cd reagent, refluxing ether 10 h). [c] Piperidinium acetate added.

Although attack by cadmium reagents at N–O bonds may be general, there appear to have been no further investigations in this area.

5. Diazo Compounds

In a study on the generation of organometallic diazoalkanes, Lorbert obtained evidence for the cadmium enolate of diazoacetic ester. The reaction involved metalation of diazomethane or ethyl diazoacetate with di[bis(trimethylsilylamino)cadmium[146] at −35 °C (eq 66 and 67). Cation exchange between lithiodiazomethane and cadmium chloride failed (eq 68).

$$Cd[N(Si(CH_3)_3)_2]_2 + CH_2N_2 \rightarrow Cd(CN_2)_2 \quad (66)$$

$$Cd[N(Si(CH_3)_3)_2]_2 + N_2CHCO_2C_2H_5 \rightarrow Cd[C(N_2)CO_2C_2H_5]_2 \quad (67)$$

$$CdCl_2 + LiCHN_2 \not\rightarrow Cd[CHN_2]_2 \quad (68)$$

Although the diazo-containing cadmium compounds decompose readily (cadmium diazomethane is explosive), their formation illustrates the indifferent reactivity of the diazo group (as well as esters) toward organocadmium compounds.

E. Oxides of Carbon

Very little has been reported on the interaction of carbon monoxide and carbon dioxide with cadmium reagents.[10] In one instance, in situ phenylcadmium reagent was inert toward CO;[147] in another, purified diphenylcadmium failed to react with CO_2.[144]

The halide-free, allylic cadmium reagents, however, were found to afford the corresponding acids (without rearrangement) in good yield.[148]

$$(CH_2{=}CHCH_2)_2Cd \xrightarrow{CO_2} CH_2{=}CHCH_2CO_2H \quad (69)$$

$$(CH_2{=}C(CH_3)CH_2)_2Cd \xrightarrow{CO_2} CH_2{=}C(CH_3)CH_2CO_2H \quad (70)$$

$$(CH_3CH{=}CHCH_2)_2Cd \xrightarrow{CO_2} CH_3CH{=}CHCH_2CO_2H \quad (71)$$

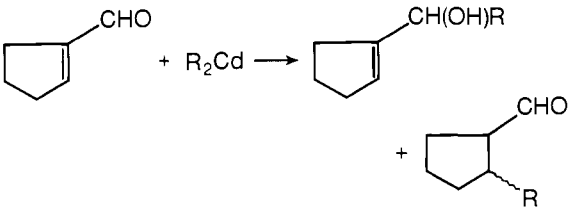
The lack of investigation in this area can be attributed to the fact that it offers no synthetic advantage over the carbonation of Grignard or lithium reagents.

V. Conjugate Addition

The recorded examples of the interaction between organocadmium reagents and α,β-unsaturated compounds have been assembled in Table IV. Most instructive is to compare the results of organocadmium reagents with the more familiar Grignard additions.

In the case of aldehydes, the cadmium reagent effects some 1,4-addition when the corresponding Grignard reagent leads exclusively to 1,2-addition.[149,150]

For the cases of crotonaldehyde with n-butylcadmium and of cyclopentene-1-carboxaldehyde with methylcadmium, it was shown that the tendency for 1,4-addition was enhanced by the presence of cuprous iodide and suppressed by increasing the Cd/aldehyde ratio.[149,150] Only with cyclopentene-1-carboxaldehyde, among those studied, however, was there substantial 1,4-addition. It accounted for about one-half the product with the ethyl- or n-butylcadmium reagent, for example.[150]



(72)

R = C_2H_5, n-C_4H_9 (Z and E)

Under similar conditions crotonaldehyde, cinnamaldehyde, cyclohexene-1-carboxaldehyde, furfural, and thiophene-2-carboxaldehyde afforded exclusively or predominantly the 1,2-adducts. These observations serve as convincing confirmation of the facile addition of cadmium reagents to aldehydes.

Ketones tend to undergo 1,4-addition somewhat more extensively than aldehydes. Furthermore, the relative amount of 1,4- to 1,2-addition is higher for cadmium than for Grignard reagents, an observation that holds for α,β-unsaturated esters and

nitriles as well. As an example, it was shown that 3-penten-2-one afforded the 1,2-adduct in 76% yield with methylmagnesium bromide, whereas the same product was formed in only trace amount with the methylcadmium reagent.[106] The mixture of

$$CH_3CH{=}CHCOCH_3 \xrightarrow[CH_3MgBr]{(CH_3)_2Cd} \begin{cases} CH_3CH{=}CHC(OH)(CH_3)_2\ (76\%) \\ \text{1,4-products}\ (100\%) \end{cases} \quad (73)$$

products from the latter case was the result entirely of a sequence of 1,4-additions.

Benzalacetophenone gave the 1,4-adduct with phenylcadmium reagent in quantitative yield;[151] although the phenyl Grignard reagent is known to produce predominantly the same product, there is, nevertheless, some 1,2-adduct as well.[152]

2,3:6,7-Dibenzotropone is recovered unchanged after treatment under forcing conditions with the ethylcadmium reagent. Fluorenone[85] and other highly conjugated cyclanones react extensively in the 1,2 manner under milder conditions.[106]

An early report by Riegel[153] indicated that the enhanced 1,4-addition with cadmium over magnesium reagents also prevailed with alkylidenemalonic esters. The saturated malonic esters from α-naphthyl reagent were isolated in higher yields from the cadmium compound in each case. It was noted, however, that piperidinium acetate facilitated the cadmium reaction, and so this salt was added to the reaction mixtures.

$$RCH{=}C(CO_2C_2H_5)_2 + (\alpha\text{-}C_{10}H_7)_2Cd$$
$$R = CH_3,\ C_2H_5,\ (CH_3)_2CH$$

$$\xrightarrow[\text{acetate}]{\text{piperidinium}} RCH(\alpha\text{-}C_{10}H_7)CH(CO_2C_2H_5)_2 \quad (74)$$

Advantage was taken of this conjugate addition to carry out the following transformation in a multistep synthetic sequence.[154]

$$(CH_3)_2CHCH{=}C(CO_2C_2H_5)CO(CH_2)_2CO_2C_2H_5 + (\alpha\text{-}C_{10}H_7)_2Cd \rightarrow$$
$$(CH_3)_2CHCH(\alpha\text{-}C_{10}H_7)CH(CO_2C_2H_5)CO(CH_2)_2CO_2C_2H_5 \quad (75)$$

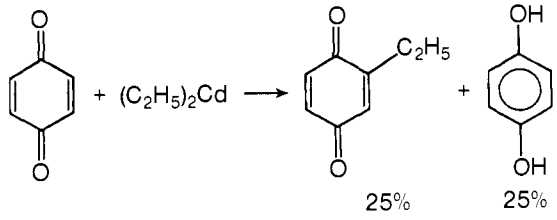
It was noted by Prout[155,156] that alkylidene cyanoacetic esters behaved in the contrary way: 1,4-addition was higher with Grignard than with cadmium reagents, the examples being the propyl, butyl, and phenyl organometallics. Only in the case of the benzyl reagents did the cadmium compound afford the 1,4-adduct in higher yields.

$$CH_3C(R){=}C(CN)CO_2C_2H_5 + R^1{}_2Cd \rightarrow CH_3CRR^1CH(CN)CO_2C_2H_5 + \text{reduction product} \quad (76)$$

$$R = CH_3,\ C_2H_5;\ R^1 = n\text{-}C_3H_7,\ n\text{-}C_4H_9,\ C_6H_5,\ C_6H_5CH_2$$

The synthesis of a series of 1,4-adducts from benzalcyanoacetic esters by this method has been the subject of a recent patent.[133]

The 1,2- and 1,4-additions in conjugated compounds are likely to be accompanied by side reactions. If the cadmium reagent contains β hydrogens, it might be expected that reduction would occur. This is particularly the case with benzoquinone,[92,93] where hydroquinone accounts for one-half the product. An example is the case of its reaction with the ethylcadmium reagent.[92] The fact, however, that hydroquinone is a major product



(77)

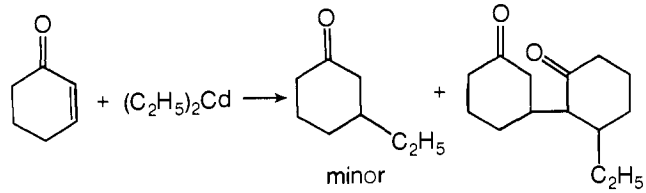
with the phenylcadmium reagent as well points to other pathways to reduction.[92]

In the case of alkylidene malonate and cyanoacetate derivatives, reduction is observed with butyl but not with phenyl or benzyl reagents.[155,156] This suggests that reduction may be taking place by means of the transfer of a β hydrogen from the alkyl group of the cadmium reagent. It is of interest, although unexplained, that the extent of reduction is higher for cadmium than for Grignard reagents.[156]

"Simple" 1,4-addition is followed by further Michael condensations with some conjugated ketones; in fact, this sequence accounts for all or most of the final products in some cases. For example, of the 1,4-addition product between 3-penten-2-one and methylcadmium reagent, all but 5% of it is the bimolecular condensation product.[106]

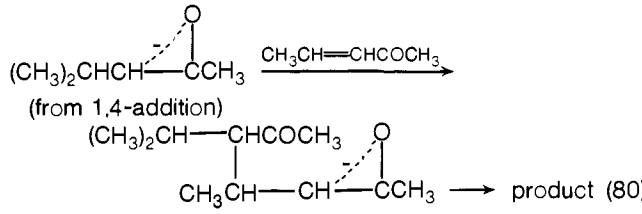
$$CH_3CH{=}CHCOCH_3 + (CH_3)_2Cd \rightarrow \underset{\text{minor}}{(CH_3)_2CHCH_2COCH_3} + \underset{\text{major}}{CH_3CH(CH(CH_3)_2)CH_2COCH_3} \quad (78)$$

Cyclohex-2-enone gives mainly the condensation product rather than the 1,4-adduct with the ethylcadmium reagent.[149]



(79)

These secondary products presumably arise by conjugate addition to starting ketone of the initially formed enolate, which was itself the product of 1,4-addition.



(80)

The fact that the condensation products predominate suggests that the Michael addition is kinetically or thermodynamically favored over the addition of cadmium reagent.

A proposal has been put forward that the competition between 1,2- and 1,4-addition in conjugated carbonyls can be correlated with the organometallic by means of the Pearson hard and soft acid–base theory.[157] According to this point of view, it can be calculated that the 4 position in an α,β-unsaturated carbonyl compound is "softer" than the 2 position. Then the "hard" metal cations (e.g., Li, K, Na, Ca) should tend to promote 1,2-addition, whereas the "soft" ones (e.g., Cd, Ag, Cu, Hg) should lead more readily to 14-addition. Metal cations of intermediate hardness should exhibit an effect somewhere between the extremes. Although the examples of comparison between cadmium and other organometallics are limited, there does indeed seem to be a correlation in the 1,2- vs. 1,4-addition for the series: Li > Mg > Cd (1,2 > 1,4).

VI. Reactions at Saturated Carbon

A. Halides

Cason and Fessenden[158] reported that some secondary and tertiary halides (2-iodooctane, 2-bromobutane, *tert*-butyl chloride, tri-*n*-propylcarbinyl chloride) were either inert toward in situ

alkylcadmium reagents or else they underwent elimination to alkenes, usually in low yield. Even allyl bromide did not react significantly with the *n*-octylcadmium reagent. More recently, Galiullina and co-workers[159] reported a high conversion of triphenylmethyl chloride to 1,1,1-triphenylethane with dimethylcadmium (presumably halide-free). This displacement or "coupling", typified by Grignard and other organometallics (Kharasch and Reinmuth), is in competition with elimination, which the organocadmium compound undergoes when the "R" of the cadmium reagent contains β hydrogens. The two contrasting pathways are illustrated in eq 81. Yields, based on un-

$$R_2Cd + (C_6H_5)_3CCl \xrightarrow{a} (C_6H_5)_3CR\ (R = Me, Et, Ph, benzyl) \quad (81)$$
$$\xrightarrow{b} (C_6H_5)_3CH + [RCdCl] + alkene\ (R\text{-}H)\ (R\text{-}Et, n\text{-}Pr, i\text{-}Bu)$$

recovered organocadmium reagent (determined by hydrolysis), were high for cadmium reagents where R = methyl, ethyl, and *n*-propyl but were not reported for R = isobutyl, phenyl, or benzyl.

The bis(triethylgermyl)cadmium compound affords, in low yield, displacement or cross-coupling products with three halides, as shown in eq 82–84. It was demonstrated by ESR spectroscopy that the reaction mixture from triphenylmethyl chloride generates free radicals and products derived from them.[160,161] Reaction of the same cadmium compound with benzyl bromide[160] affords symmetrical coupling products (eq 85), an observation also suggestive of free-radical intermediates.

$$[(C_2H_5)_3Ge]_2Cd + (C_6H_5)_3CCl \rightarrow (C_2H_5)_3GeC(C_6H_5)_3 \quad (82)$$

$$[(C_2H_5)_3Ge]_2Cd + CH_2{=}CHCH_2Br \rightarrow (C_2H_5)_3GeCH_2CH{=}CH_2 \quad (83)$$

$$[(C_2H_5)_3Ge]_2Cd + C_2H_5Br \rightarrow (C_2H_5)_4Ge \quad (84)$$

$$[(C_2H_5)_3Ge]_2Cd + C_6H_5CH_2Br \rightarrow (C_2H_5)_3GeGe(C_2H_5)_3 + C_6H_5CH_2CH_2C_6H_5 \quad (85)$$

The interaction of diethylcadmium (and -zinc) with carbon tetrachloride and chloroform leads to dichlorocarbene formation, the evidence for the divalent intermediate being the trapping product with cyclohexene and 1-chloropropene, presumed to form by an insertion of dichlorocarbene into the carbon–cadmium bond.[162,163]

$$(C_2H_5)_2Cd + CCl_4 \longrightarrow C_2H_5CdCCl_3 + C_2H_5Cl \quad (86a)$$

$$C_2H_5CdCl_3 \longrightarrow C_2H_5CdCl + :CCl_2 \quad (86b)$$

$$:CCl_2 + \text{cyclohexene} \longrightarrow \text{dichlorocarbene adduct} \quad (86c)$$

(detected by chromatography)

$$:CCl_2 + (C_2H_5)_2Cd \text{ or } C_2H_5CdCl \longrightarrow C_2H_5C(Cl_2)CdR\ (R = C_2H_5, Cl) \quad (86d)$$

$$C_2H_5C(Cl_2)CdR \longrightarrow RCdCl + [C_2H_5\ddot{C}Cl] \xrightarrow{\alpha} CH_3CH{=}CHCl\ (isolated) \quad (86e)$$

Benzyl bromide or chloride leads to substantial coupling with phenylcadmium reagents.[164,165] Of particular interest is the observation by Emptoz and Huet that bibenzyl formation disappears when one changes from in situ to halide-free diphenylcadmium, and that benzene is superior to ether as solvent.[165] Dimethylcadmium affords ethylbenzene with benzyl bromide in ether or benzene as solvent, but the reaction conditions are more extreme, and the conversion is inferior to that with diphenylcadmium.

$$C_6H_5CH_2X + R_2Cd \rightarrow C_6H_5CH_2R \quad (87)$$
$$R = Ar, CH_3$$

There has been one report of the conversion of allyl bromide to 3-phenylpropene (39%) and of 3-bromocyclohexene to 3-phenylcyclohexene (81%) with the in situ phenylcadmium reagent.[164]

$$(C_6H_5)_2Cd \xrightarrow{CH_2{=}CHCH_2Br} CH_2{=}CHCH_2C_6H_5$$
$$\text{bromocyclohexene} \longrightarrow \text{3-phenylcyclohexene} \quad (88)$$

Displacement at silicon in 3-trichlorosilylpropanenitrile is effected with purified dimethylcadmium in toluene.

$$Cl_3Si(CH_2)_2CN + (CH_3)_2Cd \rightarrow CH_3Si(Cl_2)(CH_2)_2CN \quad (89)$$

The product of monodisplacement is formed in 90% yield (69% in benzene), whereas a mixture of mono-, di-, and tri-displacement products are formed with the Grignard reagent.[131]

B. Epoxides

Only one study of the reactions of styrene oxide with cadmium reagents appears to have been carried out.[86,166,167] The products with in situ methyl, ethyl, butyl, and phenyl reagents are secondary alcohols, presumably arising from phenylacetaldehyde, an initial rearrangement product. (It has been shown that phenylacetaldehydes readily undergo addition with in situ reagents.[101]) In no case was any indication given that either of the

$$C_6H_5CH\text{—}CH_2 + R_2Cd(MgX_2) \longrightarrow [C_6H_5CH_2CHO] \longrightarrow C_6H_5CH_2CH(OH)R \quad (90)$$

alcohols from direct ring-opening—$C_6H_5CH(OH)CH_2R$, $C_6H_5CH(R)CH_2OH$—was detected. The metal salts present in the in situ reagent may promote the rearrangement of styrene oxide to phenylacetaldehyde; in any case, purified cadmium reagents were shown to be unreactive toward styrene oxide. The interaction with epoxides warrants further attention, however, for it has been noted that diethylcadmium and mercaptans serve as catalysts in the polymerization of propylene oxide.[168]

C. Competition between Displacement at Saturated Carbon and Other Reactions

An early report by Bunnett and Tarbell[169] would indicate that addition to an acid chloride is more facile than displacement of an α-halogen. The example is chloroacetyl chloride, which was converted in 26% yield to the ketone with in situ butylcadmium reagent.

$$ClCH_2COCl \rightarrow ClCH_2COC_4H_9 \quad (91)$$

The mixed carboxyl carbonic anhydride of acetoacetic acid ethylene ketal reacts in the expected manner with in situ butylcadmium reagent, to afford the corresponding ketone.[170]

$$\text{ketal-}CH_2COCOCOC_2H_5 + (C_4H_9)_2Cd \longrightarrow \text{ketal-}CH_2COC_4H_9 \quad (92)$$

The next two higher homologs, however, react preferentially by what appears to be displacement at the ketal carbon, alkoxide being the leaving group.[170,171]

TABLE V. Displacement Reactions Effected by Organocadmium Reagents in Multifunctional Compounds

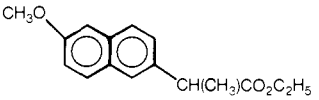
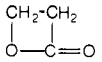
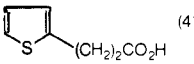
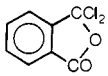
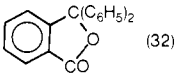
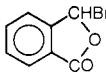
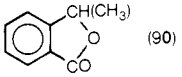
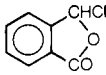
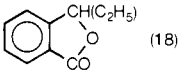
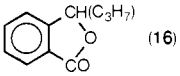
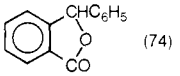
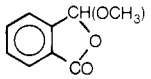
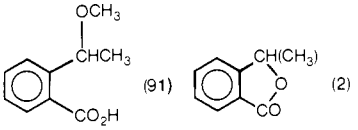
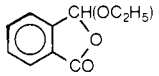
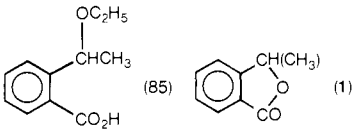
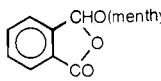
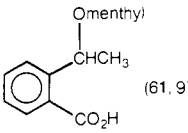
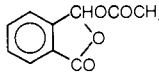
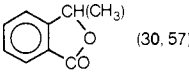
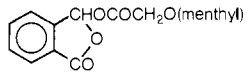
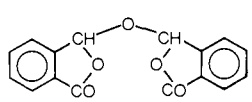
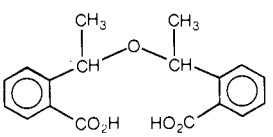
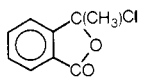
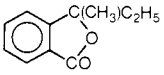
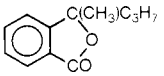
	Reactant	Cd reagent (R =)	product(s) (yield, %)	ref
1.	$C_6H_5COOCH(Cl)C_6H_5$	C_6H_5	$C_6H_5COOCH(C_6H_5)_2$ (29)	*a*
2.	$(C_6H_5COO)_2CHC_6H_5$	C_6H_5	$C_6H_5COOCH(C_6H_5)_2$ (13)	*a*
3.	$C_6H_5CO_2CH(Cl)CH{=}CHC_6H_5$	C_6H_5	$(C_6H_5)_2CHCH{=}CHC_6H_5$ (25)	*a*
4.	$BrCH_2CO_2C_2H_5$	C_6H_5	$C_6H_5CH_2CO_2C_2H_5$ (11, 26, 46, 53)	174
5.	$BrCH_2CO_2C_2H_5$	α-$C_{10}H_7$	α-$C_{10}H_7CH_2CO_2C_2H_5$ (9, 16, 62)	174
6.	$ClCH_2CO_2C_2H_5$	C_6H_5		174
7.	$CH_3CH(Br)CO_2C_2H_5$	C_6H_5	$CH_3CH(C_6H_5)CO_2C_2H_5$ (40, 58)	164, 174
8.	$CH_3CH(Br)CO_2C_2H_5$	α-$C_{10}H_7$	$CH_3CH(\alpha$-$C_{10}H_7)CO_2C_2H_5$ (55)	179
9.	$CH_3CH(Br)CO_2C_2H_5$	6-(CH_3O)-2-$C_{10}H_6$		193
10.	$(CH_3)_2C(Br)CO_2C_2H_5$	C_6H_5		174
11.	$BrCH(CO_2C_2H_5)_2$	C_6H_5	$CH_2(CO_2C_2H_5)_2$ (75) + C_6H_5Br (75)	174
12.	$C_6H_5COCH_2Br$	C_6H_5	$C_6H_5COCH_2C_6H_5$ (3–31)	174
13.	$CH_3OCH(Cl)CO_2CH_3$	C_6H_5	$CH_3OCH(C_6H_5)CO_2CH_3$ (60)	126
14.		*n*-C_4H_9	*n*-$C_4H_9(CH_2)_2CO_2H$ (32)	123
		C_6H_5	$C_6H_5(CH_2)_2CO_2H$ (77)	123
		o-$C_6H_4CH_3$	*o*-CH_3-$C_6H_4(CH_2)_2CO_2H$ (5)	123
		m-$C_6H_4CH_3$	*m*-CH_3-$C_6H_4(CH_2)_2CO_2H$ (51)	123
		2-$C_{10}H_7$	2-$C_{10}H_7$-$(CH_2)_2CO_2H$ (48)	123
		 (41)	 (41)	123
15.		C_6H_5	 (32)	*b*
16.		CH_3	 (90)	128
17.		C_2H_5	 (18)	175
18.	as above	C_3H_7	 (16)	175
19.	as above	C_6H_5	 (74)	175
20.		CH_3	 (91) (2)	129
21.		CH_3	 (85) (1)	129
22.		CH_3	 (61, 97)	129
23.		CH_3	 (30, 57)	129
24.		CH_3	as above (13, 38)	129, 180
25.		CH_3	 (22)	129
26.		C_2H_5	 (51)	175
27.	as above	C_3H_7	 (57)	175

TABLE V. (Cont)

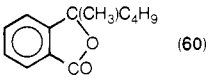
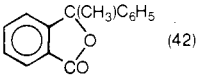
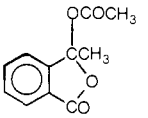
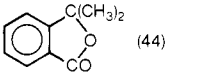
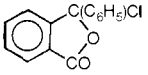
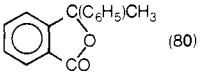
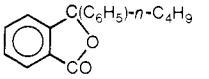
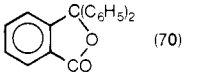
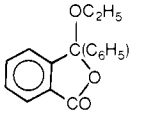
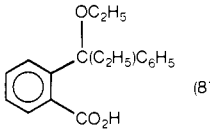
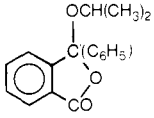
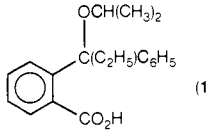
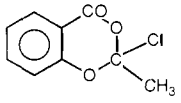
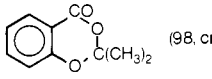
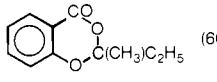
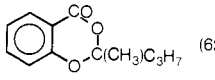
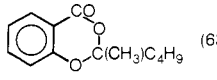
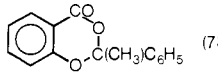
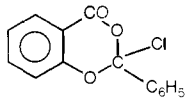
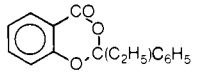
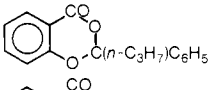
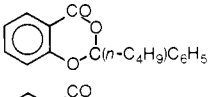
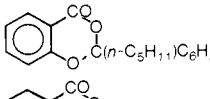
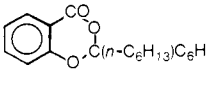
	Reactant	Cd reagent (R =)	product(s) (yield, %)	ref
28.	as above	C_4H_9	 (60)	175
29.	as above	C_6H_5	 (42)	175
30.		CH_3	 (44)	128
31.		CH_3	 (80)	175
32.	as above	CH_3	as above (88)	127
33.	as above	n-C_4H_9	 (80)	127
34.	as above	C_6H_5	 (70)	127
35.	as above	C_6H_5	as above (45)	175
36.		C_2H_5	 (87)	*a*
37.		C_2H_5	 (19)	*a*
38.	 (or chain tautomer)	CH_3	 (98, crude)	*c*
39.	as above	C_2H_5	 (60, 75)	*d*
40.	as above	C_3H_7	 (62)	*d*
41.	as above	C_4H_9	 (63)	*d*
42.	as above	+ C_6H_5	 (73)	*d*
43.	 (or chain tautomer)	CH_3	as above (64)	*e*
44.	as above	C_2H_5	 (26)	*e*
45.	as above	n-C_3H_7	 (43)	*e*
46.	as above	n-C_4H_9	 (55)	*e*
47.	as above	n-C_5H_{11}	 (57)	*e*
48.	as above	n-C_6H_{13}	 (41)	*e*

TABLE V. (Cont)

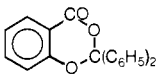
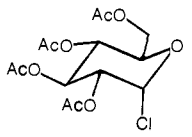
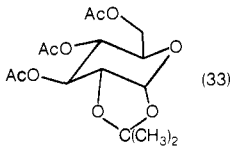
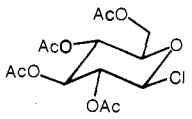
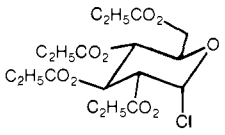
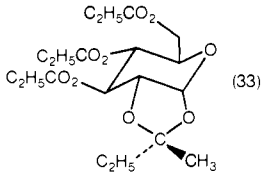
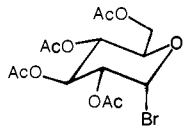
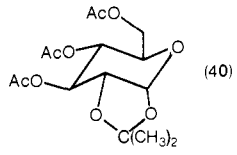
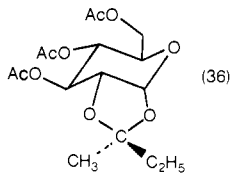
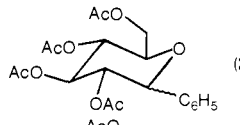
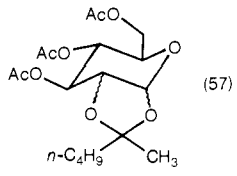
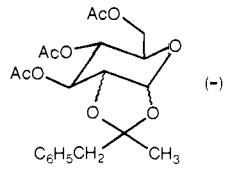
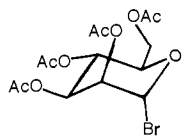
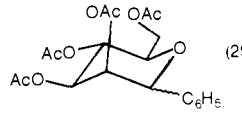
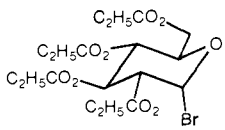
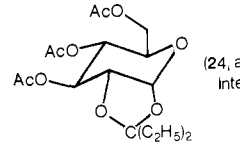
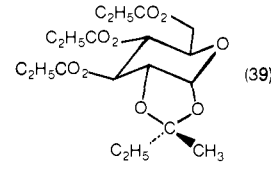
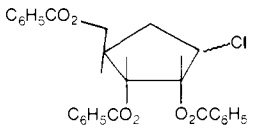
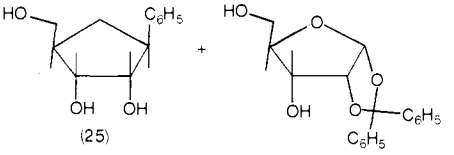
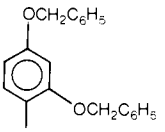
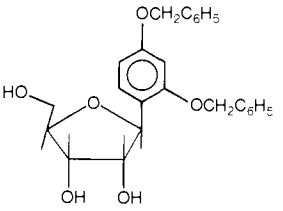
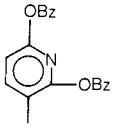
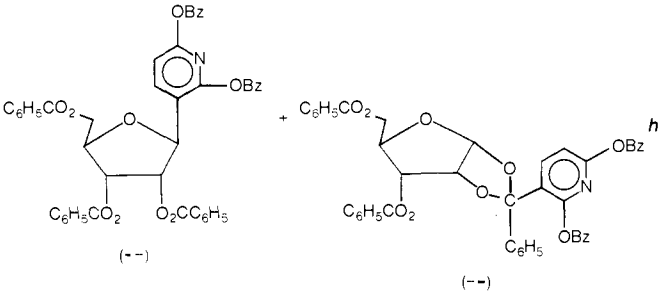
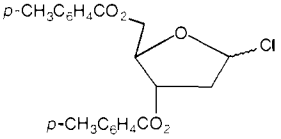
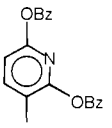
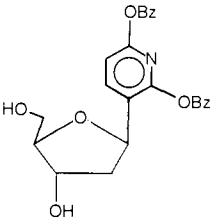
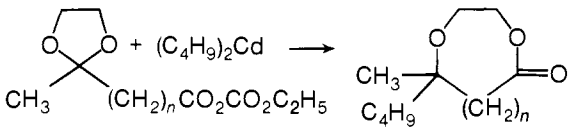
	Reactant	Cd reagent (R =)	product(s) (yield, %)	ref
49.	as above	C_6H_5	 (45)	e
50.		CH_3	 (33)	f
51.		CH_3	as above (57)	f
52.		CH_3	 (33)	f
53.		CH_3	 (40)	f
54.	as above	C_2H_5	 (36)	f
55.	as above	C_6H_5	 (23)	177
56.	as above	n-C_4H_9	 (57)	177
57.	as above	$C_6H_5CH_2$	 (-)	177
58.		C_6H_5	 (29)	177
59.		C_2H_5	 (24, after ester interchange)	f
60.	as above	CH_3	 (39)	f

TABLE V. (Cont)

	Reactant	Cd reagent (R =)	product(s) (yield, %)	ref
61.		C_6H_5	 (25) + (55) (after saponification)	178
62.	as above		 (12) (after saponification)	*g*
63.	as above		 (--) (--)	*h*
64.			 65 (after saponification)	*h*

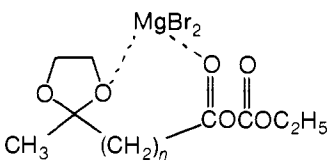
[a] P. R. Jones, C. J. Jarboe, and R. Nadeau, *J. Organomet. Chem.*, **8**, 361 (1967). [b] R. C. Fuson, S. B. Speck, and W. R. Hatchard, *J. Org. Chem.*, **10**, 55 (1945). [c] C. Rüchardt and S. Rochlitz, *Justus Liebigs Ann. Chem.*, 15 (1974). [d] M. Renson and F. Schoofs, *Bull. Soc. Chim. Belg.*, **69**, 236 (1960). [e] M. Renson and J.-C. D'Harcour, *Ibid.*, 71, 245 (1962). [f] R. G. Rees, A. R. Tatchell, and R. D. Wells, *J. Chem. Soc. C*, 1768 (1967). [g] R. A. Sharma, M. Bobek, and A. Bloch, *J. Med. Chem.*, **18**, 473 (1975). [h] M. P. Mertes, J. Zielinski, and C. Pillar, *ibid.*, **10**, 320 (1967).

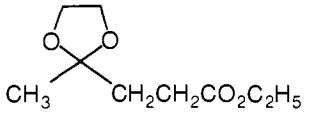
It was proposed by LeMahieu[170] that this interesting formation of eight- and nine-membered lactones depends upon coordination of $MgBr_2$ between the ketal oxygen and the carbonyl group, as depicted below. Support for this explanation is the observation that purified dimethylcadmium results, not in cleavage of the dioxalane ring, but in generation of the ester. This ethyl ester presumably forms as a result of cleavage of solvent ether, for which there is ample precedent,[7] or from ethoxide originating from the mixed anhydride.



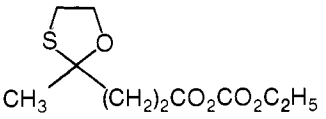
(93)

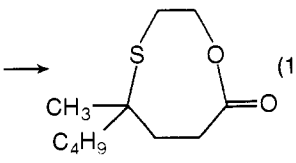
n = 2,3



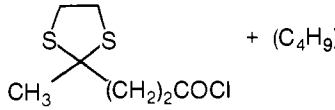


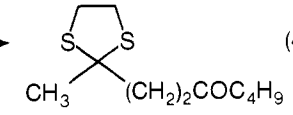
There is some indication that displacement at the ketal carbon, whatever the mechanism, is more facile when oxygen rather than sulfur is the leaving group. This is based on the following examples from LeMahieu's work.[170]





(14%) (94)





(47%) (95)

tert-Butyl 1-chloroethyl peroxide reacted with dimethylcadmium to afford the displacement product, *tert*-butyl isopropyl peroxide, in 50% yield.

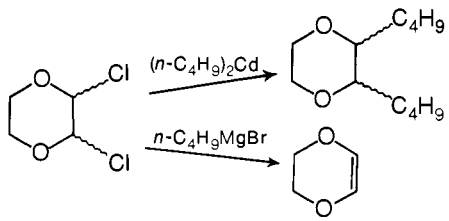
$$t\text{-}C_4H_9OOCH(Cl)CH_3 + (CH_3)_2Cd \rightarrow t\text{-}C_4H_9OOCH(CH_3)_2 \quad (96)$$

With lithium reagents the halo peroxide tended to undergo α-elimination instead.[172]

It was reported in 1963 that polychlorinated aliphatic aldehydes and ketones (of unspecified structure) for the most part undergo addition at the carbonyl, rather than displacement of halogen, with in situ cadmium reagents.[78] Chloral, for example, was reported to afford the secondary alcohol in 45–70% yield. In the cases of monochlorinated carbonyls, it was mentioned that addition did not take place, but there was no indication of other products.

$$Cl_3CCHO + R_2Cd \rightarrow Cl_3CCH(OH)R \quad (97)$$

2,3-Dichloro-1,4-dioxane undergoes displacement of halogen rather than oxygen with the butylcadmium reagent.[173] The product, 2,3-diphenyl-1,4-dioxane, isolated in 44%, was also formed from the corresponding zinc reagent. By contrast, butylmagnesium bromide caused dehalogenation to dioxene.



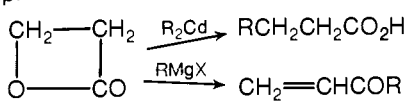
(98)

In an analogous manner, chloromethyl methyl ether formed benzyl methyl ether (34%) with the phenylcadmium reagent.[164]

$$CH_3OCH_2Cl + (C_6H_5)_2Cd \rightarrow CH_3OCH_2C_6H_5 \quad (99)$$

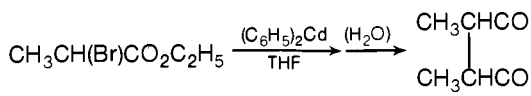
In general, esters and lactones are not attacked by addition under conditions where cadmium reagents cause displacement at saturated carbon. All the known instances of this preferential displacement over addition are assembled in Table V. Although the number of examples is limited, certain generalizations about the scope of displacement seem to hold. The site of displacement is either allylic, benzylic, or alpha to a carbonyl (ester, lactone, ketone) group. It apparently may be primary or secondary but not tertiary. The ease of displacement of leaving groups follows the order Br, Cl > OCOR > OR. In those instances where an acyloxy group can be displaced with or without ring opening, the latter prevails; thus, the "exocyclic" acyloxy group is preferentially displaced (see entries 23, 24, 30). Even the ketone function in phenacyl bromide (entry 12) survives to some extent while the bromide is displaced.[174]

Propiolactone is reactive with some organocadmium reagents, probably because of the strain relieved when the ring opens. It is of interest that ring opening proceeds by attack at the *saturated* carbon (displacement), not by addition at the carbonyl. Most Grignard reagents (except benzylic and allylic) attack the carbonyl group.[123]



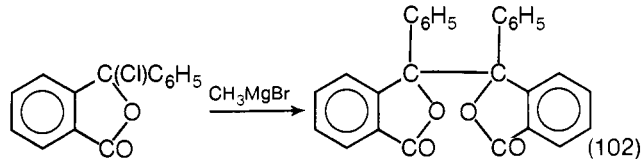
(100)

It has been noted in some instances that symmetrical coupling accompanies displacement in multifunctional compounds. For example, 2,3-dimethylsuccinic acid was isolated after hydrolytic workup from the reaction mixture from ethyl α-bromopropionate



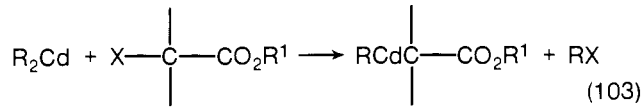
(101)

and phenylcadmium reagent in THF.[174] Similar coupling products were detected from α-bromoisobutyrate and α-bromoisovalerate esters.[164] There is some indication that symmetrical coupling is less prevalent with cadmium reagents than it is with Grignard reagents. Thus, whereas 3-chloro-3-phenylphthalide (the ring tautomer of *o*-benzoylbenzoyl chloride) afforded some of the coupling product, 3-3′-diphenylbiphthalidyl with methylmagnesium bromide, none was found when the reagent was in situ dimethylcadmium.[175]



(102)

An alternative course of the reaction with α-halo esters and cadmium reagents is dehalogenative enolization.



(103)

Cason and Fessenden reported formation of the β-keto ester product from ethyl α-bromoisobutyrate in the presence of *n*-butylcadmium or *n*-dodecylcadmium reagent.[158] It seems most plausible that the β-keto ester is a Claisen condensation product from the enolate.

$$BrC(CH_3)_2CO_2C_2H_5 + R_2Cd \rightarrow (CH_3)_2CHCOC(CH_3)_2CO_2C_2H_5 \quad (104)$$

The enolate, resembling the classical Reformatsky reagent, is probably the intermediate in the condensation between α-bromo esters and ketones, induced by cadmium reagents.

$$CH_3CO\text{-}n\text{-}C_6H_{13} + BrCH(CH_3)CO_2C_2H_5 + (n\text{-}C_3H_7)_2Cd \rightarrow \underset{n\text{-}C_6H_{13}}{\overset{CH_3}{\diagdown\!\diagup}}C(OH)CH(CH_3)CO_2C_2H_5 \quad \text{(ref 158)} \quad (105)$$

(74%)

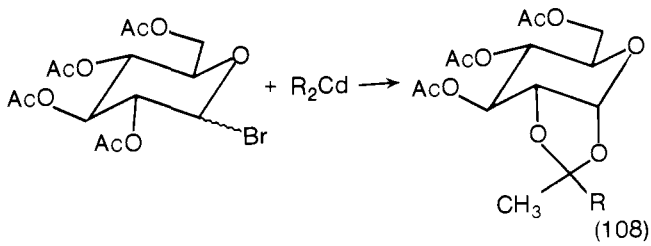
$$CH_3COC_6H_5 + BrCH_2CO_2(\text{menthyl}) + (n\text{-}C_3H_7)_2Cd \xrightarrow{H_2O} \underset{C_6H_5}{\overset{CH_3}{\diagdown\!\diagup}}C(OH)CH_2CO_2H \quad \text{(ref 176)} \quad (106)$$

(68%)

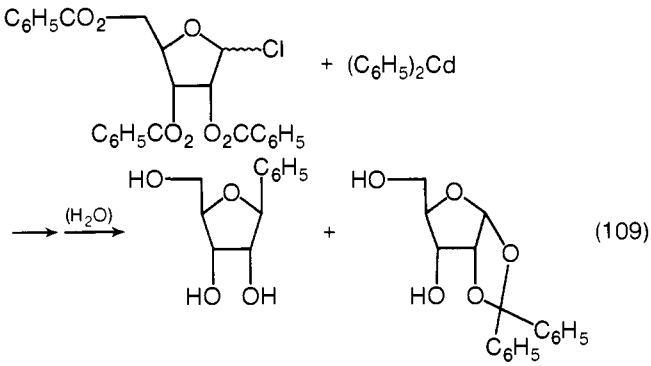
Similar Claisen products were not found in cases where the phenylcadmium reagent was employed with simple α-halo esters,[164,174] but the dehalogenative enolization with bromomalonic ester was extensive[174] and bromobenzene was shown to be produced in equimolar amount.[174] Presumably the cadmium enolate $C_6H_5CdCH(CO_2C_2H_5)_2$ is generated, along with bromobenzene, before the hydrolytic step.

$$BrCH(CO_2C_2H_5)_2 + (C_6H_5)_2Cd \xrightarrow{H_2O} CH_2(CO_2C_2H_5)_2 + C_6H_5Br \quad (107)$$

An interesting side reaction in displacements in the hexose and pentose series is one involving neighboring group participation (entries 50–63). The first recorded example was the formation of bicyclic ketals from an acetate-protected glucopyranosyl bromide[177] (entries 55 and 56). Although Hurd and Holysz observed that neighboring group participation occurred with butyl- and benzylcadmium reagents and not the phenyl re-


(108)

agent,[177] it has subsequently been shown that similar products can be formed in the ribose series with the phenyl reagent as well. An example is the behavior of the benzoyl-protected ribofuranosyl chloride[178] (entry 61).


(109)

D. Mechanism

Very little information is available which can be used in support of one or more mechanisms for displacement at saturated carbon. The order of ease of leaving group displacement—Cl, Br > OCOR > OR—is in line with a nucleophilic process. On the other hand, there is evidence from ESR spectroscopy for the formation of free radicals in two instances.[160,164]

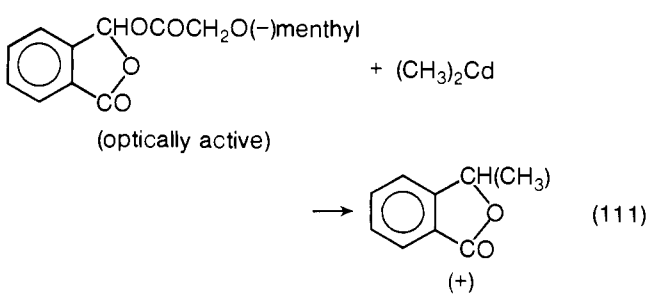
Both stereoselective and nonstereoselective displacements have been recorded. Optically active α-bromopropionate esters react with phenyl[164] and α-naphthyl[179] cadmium reagents to afford racemic α-arylpropionate esters.

$$\underset{\text{(optically active)}}{CH_3CH(Br)CO_2R} + Ar_2Cd \rightarrow \underset{\text{(racemic)}}{CH_3CH(Ar)CO_2R} \quad (110)$$

$$Ar = C_6H_5,\ \alpha\text{-}C_{10}H_7$$

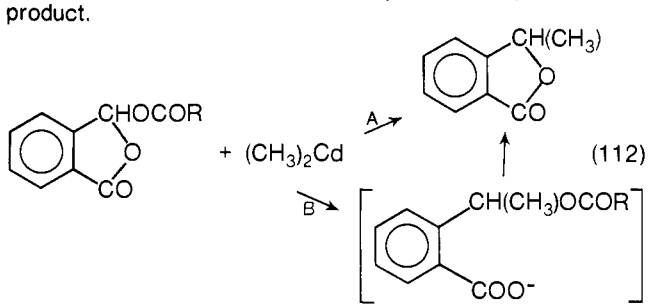
It was shown that both the starting ester[164,179] and product[179] were optically stable under the reaction conditions. Consistent with this finding is the fact that the reaction with phenylcadmium reagent generates free radicals, so an electron-transfer process[164] is a plausible pathway for this conversion.

In a different series, it was found that 3-[(−)-menthoxyacetoxy]phthalide underwent displacement with the methylcadmium reagent with formation of (+)-3-methylphthalide.[180]

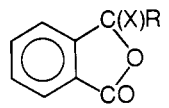

(111)

Although the absolute configuration of the 3-methylphthalide is known to be *R*,[181] it is not known whether the displacement proceeded with net retention or inversion, inasmuch as the configuration and optical purity of the starting material could not be determined.

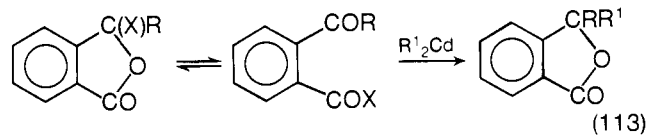
The formation of 3-methylphthalide could occur "directly", as represented in path A (eq 112), or "indirectly" by sequential displacement of endocyclic and exocyclic acyloxy groups, as represented in path B. In either case, the steps must be concerted to account for retention of optical activity in the final product.


(112)

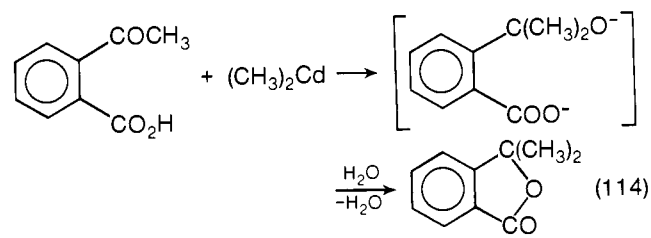
Other phthalide compounds with a potential leaving group "X" in the 3 position:



may be attacked by cadmium reagents in a similar fashion, in which case the displacements would be stereoselective. The possibility that the 3-substituted phthalide reverts to the chain tautomer, which is then attacked by cadmium reagent, is ruled out in cases where the product retains optical activity.


(113)

One exception to this is the case of *o*-acylbenzoic acids (X = OH), which probably react by addition to the ketone in the chain tautomeric form.[128,182] An example is formation of 3,3-dimethylphthalide from *o*-acetylbenzoic acid on prolonged treatment. A displacement pathway would require that the leaving group be "O^{2-}".


(114)

VII. Rearrangements

Rearrangement in the alkyl or aryl moiety of the cadmium reagent seems to be an area which has received little attention.

A. Allylic Compounds

Of the few rearrangements which have been reported, most have been observed in allylic structures. From recent reviews of allylic organometallics,[124,183-185] it is evident that rearrangements are known to occur more widely in allylic compounds of lithium, sodium, magnesium, and even zinc, than in those containing cadmium.

The products from "crotyl" cadmium reagent (prepared from crotyl bromide, ["$(CH_3CH{=}CHCH_2)Cd$"] with aldehydes and ketones have been assigned the 2-butenyl structures. These assignments appear to be based only on infrared and not NMR

spectral analysis. As an example, the in situ crotylcadmium reagent is reported to afford 2,2,4-trimethyl-5-hexen-3-ol with pivalaldehyde.[103,120] Other carbonyl compounds which give the "rearranged" alcohols are methyl ethyl ketone, diethyl ketone, butyraldehyde, and benzaldehyde.

$$(CH_3CH{=}CHCH_2)_2Cd(Br,Br) + (CH_3)_3CCHO \longrightarrow (CH_3)_3CCH(OH)CH(CH_3)CH{=}CH_2 \quad (115)$$

The crotylzinc reagent, halide-free, prepared from the boron compound, is reported[102,105] to decompose with deposition of metallic cadmium under comparable reaction conditions. Subjected to air oxidation, it affords a mixture of *Z* and *E* crotyl alcohols, but-1-en-3-ol, and C_8 coupling products.[186] The halide-free allylic cadmium reagents prepared from boron compounds are carbonated quantitatively; the crotyl compound affords unrearranged 3-pentenoic acid.[148]

$$(CH_3CH{=}CHCH_2)_2Cd \xrightarrow{CO_2} CH_3CH{=}CHCH_2CO_2H \quad (116)$$

By contrast, in situ crotylcadmium reagent is hydrolyzed with water to a mixture of alkenes, the composition of which depends slightly on the solvent.[187]

$$(CH_3CH{=}CHCH_2)_2Cd(Br,Cl) \xrightarrow{H_2O} \underset{(66\text{–}77\%)}{CH_3CH_2CH{=}CH_2} + \underset{(10\text{–}17\%)}{trans\text{-}CH_3CH{=}CHCH_3} + \underset{(13\text{–}20\%)}{cis\text{-}CH_3CH{=}CHCH_3} \quad (117)$$

Propargyl bromide and metallic cadmium in THF–HMPT give rise to a solution whose infrared spectrum exhibits a significant band at 1903 cm^{-1}, which was interpreted by Moreau and

$$HC{\equiv}CCH_2Br + Cd \xrightarrow{THF\text{-}HMPT} [H_2C{=}C{=}CHCdBr] \xrightarrow{(C_2H_5)_2CO} \underset{(\sim 11\%\ yield)}{(C_2H_5)_2C(OH)CH{=}C{=}CH_2} \quad (118)$$

Gaudemar as evidence for the allenic structure. In accord with this explanation, the solution reacts with diethyl ketone to afford a mixture of alcohols (15% yield), of which 75% is the allenic alcohol.[95]

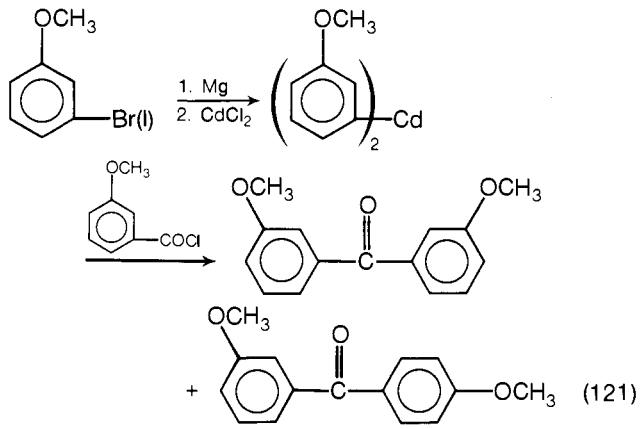
Although benzylcadmium reagents have received only cursory attention, they appear to give unrearranged (benzyl) products, in contrast to the benzyl Grignard reagents. As early as 1939, Gilman and Nelson reported formation in low yield of "normal" products from in situ benzylcadmium with formaldehyde and acetyl chloride.[188] The addition to benzil likewise proceeds without rearrangement.[112]

$$(C_6H_5CH_2)_2Cd(Cl,Cl) \xrightarrow{H_2CO} C_6H_5CH_2CH_2OH\ (8\%) \qquad (C_6H_5CH_2)_2Cd(Cl,Cl) \xrightarrow{CH_3COCl} C_6H_5CH_2COCH_3\ (18\%) \quad (119)$$

$$\underset{\text{in situ}}{C_6H_5CH_2CdCl} + (C_6H_5CO)_2 \xrightarrow{N_2} C_6H_5C(=O)C(OH)(CH_2C_6H_5)C_6H_5\ (70\%) \quad (120)$$

B. Aryl Compounds

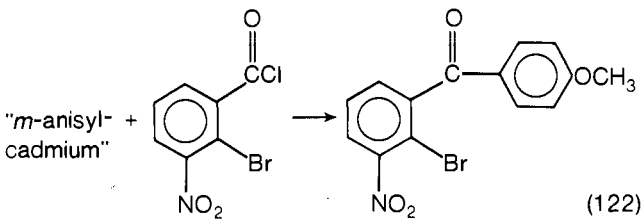
A rearrangement in the aryl moiety of an in situ arylcadmium compound was first reported by Klemm, Mann, and Lind in 1958.[189] They found that the anisylcadmium reagent, prepared from *m*-bromo- or *m*-iodoanisole, reacted with *m*-methoxybenzoyl chloride to afford, in low yield, a mixture of 3,3′-dimethoxybenzophenone (the "normal" product) and the 3,4′ isomer.



(121)

Dauben and Collette[190] observed the same peculiar behavior of the "*m*-anisyl" cadmium reagent. Rearranged, *p*-anisyl products were identified in reactions with 1-cyclohexenecarbonyl chloride, acetyl chloride, β-carbomethoxypropionyl chloride, and acetic anhydride, but only "normal" products could be found in reactions with succinic anhydride and biacetyl. The fact that both normal and rearranged products result from the *m*-anisylcadmium reagent suggests that rearrangement must be taking place during combination of the reagent with the carbonyl compound—not during formation of the Grignard or cadmium reagent. In fact, the *m*-anisyl Grignard reagent gives normal products.[189]

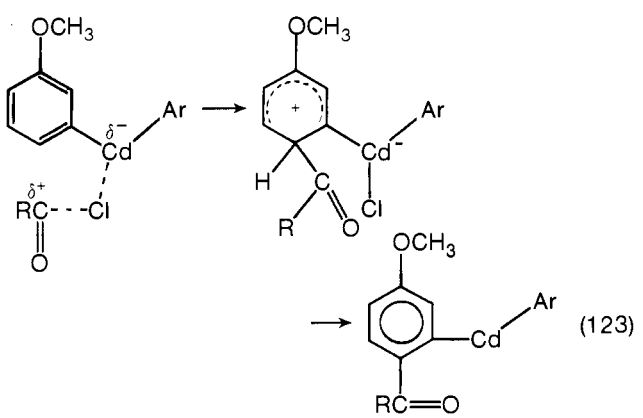
A third research group observed rearrangement accompanying the condensation of *m*-anisylcadmium reagent with an acid chloride (2-bromo-3-nitrobenzoyl chloride) but not with 3-ni-



(122)

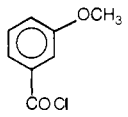
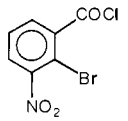
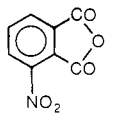
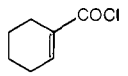
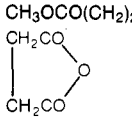
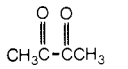
trophthalic anhydride.[191] The reactions of *m*-anisylcadmium reagent are summarized in Table VI.

Clearly, the coreactant with the cadmium reagent plays a role in this curious rearrangement. Klemm, Mann, and Lind[189] and Dauben and Collette[190] both suggested a mechanism in which the acylating agent (acid chloride or anhydride) is attacking the position para to the methoxyl, in a Friedel–Crafts-like reaction, the cadmium function serving as a Lewis acid:



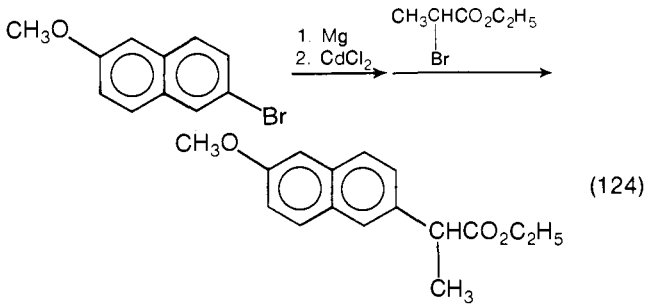
(123)

TABLE VI. Reactions of *m*-Anisylcadmium Reagent

Coreactant	Products[a]	Ref
	n, r	189
	r	191
	n	191
	r	190
CH_3COCl	n, r	190
$(CH_3CO)_2O$	n, r	190
$CH_3OCO(CH_2)_2COCl$	r	190
	n	190
	n	190

[a] n = normal; r = rearranged.

This would be consistent with the observation that *o*- and *p*-anisylcadmium reagents show no tendency for rearrangement. Apparently the *m*-anisyl moiety is the only one to date which gives rise to rearrangement.[192] Even the cadmium reagent from 6-methoxy-2-bromonaphthalene gives the normal product with ethyl 2-bromopropanoate.[193] This reaction, however, may be free-radical,[164] and the same mechanistic interpretation would not apply.



(124)

VIII. Redistributions

The term redistribution[194] connotes here the exchange of metals or alkyl or aryl substituents between two organometallics. For redistributions involving cadmium reagents, the use of NMR spectroscopy has been most effective, for preexchange lifetimes can be estimated from the splitting of protons[195] or ^{13}C[67] with the ^{111}Cd and ^{113}Cd nuclei.[196] The recent development of instrumentation for ^{113}Cd Fourier transform NMR spectroscopy[197,198] has provided a promising alternative spectroscopic method for studying redistributions of cadmium compounds.

A. Homoexchange

The fact that the ^1H NMR spectrum of neat dimethylcadmium consists of five lines in ether or hydrocarbon solvents at ambient temperatures demonstrates that homoexchange is slow under these conditions.[196,199,200] The coalescence temperature is about 100 °C, corresponding to an energy of activation of 15.7 kcal/mol for the exchange.[201] Introduction of more polar solvents, THF, pyridine, triethylamine, methanol, etc., greatly increases the rate of exchange.[22,196,199-202]

The proton-decoupled ^{113}Cd FT NMR spectrum of an equimolar mixture of dimethyl- and diethylcadmium consists of three lines with intensities 1:2:1, the center line being intermediate in position between those of dimethylcadmium and diethylcadmium.[197] This has been explained as being the result of a statistical redistribution to $CH_3Cd(C_2H_5)$ under the conditions of the experiment (temperature not designated). The fact that the proton-coupled spectrum is highly resolvable is consistent with a "slow" exchange, approximated to be $4.5 \times 10^2\ s^{-1}$ as an upper limit. The ^{113}Cd chemical shift in dimethylcadmium is displaced by solvents both upfield (polar, aprotic solvents) and downfield (hydrocarbons, methylene chloride). This suggests the importance of coordination of cadmium reagents with solvents, which would be expected to facilitate exchange.

In an ^1H NMR study of the exchange between dimethyl- and divinylcadmium,[38] indirect evidence was advanced for the formation of methylvinylcadmium, and it was concluded that vinyl exchange was much faster than methyl exchange.

The homoexchange of dimethylcadmium in benzene or toluene is catalyzed by alcohols or phenols, which decompose the cadmium reagent to a mixed alkoxide.[203] The process with methanol requires at least several minutes at ambient temperature.

$$(CH_3)_2Cd + CH_3OH \rightarrow CH_3CdOCH_3 + CH_4 \qquad (125)$$

The mode of catalysis appears not to be a rapid exchange between the dimethylcadmium and methylcadmium methoxide, for distinct resonance lines for the two are observed in the ^1H NMR spectrum below 80 °C. The catalytic effect of added OH-containing agents was deduced by observing the temperature at which the resonance lines collapsed.[22] From these results the catalytic effect was ordered as follows: $C_6H_5OH > C_2H_5OH > CH_3OH > (CH_3)_2CHOH$.

Exchange between dimethylcadmium and cadmium bromide in THF is even faster than the self-exchange of dimethylcadmium in the same solvent.[201] Evidence for the Schlenk-type equilibrium came from the ^1H NMR spectrum at −110 °C.

$$(CH_3)_2Cd + CdBr_2 \rightleftarrows 2CH_3CdBr \qquad (126)$$

Although it might be expected that a similar exchange in ether would be somewhat slower, this same disproportionation reaction has been the basis for the preparation of "RCdX" reagents.[53,70,204]

B. Heteroexchange

Some generalizations about the redistributions of organocadmium reagents with other organometallics—heteroexchange—seem well grounded. Exchange with "active" organometallics (Li, Mg, Al, B) is rapid; that with organozinc and organomercury compounds is relatively slow.[205]

Several cases of redistributions with organolithium compounds have been examined. A "fast" exchange between ethyllithium and diethylcadmium in benzene was observed,[206] in contrast to the "very slow" exchange between ethyllithium and diethylmercury. An ate complex $(C_2H_5)_3LiCd$ was observed from the former pair when traces of ether or THF were introduced. The following rapid redistribution between methyllithium and dimethylcadmium in THF and ether has been proposed to accommodate the ^1H and ^7Li NMR results.[207]

$$CH_3Li + (CH_3)_2Cd \rightleftharpoons (CH_3Li)_2(CH_3)_2Cd + (CH_3Li)_3(CH_3)_2Cd \qquad (127)$$

It is to be noted that the exchange was faster in ether than in THF, an observation in contrast to the homoexchange of dimethylcadmium. Lithium and methyl exchange were comparable in rates, and the ease of exchange of methyllithium with other or-

ganometallics was found to be: $Me_2Cd > Me_2Zn > Me_2Mg$. The preexchange lifetime for a 1:1 mixture of dimethylmagnesium and dimethylcadmium in THF, for example, was estimated to be less than 0.007 s at 28 °C.[200] Apparently a rapid exchange occurs between "C_2H_5CdI" (a solid from diethylcadmium and cadmium iodide) and *n*-propylmagnesium bromide, for the mixture became a clear solution, which, after distillation afforded the unsymmetrical dialkylcadmium.[208]

$$C_2H_5CdI + n\text{-}C_3H_7MgBr \rightarrow C_2H_5Cd\text{-}n\text{-}C_3H_7 \quad (128)$$

The preexchange lifetime of methyl groups in the trimethylaluminum–dimethylcadmium system at room temperature is estimated to be 0.09 s in benzene,[209] whereas that in the dimethylzinc–dimethylcadmium pair at 25 °C is 0.19 s in the same solvent.[210] Thiele's synthesis of diallylcadmium depends on the rapid exchange between dimethylcadmium and triallylboron.[26] The rates of redistributions in methylene chloride between dimethylcadmium and the methyl derivatives of group 3A metals gallium and indium are both faster than that between dimethylcadmium and dimethylzinc, in cyclohexane the rate for $(CH_3)_3Ga$ being somewhat faster than that for $(CH_3)_3In$.[211]

Both ^1H and ^{19}F NMR spectroscopy have been used to examine the exchange in pyridine or diglyme between dimethylcadmium and perfluorodimethylmercury.[212]

$$(CH_3)_2Cd + (CF_3)_2Hg \rightarrow CH_3CdCF_3 + (CF_3)_2Cd + CH_3HgCF_3 + (CH_3)_2Hg \quad (129)$$

Equilibrium was established "rather quickly" at 34 °C. By noting the change in composition of the four products with varying amounts of initial cadmium and mercury compounds, it was concluded that CH_3CdCF_3 exchanges more slowly than dimethylcadmium. The rapid exchange with the perfluorinated mercury compound is exceptional, mercury compounds generally being slow. At the other extreme is divinylmercury, which was exchanged with dimethylcadmium at 60 °C in a sealed tube for 5 days.[38]

IX. Miscellaneous Reactions

A. Reactions with Oxygen and Peroxides

Although the reactions of organometallics with oxygen and peroxides have been reviewed in recent years,[213-215] only brief sections covering cadmium compounds were included.

It has been claimed that diethylcadmium forms a "bisperoxide" $(C_2H_5)_2Cd\cdot 2O_2$ reversibly in heptane,[216] the evidence for the adduct being an intense ultraviolet band at 276 nm and an infrared band at 790 cm^{-1}. The experiments were carried out in a vacuum line. In ether solution dimethylcadmium forms the monoperoxy cadmium compound, whereas diethylcadmium and di-*n*-butylcadmium are converted to diperoxy derivatives.[134,217] The fact that peroxide formation was inhibited by galvinoxyl sug-

$$R_2Cd + O_2 \rightarrow \underset{(R = CH_3)}{ROOCdR} + \underset{(R = C_2H_5,\ n\text{-}C_4H_9)}{(ROO)_2Cd} \quad (130)$$

gested that the reaction could be formulated as a free-radical chain mechanism not involving a long-lived oxygen complex.[218] Hydroperoxides have been synthesized by controlled oxidation of organocadmium reagents with oxygen and hydrolysis of the resulting peroxide.[219,220] The reaction, illustrated with *n*-butylcadmium chloride[219]

$$n\text{-}C_4H_9CdCl + O_2 \longrightarrow [n\text{-}C_4H_9OOCdCl] \xrightarrow{H^+} n\text{-}C_4H_9OOH\ (94\%) \quad (131)$$

was also carried out with dibutylcadmium (95%), octylcadmium chloride (90%), and benzylcadmium chloride (86%). It was noted that the yield (42%) of cyclohexyl peroxide from the cadmium reagent was higher than that achieved directly from the Grignard reagent.[220] The corresponding hydroperoxides from menthyl- and bornylcadmium reagents were prepared in 28 and 39% yield, respectively.[220] Under conditions apparently less carefully controlled, air oxidation of aliphatic cadmium reagents leads to alcohols, probably by a sequence of oxidation and disproportionation.

$$n\text{-}C_4H_9CdBr\ (\text{solid}) \xrightarrow{O_2} \underset{60\%}{n\text{-}C_4H_9OH}\ (\text{ref } 221) \quad (132)$$

$$\text{"crotyl cadmium reagent"} \xrightarrow{O_2} \underset{(E \text{ and } Z)}{CH_3CH{=}CHCH_2OH}\ (\text{ref } 186) + CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH{=}CH_2 + C_8H_{14} \quad (133)$$

There seems to be very little information about the behavior of arylcadmium reagents toward oxygen. Diphenylcadmium in benzene gave some phenol but mainly biphenyl, which was shown from labeling studies to come from radical attack on benzene.[222] Oxidation of diphenylcadmium in chloroform or carbon tetrachloride gave, in addition to the above products, some benzoic acid (after hydrolysis), presumably from benzotrichloride.

$$(C_6H_5)_2Cd + O_2 \xrightarrow{C_6H_6} (C_6H_5)_2 + C_6H_5OH \quad (134)$$

$$(C_6H_5)_2Cd + O_2 \xrightarrow[\text{or } CCl_4]{CHCl_3} (C_6H_5)_2 + C_6H_5OH + C_6H_5CO_2H \quad (135)$$

Although few examples have been reported, it would appear that sulfur inserts itself between carbon and cadmium in an analogous way. The products may be salts,[223] mercaptans, or disulfides.[221]

An alternative route to peroxy cadmium compounds is the reaction of purified alkylcadmium reagents with hydroperoxides, which might be visualized as a nucleophilic displacement by the cadmium reagent on hydrogen.[217]

$$R_2Cd + R'OOH \rightarrow RH + RCdOOR' \quad (136a)$$

$$RCdOOR' + R'OOH \rightarrow RH + (R'O)_2Cd \quad (136b)$$

Either 1 or 2 equiv of hydrocarbon from the cadmium reagent is generated, the methyl reagent being less reactive than the ethyl or *n*-butyl reagents.[134,217]

Diphenylcadmium reacts with *tert*-butyl hydroperoxide to form the cadmium peroxide and alkoxide, the latter being a secondary product from the former.[224]

Presumably benzene was formed as well. With dibenzoyl peroxide the diphenyl reagent affords phenyl benzoate, phenylcadmium benzoate, and cadmium dibenzoate.[224]

$$(C_6H_5)_2Cd + (CH_3)_3COOH \rightarrow [(CH_3)_3COO]_2Cd + [(CH_3)_3CO]_2Cd \quad (137)$$

$$(C_6H_5)_2Cd + (C_6H_5COO)_2 \rightarrow C_6H_5CO_2C_6H_5 + C_6H_5CdOCOC_6H_5 + Cd(OCOC_6H_5)_2 \quad (138)$$

Dimethylcadmium and *tert*-butylperoxy radicals, generated thermally from di-*tert*-butyl hyponitrite, react to form methyl radicals, which are detected by ESR spectroscopy.[225]

The reaction of alkylcadmium reagents with hydrogen peroxide has been described, but the products were incompletely characterized.[134]

B. Thermal Reactions

Diethylcadmium decomposes at 250–290 °C to deposit

metallic cadmium metal in 99.5% purity.[226] Under considerably milder conditions other cadmium reagents have been reported to decompose. Diphenylcadmium, for example, deposited metallic cadmium in refluxing ether;[227] (*S*)-di(2-methyl-1-butyl)-cadmium is said to decompose at room temperature with separation of cadmium, although it could be distilled at 55–60 °C (0.04 Torr).[228] It is of interest that this reagent is optically stable when heated at 103 °C for 3 h; racemization occurred only to the extent of 1.5%.[228] Thus, whatever the mode of decomposition may be, it does not involve β-elimination followed by readdition.

$$[CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2]_2Cd \longrightarrow [CH_3CH_2C(CH_3){=}CH_2] \not\longrightarrow [CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2]_2Cd \quad (139)$$

(*S*) (*R*,*S*)

Thermal decomposition of diphenylcadmium in ^{14}C-labeled benzene at 215–220 °C for about 80 h afforded, after removal of solvent and hydrolysis, benzene (50%) and biphenyl (50%), each containing a small amount of radioactive label.[229]

The products from thermal decomposition of dimethylcadmium vapor at 260 °C are cadmium metal, methane, ethane, ethylene, and a solid polymethylene.[230]

$$(CH_3)_2Cd \rightarrow Cd^0 + CH_4 + C_2H_6 + C_2H_4 + (CH_2)_x \quad (140)$$

The activation energy for rupture of the first C–Cd bond in the homogeneous reaction is 43 kcal and for rupture of the second C–Cd bond is 21 kcal. Evidence points to the initial generation of methyl radicals.[231,232]

$$(CH_3)_2Cd \xrightarrow{\Delta} Cd^0 + 2CH_3 \quad (141)$$

Rates of pyrolysis of dimethylcadmium have been measured in a flow system with benzene and toluene as carriers.[233,234]

C. Photolysis

Photolysis of purified dimethylcadmium results in formation of cadmium metal.[235,236] The metal film is deposited only where the ultraviolet radiation is incident on the walls of the system.[235] It has been concluded that asymmetric dissociation of the molecule, involving breaking of a C–Cd bond, is the preferred mode.[236–238] In one photolysis study of dimethylcadmium, ionization thresholds were measured for the principal ions by ultraviolet and mass spectroscopy.[239] From the heats of formation so determined, the bond dissociation energy for dimethylcadmium was calculated to be 69 kcal/mol.

The photolysis of diphenylcadmium in dioxane affords benzene, biphenyl, and "a little" dimeric coupling product from the solvent. In ^{14}C-labeled benzene, the photolysis of diphenylcadmium leads to unlabeled benzene (after removal of solvent and hydrolysis) and biphenyl with some radioactive label.[229]

D. Electrolysis

Alkyl-, cycloalkyl-, and arylcadmium reagents (presumably in situ), when subjected to electrolysis, lead to coupling products. Magnesium, lithium, and zinc compounds behave similarly in this transformation, presumed to be the result of dimerization of radicals generated by oxidation at the anode.[240,241]

$$R_2Cd \xrightarrow{\text{electrolysis}} R_2 \quad (142)$$

As a preparative method there is no advantage in electrolyzing cadmium reagents over the more readily available magnesium and lithium reagents, with the exception of a few long-chain alkanes. Dotriacontane and hexatriacontane, for example, are produced in higher yield by coupling of the hexadecyl and octadecylcadmium reagents, respectively, than from other organometallics.[241] Several terpene derivatives were coupled, including farnesyl halide, which afforded squalene, albeit in only 25% yield. The geranyl and menthyl reagents of magnesium and lithium coupled more efficiently than those of cadmium.

In the case of aryl coupling, the question arises as to what extent dimerization occurs during generation of the organometallics, for biaryls are inevitably produced at this stage.

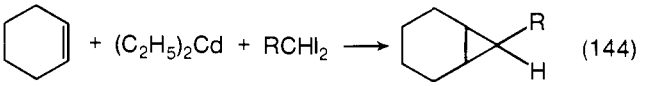
E. Generation of Carbenes from *gem*-Dihalides

The interaction of diethylcadmium (and zinc) with carbon tetrachloride and chloroform leads to dichlorocarbene formation, the evidence for the divalent intermediate being the trapping product with cyclohexene and 1-chloropropene, presumed to form by an insertion of dichlorocarbene into the carbon–cadmium bond.[162,163] (see eq 86a–e).

The combination of diethylcadmium and *gem*-diiodo alkanes is considered a source of an in situ cadmium carbenoid, similar

$$RCHI_2 + (C_2H_5)_2Cd \longrightarrow [C_2H_5CdCH(R)I] + C_2H_5I \quad (143)$$

to the Simmons–Smith reagent. When the reaction is carried out in the presence of alkenes, cyclopropanes are formed.[242] Thus, for example, norcaranes were formed from cyclohexene.

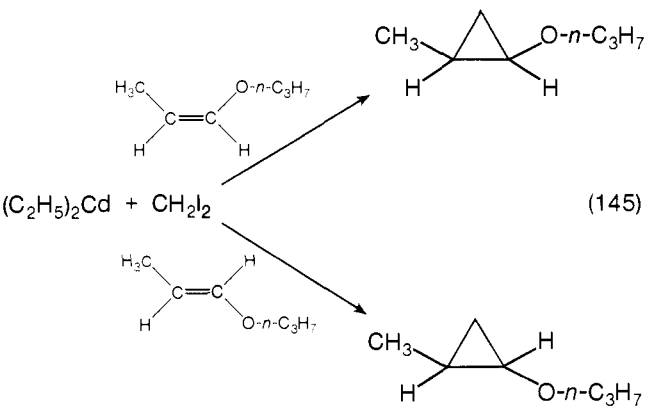


(144)

R = H, CH_3, C_6H_5

The addition of substituted carbenoids to cyclohexene (R = methyl, phenyl) is less stereoselective in favor of the syn isomer than is the corresponding zinc carbenoid; in fact, the anti isomer predominates slightly in the product from 1,1-diodoethane (R = CH_3).

Configuration in the alkene is maintained, as is illustrated in eq 145 with the two enol ethers of propanal.



(145)

Reaction of mono-arylacetylenes with the carbenoid reagents led either to allene or a mixture of allene and homologous, internal acetylene (eq 146). By contrast, metalation (with evolution of ethane) was the predominant course of the reaction when diethylzinc was substituted for diethylcadmium.[242]

$$ArC{\equiv}CH + RCHI_2 + (C_2H_5)_2Cd \rightarrow ArCH{=}C{=}CHR + ArC{\equiv}CCH_2R \quad (146)$$

Ar = C_6H_5, *p*-$CH_3C_6H_4$, *p*-BrC_6H_4; R = H, CH_3

F. Reactions with Sulfur-Containing Functional Groups

1. Sulfonyl Chlorides

Gilman and Nelson first noted that the in situ phenylcadmium reagent (from bromide-free Ar_2Mg) and benzenesulfonyl chloride

led to formation of diphenyl sulfone (15%), benzenesulfinic acid, and chlorobenzene (15%).[6] This reaction was apparently not investigated further until 1957, when Henze and Artman explored its utility as a synthetic route to sulfones.[243] The yields of diaryl sulfones from a variety of arenesulfonyl chlorides generally ranged from 30 to 46%, although in one case (*p*-chlorophenyl cadmium reagent and benzenesulfonyl chloride) it was as high as 61%. Arenesulfinic acid was a by-product in almost all instances. The reaction failed to give any ethyl phenyl sulfone from diethylcadmium (in situ) and benzenesulfonyl chloride, ethyl chloride being isolated as the product instead.

$$Ar_2Cd + Ar'SO_2Cl \rightarrow ArSO_2Ar' + Ar'SO_2H \quad (147)$$

Quite recently these general results have been confirmed;[244-246] that is, sulfones are obtained in moderate to low yield along with arenesulfinic acids from arenesulfonyl chlorides and arylcadmium reagents. The reaction either fails or affords very little (8%) aryl alkyl sulfone if either the cadmium reagent or sulfonyl chloride is aliphatic.

2. Sulfinate Esters

The in situ dimethylcadmium reagent is reported to give sulfoxide in 20% yield with (−)-menthyl *p*-toluenesulfinate;[247] it is thus of no advantage over the Grignard route to sulfoxides.

$$CH_3C_6H_4SO_2(-)\text{-menthyl} + (CH_3)_2Cd \rightarrow CH_3C_6H_4SOCH_3 \quad (148)$$

3. Thioketones

Thiobenzophenone is converted to a variety of products with the ethylcadmium reagent in THF, and about one-half the starting material is recovered.[248] Similar products are formed with the *n*-propylcadmium reagent.

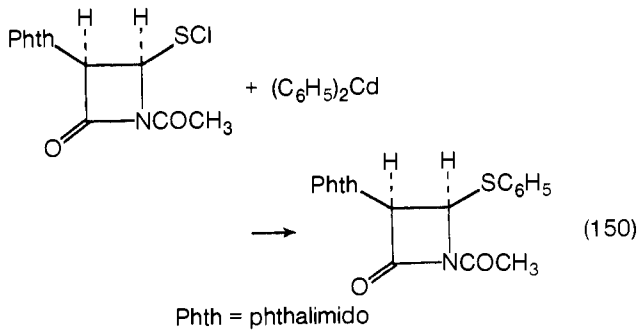
$$(C_6H_5)_2C{=}S + (C_2H_5)_2Cd \rightarrow (C_6H_5)_2CHSC_2H_5 + \underset{\diagup\ \diagdown}{(C_6H_5)_2C\text{—}C(C_6H_5)_2} + (C_6H_5)_2C{=}CHCH_3 + (C_6H_5)_2CH_2 \quad (149)$$

(S)

With diethylcadmium and ether as solvent, the thiirane is formed in 90% yield. The presence of free radicals was confirmed by ESR spectroscopy.

4. Sulfenyl Chlorides

A displacement with diphenylcadmium in THF at a sulfenyl chloride was used to generate a sulfide in a penicillin synthesis. The selectivity for reaction at the sulfenyl chloride over that at any of the imide functions is difficult to assess, however, inasmuch as the yield was only 3%.[249]

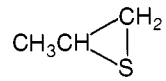


(150)

Phth = phthalimido

G. Polymerizations

Dialkylcadmium reagents have been used as catalysts for vinyl polymerizations.[250] It was shown that in the polymerization of styrene and acrylonitrile, di-*n*-butylcadmium was intermediate in "intrinsic reactivity" between diethylzinc and diethylmercury.[251] Diethylcadmium has been used as one component of the catalyst for polymerization of allyl thioglycidyl ether and 1,2-butylene sulfide.[252] The dimethyl or diethyl reagent catalyzes formation of an optically active polymer from



and an optically active alcohol.[253]

Polymerization of propylene oxide is catalyzed by a diethylcadmium–CH_3COSH combination, which is superior to diethylcadmium combined with alcohol, mercaptan, or carboxylic acid.[254]

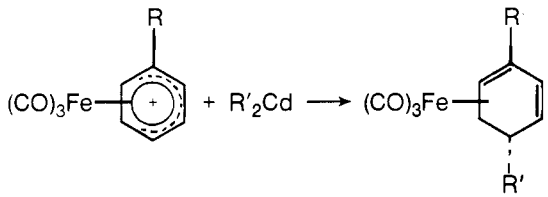
Cadmium alkoxides ($ROCdC_2H_5$), from optically active alcohols and diethylcadmium, have been used in initiating vinyl polymerizations.[255]

H. Other

Decaborane ($B_{10}H_{14}$) is metalated with diethylcadmium in ether to form $CdB_{10}H_{12}{\cdot}2Et_2O$, a compound which presumably contains internally bridged Cd–B bonds.[256]

Chlorine azide forms cadmium azides with dimethylcadmium, diethylcadmium, and ethoxymethylcadmium.[257] Presumably the by-product in each case is alkyl chloride.

Alkylations of tricarbonylcyclohexadienyliron cationic complexes are possible with organocadmium (and zinc) reagents, whereas Grignard and lithium reagents lead to coupling.



(151)

The yields, generally superior with cadmium over zinc reagents, ranged from 40% (R′ = 1-propenyl) to 83% (R′ = allyl, benzyl). The alkylations are both regio- and stereoselective; attack from the side opposite the $Fe(CO)_3$ is consistent with an irreversible nucleophilic reaction.[258]

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X. References

(1) E. Schüler, *Justus Liebigs Ann. Chem.*, **87**, 34 (1853).
(2) F. L. Sonnenschein, *J. Prakt. Chem.*, **67**, 169 (1856).
(3) J. A. Wanklyn, *J. Chem. Soc.*, **9**, 193 (1857).
(4) P. Löhr, *Justus Liebigs Ann. Chem.*, **261**, 48–87 (1891).
(5) E. Krause, *Ber.*, **50**, 1813 (1917).
(6) H. Gilman and J. F. Nelson, *Recl. Trav. Chim. Pays-Bas*, **55**, 518 (1936).
(7) J. Cason, *Chem. Rev.*, **40**, 15 (1947).
(8) D. A. Shirley, *Org. React.*, **8**, 28 (1954).
(9) N. I. Sheverdina and K. A. Kocheshkov, "The Organic Compounds of Zinc and Cadmium", North-Holland Publishing Co., Amsterdam, 1967.
(10) K. Nützel, in Houben-Weyl, "Methoden der Organischen Chemie", 4th ed, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1973, XIII/2a, pp 859-949.
(11) J. Kollonitsch, *Nature (London)*, **188**, 140 (1960).
(12) J. Kollonitsch, *J. Chem. Soc. A*, 453 (1966).
(13) J. Kollonitsch, *J. Chem. Soc. A*, 456 (1966).
(14) J. B. Smart, *Annu. Rep. Inorg. Gen. Synth.*, 288 (1973).
(15) K. C. Bass, *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One*, **4**, 41 (1972).
(16) A. J. Bloodworth, *MTP Int. Rev. Sci.: Inorg. Chem., Ser. Two*, **4**, 271 (1975).
(17) J. D. Smith and D. R. M. Walton, *Adv. Organomet. Chem.*, **13**, 453 (1975).
(18) R. G. Jones and H. Gilman, *Chem. Rev.*, **54**, 835 (1954).
(19) E. Krause and A. von Grosse, "Die Chemie der Metall-organischen Verbindungen", Edwards Brothers, Ann Arbor, Mich., 1943.
(20) J. Cason, *J. Am. Chem. Soc.*, **68**, 2078 (1946).
(21) M. Schmelsser and M. Weidenbruch, *Chem. Ber.*, 100, 2306 (1967).
(22) E. A. Jefferey and T. Mole, *Aust. J. Chem.*, **21**, 1187 (1968).

(23) A. G. Kali-Chemie, British Patent 768,765 (1957); *Chem. Abstr.*, **52**, 421e (1958).
(24) B. Bartocha, C. M. Douglas, and M. Y. Gray, *Z. Naturforsch., Teil B*, **14**, 809 (1959).
(25) O. G. Yashina, T. D. Kaigoradova, T. V. Zara, and L. I. Vereshchagin, *Zh. Org. Khim.*, **4**, 1904 (1968); *Chem. Abstr.*, **70**, 28341f (1969).
(26) K.-H. Thiele and J. Köhler, *J. Organomet. Chem.*, **7**, 365 (1967).
(27) C. Agami and C. Prevost, *C.R. Acad. Sci., Ser. C*, **263**, 304 (1966).
(28) G. Soussan and P. Freon, *Bull. Soc. Chim. Fr.*, 4228 (1972).
(29) G. Soussan and P. Freon, *Bull. Soc. Chim. Fr.*, 4233 (1972).
(30) D. J. Holter and V. I. Stenberg, *Proc. N. Dakota Acad. Sci.*, **17**, 31 (1963); *Chem. Abstr.*, **60**, 5533d (1964).
(31) J. Chenault and F. Tatibouët, *C.R. Acad. Sci., Ser. C*, **262**, 499 (1966).
(32) J. Chenault and F. Tatibouët, *C.R. Acad. Sci., Ser. C*, **264**, 213 (1967).
(33) M. Gaudemar, *C.R. Acad. Sci., Ser. C*, **268**, 1439 (1969).
(34) R. O. Murdock and K. J. Klabunde, *J. Org. Chem.*, **41**, 1076 (1976).
(35) J. J. Habeeb, A. Osman, and D. G. Tuck, *J. Chem. Soc., Chem. Commun.*, 379 (1976).
(36) D. F. Evans and R. F. Phillips, *J. Chem. Soc., Dalton Trans.*, 978 (1973).
(37) D. J. Foster and E. Tobler, U.S. Patent 3,087,947 (1963); *Chem. Abstr.*, **59**, 10119d (1963).
(38) H. D. Visser, L. P. Stodulski, III, and J. P. Oliver, *J. Organomet. Chem.*, **24**, 563 (1970).
(39) G. B. Deacon and J. C. Parrott, *J. Organomet. Chem.*, 22, 287 (1970).
(40) R. Nast and C. Richers, *Z. Anorg. Allgem. Chem.*, **319**, 320 (1963).
(41) O. Y. Okhlobystin and L. I. Zakharkin, *Zh. Obshch. Khim.*, **36**, 1734 (1966); *Chem. Abstr.*, **66**, 65606j (1967).
(42) O. G. Yashina and L. I. Vereshchagin, *Zh. Org. Khim.*, **4**, 2104 (1968); *Chem. Abstr.*, **70**, 67812e (1969).
(43) O. G. Yashina, T. V. Zarva, and L. I. Vereshchagin, *Zh. Org. Khim.*, **3**, 219 (1967); *Chem. Abstr.*, **66**, 94664g (1967).
(44) M. N. Bochkarev, L. P. Maiorova, L. N. Bochkarev, and N. S. Vyazankin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 10, 2353 (1971); *Chem. Abstr.*, **76**, 46262j (1972).
(45) G. A. Razuvaev, V. T. Bychkov, and N. S. Vyazankin, *Dokl. Akad. Nauk. SSSR* 211, 116 (1973); *Chem. Abstr.*, **79**, 105365g (1973).
(46) G. Emptoz, E. Henry-Basch, H. Coudane, and P. Freon, *C.R. Acad. Sci., Ser. C*, **262**, 655 (1966).
(47) A. Jubier, E. Henry-Basch, and P. Freon, *C.R. Acad. Sci., Ser. C*, **267**, 842 (1968).
(48) A. Jubier, G. Emptoz, E. Henry-Basch, and P. Freon, *Bull. Soc. Chim. Fr.*, 2032 (1969).
(49) G. Emptoz and F. Huet, *J. Organomet. Chem.*, **55**, C61 (1973).
(50) K. A. Kocheshkov, N. I. Sheverdina, and I. E. Paleeva, *Bull. Soc. Chim. Fr.*, 1472 (1963).
(51) I. E. Paleeva, N. I. Sheverdina, and K. A. Kocheshkov, *Dokl. Akad. Nauk SSSR*, **157**, 626 (1964); *Chem. Abstr.*, **61**, 9520a (1964).
(52) J. R. Sanders and E. C. Ashby, *J. Organomet. Chem.*, **25**, 277 (1970).
(53) N. I. Sheverdina, I. E. Paleeva, E. D. Delinskaya, and K. A. Kocheshkov, *Dokl. Akad. Nauk SSSR*, **143**, 1123 (1962); *Chem. Abstr.*, **57**, 4690b (1962).
(54) G. A. Razuvaev, V. N. Pankratova, and A. M. Bobrova, *Zh. Obshch. Khim.*, **38**, 1723 (1968); *Chem. Abstr.*, 70, 20189s (1969).
(55) W. Strohmeier, *Chem. Ber.*, **88**, 1218 (1955).
(56) H. S. Gutowsky, *J. Am. Chem. Soc.*, **71**, 3194 (1949).
(57) L. LeGuilly, J. Chenault, and F. Tatibouët, *C.R. Acad. Sci., Ser. C*, **260**, 6634 (1965).
(58) H. Coudane, E. Henry-Basch, J. Michel, B. Marx, F. Huet, and P. Freon, *C.R. Acad. Sci., Ser. C*, **262**, 861 (1966).
(59) K. Cavanagh and D. F. Evans, *J. Chem. Soc. A*, 2890 (1969).
(60) K. S. Rao, B. P. Stoicheff, and R. Turner, *Can. J. Phys.*, **38**, 1516 (1960).
(61) T. Shimanouchi, *J. Phys. Chem. Ref. Data*, **3**, 269 (1974); *Chem. Abstr.*, **81**, 97200y (1974).
(62) H. D. Kaesz and F. G. A. Stone, *Spectrochim. Acta*, 360 (1959).
(63) A. M. W. Bakke, *J. Mol. Spectrosc.*, **41**, 1 (1972).
(64) C. R. McCoy and A. L. Allred, *J. Inorg. Nucl. Chem.*, **25**, 1219 (1963).
(65) M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Adv. Organomet. Chem.*, **3**, 1 (1965).
(66) H. D. Visser and J. P. Oliver, *J. Organomet. Chem.*, **40**, 7 (1972).
(67) B. E. Mann, *Adv. Organomet. Chem.*, 12, 135 (1974).
(68) F. J. Weigert, M. Winokur, and J. D. Roberts, *J. Am. Chem. Soc.*, **90**, 1566 (1968).
(69) A. B. Garrett, A. Sweet, W. L. Marshall, D. Riley, and A. Touma, *Rec. Chem. Progr.*, **13**, 155 (1952).
(70) I. E. Paleeva, N. I. Sheverdina, and K. A. Kocheshkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1263 (1967); *Chem. Abstr.*, **68**, 22031s (1968).
(71) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).
(72) S. C. Watson and J. F. Eastham, *J. Organomet. Chem.*, **9**, 165 (1967).
(73) K.-H. Thiele, *Z. Anorg. Allgem. Chem.*, **330**, 8 (1964).
(74) H. Schmidbaur and W. Wolfsberger, *Synth. Inorg. Met.-Org. Chem.*, 1, 111 (1971).
(75) T. Eicher in "The Chemistry of the Carbonyl Group", S. Patai, Ed., Wiley-Interscience, New York, N.Y., 1966, pp 621–693.
(76) M. Cais and A. Mandelbaum in ref 75, pp 303–330.
(77) N. O. V. Sonntag, *Chem. Rev.*, **52**, 237 (1953).
(78) F. Tatibouët and P. Freon, *Bull. Soc. Chim. Fr.*, 1496 (1963).
(79) G. Soussan, *C.R. Acad. Sci., Ser. C*, **268**, 267 (1969).
(80) G. Soussan and P. Freon, *C.R. Acad. Sci., Ser. C*, **271**, 211 (1970).
(81) C. Bernardon, E. Henry-Basch, and P. Freon, *C.R. Acad. Sci., Ser. C*, **266**, 1502 (1968).
(82) F. Huet, E. Henry-Basch, and P. Freon, *Bull. Soc. Chim. Fr.*, 1415 (1970).
(83) F. Huet, E. Henry-Basch, and P. Freon, *Bull. Soc. Chim. Fr.*, 1426 (1970).
(84) G. Soussan, *C.R. Acad. Sci., Ser. C*, **263**, 954 (1966).
(85) F. Huet, J. Michel, C. Bernardon, and E. Henry-Basch, *C.R. Acad. Sci., Ser. C*, **262**, 1328 (1966).
(86) E. Henry-Basch, J. Deniau, G. Emptoz, F. Huet, B. Marx, and J. Michel, *C.R. Acad. Sci., Ser. C*, **262**, 598 (1966).
(87) E. Henry-Basch, F. Huet, B. Marx, and P. Freon, *C.R. Acad. Sci., Ser. C*, **260**, 3694 (1965).
(88) E. Henry-Basch, J. Michel, F. Huet, B. Marx, and P. Freon, *Bull. Soc. Chim. Fr.*, 927 (1965).
(89) D. Abenhaim, *C.R. Acad. Sci., Ser. C*, **267**, 1426 (1968).
(90) M. Gocmen and H. Coudane, *C.R. Acad. Sci., Ser. C*, **269**, 467 (1969).
(91) E. Henry-Basch, J. Michel, and P. Freon, *C.R. Acad. Sci., Ser. C*, **260**, 5809 (1965).
(92) M. Langlais, A. Buzas, and P. Freon, *C.R. Acad. Sci., Ser. C*, **253**, 2364 (1961).
(93) M. Langlais, A. Buzas, and P. Freon, *C.R. Acad. Sci., Ser. C*, **254**, 1442 (1962).
(94) J. Michel, E. Henry-Basch, and P. Freon, *C.R. Acad. Sci., Ser. C*, **258**, 6171 (1964).
(95) J. L. Moreau and M. Gaudemar, *Bull. Soc. Chim. Fr.*, 2175 (1970).
(96) F. Tatibouët and P. Freon, *C.R. Acad. Sci., Ser. C*, **248**, 3447 (1959).
(97) F. Tatibouët and P. Freon, *C.R. Acad. Sci., Ser. C*, **249**, 1361 (1959).
(98) F. Tatibouët and P. Freon, *C.R. Acad. Sci., Ser. C*, **250**, 145 (1960).
(99) H. J. Bruer and R. Haller, *Tetrahedron Lett.*, 5227 (1972).
(100) P. R. Jones, E. G. Goller, and W. J. Kauffman, *J. Org. Chem.*, **34**, 3566 (1969).
(101) P. R. Jones, E. J. Goller, and W. J. Kauffman, *J. Org. Chem.*, **36**, 3311 (1971).
(102) D. Abenhaim, E. Henry-Basch, and P. Freon, *C.R. Acad. Sci., Ser. C*, **264**, 1313 (1967).
(103) D. Abenhaim and E. Henry-Basch, *C.R. Acad. Sci., Ser. C*, **267**, 87 (1968).
(104) D. Abenhaim, E. Henry-Basch, and P. Freon, *Bull. Soc. Chim. Fr.*, 4038 (1969).
(105) R. Pinson, Jr., and S. L. Friess, *J. Am. Chem. Soc.*, **72**, 5333 (1950).
(106) M. Gocmen, G. Soussan, and P. Freon, *Bull. Soc. Chim. Fr.*, 562 (1973).
(107) J. A. Nieuwland and S. F. Daly, *J. Am. Chem. Soc.*, **53**, 1842 (1931).
(108) G. W. Stacy and R. M. McCurdy, *J. Am. Chem. Soc.*, **76**, 1914 (1954).
(109) G. W. Stacy, R. A. Mikulec, S. L. Razniak, and L. D. Starr, *J. Am. Chem. Soc.*, **79**, 3587 (1957).
(110) P. Freon and E. Henry-Basch, *C.R. Acad. Sci., Ser. C*, **242**, 1627 (1956).
(111) J. F. Eastham and D. J. Feeney, *J. Org. Chem.*, **23**, 1826 (1958).
(112) P. R. Jones, P. D. Sherman, and K. Schwarzenberg, *J. Organomet. Chem.*, 10, 521 (1967).
(113) E. C. Ashby and J. T. Laemmle, *Chem. Rev.*, **75**, 521–546 (1975).
(114) W. J. Houlihan, *J. Org. Chem.*, **27**, 3860 (1962).
(115) H. O. House and W. L. Respess, *J. Org. Chem.*, **30**, 301 (1965).
(116) P. R. Jones, W. J. Kauffman, and E. J. Goller, *J. Org. Chem.*, **36**, 186 (1971).
(117) E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, N.Y., 1962, p 69.
(118) G. J. Karabatsos, *J. Am. Chem. Soc.*, **89**, 1367 (1967).
(119) M. Cherest, H. Felkin, and N. Prudent, *Tetrahedron Lett.*, 2199 (1968).
(120) D. Abenhaim, E. Henry-Basch, and P. Freon, *Bull. Soc. Chim. Fr.*, 4043 (1969).
(121) J. Canceill, J. Gabard, and J. Jacques, *Bull. Soc. Chim. Fr.*, 231 (1968).
(122) P. R. Jones and D. A. Walsh, unpublished results, University of New Hampshire.
(123) C. G. Stuckwisch and J. V. Bailey, *J. Org. Chem.*, **28**, 2362 (1963).
(124) G. Courtois and L. Miginiac, *J. Organomet. Chem.*, **69**, 1 (1974).
(125) T. Tanabe, *Bull. Chem. Soc. Jpn.*, **46**, 2233 (1973).
(126) H. Gross and J. Freiberg, *Chem. Ber.*, **99**, 3260 (1966).
(127) F. N. Jones and C. R. Hauser, *J. Org. Chem.*, **27**, 3364 (1962).
(128) P. R. Jones and A. A. Lavigne, *J. Org. Chem.*, **25**, 2020 (1960).
(129) P. R. Jones and C. J. Jarboe, *J. Organomet. Chem.*, **24**, 555 (1970).
(130) K. Soga, H. Imamura, and S. Ikeda, *Makromol. Chem.*, **176**, 807 (1975); *Chem. Abstr.*, **82**, 156818b (1975).
(131) G. D. Cooper and M. Prober, *J. Org. Chem.*, **25**, 240 (1960).
(132) J. Michel and E. Henry-Basch, *C.R. Acad. Sci., Ser. C*, **262**, 1274 (1966).
(133) I. Pitta da Rocha, A. Boucherle, and Luu Duc Cuong, *Eur. J. Med. Chem.-Chim. Ther.*, **9**, 462 (1974); *Chem. Abstr.*, **82**, 155672n (1975).
(134) A. G. Davies and J. E. Packer, *J. Chem. Soc.*, 3164 (1959).
(135) L. Le Guilly, R. Setton, and F. Tatibouët, *J. Organomet. Chem.*, **40**, C5 (1972).
(136) J. Thomas, E. Henry-Basch, and P. Freon, *C.R. Acad. Sci., Ser. C*, **267**, 176 (1968).
(137) J. Thomas, *Bull. Soc. Chim. Fr.*, 1300 (1973).
(138) J. Thomas and P. Freon, *C.R. Acad. Sci., Ser. C*, **267**, 1850 (1968).
(139) J. Thomas, E. Henry-Basch, and P. Freon, *Bull. Soc. Chim. Fr.*, 109 (1969).
(140) J. Thomas, *Bull. Soc. Chim. Fr.*, 1296 (1973).
(141) J. C. Fiaud and H. B. Kagan, *Tetrahedron Lett.*, 1019 (1971).
(142) J. Chenault and F. Tatibouët, *C.R. Acad. Sci., Ser. C*, **267**, 1492 (1968).
(143) T. Wizemann, H. Mueller, D. Seybold, and K. Dehnicke, *J. Organomet. Chem.*, 20, 211 (1969).
(144) A. N. Nesmeyanov and L. G. Makarova, *J. Gen. Chem. USSR*, **7**, 2649 (1937).
(145) M. H. Abraham, J. H. N. Garland, J. A. Hill, and L. F. Larkworthy, *Chem. Ind. (London)*, 1615 (1962).
(146) J. Lorberth, *J. Organomet. Chem.*, **27**, 303 (1971).

(147) M. Ryang, K. Yoshida, H. Yokoo, and S. Tsutsumi, *Bull. Chem. Soc. Jpn.*, **38**, 636 (1965).
(148) K.-H. Thiele, J. Köhler, and P. Zdunneck, *Z. Chem.*, **7**, 307 (1967).
(149) M. Gocmen and G. Soussan, *J. Organomet. Chem.*, **61**, 19 (1973).
(150) M. Gocmen, G. Soussan, and P. Freon, *Bull. Soc. Chim. Fr.*, 1310 (1973).
(151) G. Wittig, F. J. Meyer, and G. Lange, *Justus Liebigs Ann. Chem.*, **571**, 167 (1951).
(152) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances", Prentice-Hall, New York, N.Y., 1954, p 385.
(153) B. Riegel, S. Siegel, and W. M. Lilienfeld, *J. Am. Chem. Soc.*, **68**, 984 (1946).
(154) B. Riegel, S. Siegel, and D. Kritchevsky, *J. Am. Chem. Soc.*, **70**, 2950 (1948).
(155) F. S. Prout, *J. Am. Chem. Soc.*, **74**, 5915 (1952).
(156) F. S. Prout, E. P. Y. Huang, R. J. Hartman, and C. J. Korpics, *J. Am. Chem. Soc.*, **76**, 1911 (1954).
(157) O. Eisenstein, J. M. Lefour, C. Minot, N. T. Anh, and G. Soussan, *C.R. Acad. Sci., Ser. C*, **274**, 1310 (1972).
(158) J. Cason and R. J. Fessenden, *J. Org. Chem.*, 22, 1326 (1957).
(159) R. F. Galiullina, V. N. Pankratova, L. P. Stepovik, and A. D. Chernova, *J. Gen. Chem. USSR*, **46**, 100 (1976).
(160) N. S. Vyazankin, V. T. Bychov, O. V. Linzina, L. V. Aleksandrova, and G. A. Razuvaev, *J. Organomet. Chem.*, **31**, 311 (1971).
(161) V. T. Bychkov, N. S. Vyazankin, G. A. Abakumov, O. V. Linzina, and G. A. Razuvaev, *Dokl. Akad. Nauk SSSR*, **202**, 593 (1972); *Chem. Abstr.*, **76**, 139726d (1972).
(162) V. I. Shcherbakov, R. F. Galiullina, Yu. N. Krasnov, and V. N. Pankratova, *J. Gen. Chem. ussr*, **41**, 2063 (1971).
(163) V. I. Shcherbakov and S. F. Zhil'tsov, *Nov. Khim. Karbenov, Mater. Vses. Soveshch. Khim. Karbenov Ikh Analogov, 1st 1972*, 162 (1973); *Chem. Abstr.*, **82**, 43559z (1975).
(164) P. R. Jones and S. J. Costanzo, *J. Org. Chem.*, **38**, 3189 (1973).
(165) G. Emptoz and F. Huet, *Bull. Soc. Chim. Fr.*, 7-8 (Pt 2), 1695 (1974).
(166) J. P. Deniau, E. Henry-Basch, and P. Freon, *C.R. Acad. Sci., Ser. C*, **264**, 1560 (1967).
(167) J. Deniau, E. Henry-Basch, and P. Freon, *Bull. Soc. Chim. Fr.*, 4414 (1969).
(168) O. Nakasugi, M. Ishimori, and T. Tsuruta, *Bull. Chem. Soc. Jpn.*, **47**, 871 (1974).
(169) J. F. Bunnett and D. S. Tarbell, *J. Am. Chem. Soc.*, **67**, 1944 (1945).
(170) R. A. LeMahieu, *J. Org. Chem.*, **32**, 4149 (1967).
(171) C. K. Warren and B. C. L. Weedon, *J. Chem. Soc.*, 3972 (1958).
(172) G. A. Razuvaev, S. N. Zaburdyaeva, and V. A. Dodonov, *Zh. Org. Khim.*, **7**, 2484 (1971); *Chem. Abstr.*, **76**, 71947u (1972).
(173) R. K. Summerbell and L. N. Bauer, *J. Am. Chem. Soc.*, **58**, 759 (1936).
(174) P. R. Jones and J. R. Young, *J. Org. Chem.*, **33**, 1675 (1968).
(175) M. Renson, *Bull. Soc. Chim. Belg.*, **70**, 77 (1961).
(176) M. H. Palmer and J. A. Reid, *J. Chem. Soc.*, 931 (1960).
(177) C. D. Hurd and R. P. Holysz, *J. Am. Chem. Soc.*, **72**, 2005 (1950).
(178) R. S. Klein, M. P. Kotick, K. A. Watanabe, and J. J. Fox, *J. Org. Chem.*, **36**, 4113 (1971).
(179) A. R. Van Horn, private communication, 1970.
(180) P. R. Jones and C. J. Jarboe, *Tetrahedron Lett.*, 1849 (1969).
(181) U. Nagai, T. Shishido, R. Chiba, and H. Mitsuhashi, *Tetrahedron*, **21**, 1701 (1965).
(182) P. R. Jones and S. L. Congdon, *J. Am. Chem. Soc.*, **81**, 4291 (1959).
(183) R. A. Benkeser, *Synthesis*, 347 (1971).
(184) E. A. Hill, *J. Organomet. Chem.*, **91**, 123 (1975).
(185) E. A. Hill, *Adv. Organomet. Chem.*, **16**, 131 (1977).
(186) S. Czernecki, C. Georgoulis, B. Gross, and C. Prevost, *C.R. Acad. Sci., Ser. C*, **266**, 1617 (1968).
(187) C. Agami, M. Andrac-Taussig, and C. Prevost, *Bull. Soc. Chim. Fr.*, 2596 (1966).
(188) H. Gilman and J. F. Nelson, *J. Am. Chem. Soc.*, **61**, 741 (1939).
(189) L. H. Klemm, R. Mann, and C. D. Lind, *J. Org. Chem.*, **23**, 349 (1958).
(190) W. G. Dauben and J. W. Collette, *J. Am. Chem. Soc.*, **81**, 967 (1959).
(191) J. Walravens and R. H. Martin, *Bull. Soc. Chim. Belg.*, **69**, 165 (1960).
(192) W. G. Dauben and H. Tilles, *J. Org. Chem.*, **15**, 785 (1950).
(193) I. T. Harrison, U.S. Patent 3,658,858 (1972); *Chem. Abstr.*, **77**, 5614c (1972).
(194) K. Moedritzer, in "Organometallic Reactions", Vol. 2, E. I. Becker and M. Tsutsui, Ed., Wiley-Interscience, New York, N.Y., 1971, p 1.
(195) M. P. Klein and J. S. Waugh, *Phys. Rev.*, **116**, 960 (1959).
(196) N. S. Ham and T. Mole, *Progr. Nucl. Magn. Reson. Spectros.*, **4**, 91 (1969).
(197) A. D. Cardin, P. D. Ellis, J. D. Odom, and J. W. Howard, Jr., *J. Am. Chem. Soc.*, **97**, 1672 (1975).
(198) G. E. Maciel and M. Borzo, *J. Chem. Soc., Chem. Commun.*, 394 (1973).
(199) J. P. Oliver, *Adv. Organomet. Chem.*, **8**, 167 (1970).
(200) R. E. Dessy, F. Kaplan, G. R. Coe, and R. M. Salinger, *J. Am. Chem. Soc.*, **85**, 1191 (1963).
(201) W. Bremser, M. Winokur, and J. D. Roberts, *J. Am. Chem. Soc.*, **92**, 1080 (1970).
(202) J. Soulati, K. L. Henold, and J. P. Oliver, *J. Am. Chem. Soc.*, **93**, 5694 (1971).
(203) N. S. Ham, E. A. Jefferey, T. Mole, J. K. Saunders, and S. N. Stuart, *J. Organomet. Chem.*, **8**, P7 (1967).
(204) N. I. Sheverdina, I. E. Paleeva, E. D. Delinskaya, and K. A. Kocheshkov, *Dokl. Akad. Nauk SSSR*, **125**, 348 (1959); *Chem. Abstr.*, **53**, 19853 (1959).
(205) E. C. Ashby, *Ann. N.Y. Acad. Sci.*, **159**, 131 (1969); *Chem. Abstr.*, **71**, 70661f (1969).
(206) S. Toppet, G. Slinckx, and G. Smets, *J. Organomet. Chem.*, **9**, 205 (1967).
(207) L. M. Seitz and B. F. Little, *J. Organomet. Chem.*, **18**, 227 (1969).
(208) I. E. Paleeva, N. I. Sheverdina, E. D. Delinskaya, and K. A. Kocheshkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1083 (1967); *Chem. Abstr.*, **68**, 29829s (1968).
(209) A. L. Allred and C. R. McCoy, *Tetrahedron Lett.*, No. 27, 25 (1960).
(210) C. R. McCoy and A. L. Allred, *J. Am. Chem. Soc.*, **84**, 912 (1962).
(211) K. Henold, J. Soulati, and J. P. Oliver, *J. Am. Chem. Soc.*, **91**, 3171 (1969).
(212) B. L. Dyatkin, B. I. Martynov, I. L. Knunyants, S. R. Sterlin, L. A. Fedorov, and Z. A. Stumbrevichute, *Tetrahedron Lett.*, 1345 (1971).
(213) T. G. Brilkina and V. A. Shushuna, "Reactions of Organometallic Compounds with Oxygen and Peroxides", CRC Press, Cleveland, Ohio, 1969.
(214) G. A. Razuvaev, V. A. Shushunov, V. A. Dodonov, and T. G. Brilkina, in D. Swern, Ed., *Org. Peroxides*, **3**, 141 (1972).
(215) Y. A. Alexandrov and V. P. Maslennikov, *J. Organomet. Chem. Libr.*, **3**, 75 (1977).
(216) Y. A. Alexandrov, G. N. Figurova, and G. A. Razuvaev, *J. Organomet. Chem.*, **57**, 71 (1973).
(217) A. G. Davies and J. E. Packer, *Chem. Ind. (London)*, 1177 (1958).
(218) A. G. Davies and B. P. Roberts, *J. Chem. Soc. B*, 1074 (1968).
(219) H. Hock and F. Ernst, *Chem. Ber.*, **92**, 2716 (1959).
(220) K. P. Long, Ph.D. Thesis, University of New Hampshire, 1970.
(221) L. LeGuilly and F. Tatibouët, *C.R. Acad. Sci., Ser. C*, **262**, 217 (1966).
(222) V. N. Pankratova, V. N. Latyaeva, and G. A. Razuvaev, *Zh. Obshch. Khim.*, **35**, 900 (1965); *Chem. Abstr.*, **63**, 6805h (1965).
(223) V. T. Bychkov, N. S. Vyazankin, O. V. Linzina, L. V. Aleksandrova, and G. A. Razuvaev, *Izk. Akad. Nauk SSSR, Ser. Khim.*, 2614 (1970); *Chem. Abstr.*, **75**, 6050m (1971).
(224) G. A. Razuvaev, V. N. Pankratova, V. A. Muraev, and I. V. Bykova, *Zh. Obshch. Khim.*, **39**, 2490 (1969); *Chem. Abstr.*, **72**, 79183e (1970).
(225) A. G. Davies and B. P. Roberts, *J. Organomet. Chem.*, **19**, P17 (1969).
(226) L. M. Dyagileva, A. K. Kazhaeva, Y. A. Aleksandrov, and B. F. Surin, *Tr. Khim. Khim. Tekhnol.*, 144 (1973); *Chem. Abstr.*, **80**, 123750d (1974).
(227) R. C. Elderfield and V. B. Meyer, *J. Am. Chem. Soc.*, **76**, 1883 (1954).
(228) L. Lardicci, L. Lucarini, P. Palagi, and P. Pino, *J. Organomet. Chem.*, **4**, 341 (1965).
(229) G. A. Razuvaev and V. N. Pankratova, *J. Gen. Chem. USSR*, **36**, 1698 (1966).
(230) C. M. Laurie and L. H. Long, *Trans. Faraday Soc.*, **53**, 1431 (1957).
(231) R. Ganesan, *Z. Phys. Chem.*, **31**, 328 (1962).
(232) L. H. Long, *J. Chem. Soc.*, 3410 (1956).
(233) M. Krech and S. J. Price, *Can. J. Chem.*, **43**, 1929 (1965).
(234) S. J. W. Price and A. F. Trotman-Dickenson, *Trans. Faraday Soc.*, **53**, 939 (1957).
(235) M. W. Jones, L. J. Rigby, and D. Ryan, *Nature (London)*, **212**, 177 (1966).
(236) C. Jonah, P. Chandra and R. Bersohn, *J. Chem. Phys.*, **55**, 1903 (1971).
(237) M. Tamir, U. Halavee, and R. D. Levine, *Chem. Phys. Lett.*, **25**, 38 (1974).
(238) R. Bersohn, *Isr. J. Chem.*, 11, 675 (1973).
(239) G. Distefano and V. H. Dibeler, *Int. J. Mass Spectrom. Ion Phys.*, **4**, 59 (1970); *Chem. Abstr.*, **73**, 24493w (1970).
(240) J. L. Morgat and R. Pallaud, *C.R. Acad. Sci., Ser. C*, **260**, 574 (1965).
(241) J. L. Morgat and R. Pallaud, *C.R. Acad. Sci., Ser. C*, **260**, 5579 (1965).
(242) J. Furukawa, N. Kawabata, and T. Fujita, *Tetrahedron*, **26**, 243 (1970).
(243) H. R. Henze and N. E. Artman, *J. Org. Chem.*, 22, 1410 (1967).
(244) A. I. Khodair, A. Osman, and A. A. Abdel-Wahab, *Int. J. Sulfur Chem.*, **8**, 613 (1976).
(245) A. I. Khodar, A. Swelim, and A. A. Abdel-Wahab, *Phosphorus Sulfur*, 2, 165 (1976).
(246) A. I. Khodair, A. Swelim, and A. A. Abdel-Wahab, *Phosphorus Sulfur*, **2**, 169 (1976).
(247) N. N. Hatch, B.S. Thesis, University of New Hampshire, 1969.
(248) M. Dagonneau and J. Vialle, *Tetrahedron*, **30**, 3119 (1974).
(249) J. C. Sheehan, D. Ben-Ishai, and J. U. Piper, *J. Am. Chem. Soc.*, **95**, 3064 (1973).
(250) T. Makimoto and K. Fujii, Japanese Patent 74 31,554 (1974); *Chem. Abstr.*, **82**, P58551q (1975).
(251) T. Huff and E. Perry, *J. Polym. Sci., Part A1*, 1553 (1963).
(252) R. H. Gobran and S. W. Osborn, German Patent 1,545,025 (1974); *Chem. Abstr.*, **82**, P32171r (1975).
(253) A. Deffieux, M. Sepulchre, N. Spassky, and P. Sigwalt, *Makromol. Chem.*, **175**, 339 (1974); *Chem. Abstr.*, **81**, 64079n (1974).
(254) M. Ishimori, O. Nakasugi, K. Yokobori, and T. Tsuruta, *Makromol. Chem.*, **171**, 41 (1973); *Chem. Abstr.*, **80**, 60267d (1974).
(255) A. Deffieux, M. Sepulchre, and N. Spassky, *J. Organomet. Chem.*, **80**, 311 (1974).
(256) N. N. Greenwood and N. F. Travers, *J. Chem. Soc. A*, 880 (1967).
(257) H. Mueller and K. Dehnicke, *Bol. Soc. Chil. Quim.*, **19**, 17 (1972); *Chem. Abstr.*, **78**, 84507 (1973).
(258) A. J. Birch and A. J. Pearson, *Tetrahedron Lett.*, 2379 (1975).