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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 1946⁷ 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 compounds¹⁰ 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 Kollonitsch¹¹⁻¹³ 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 ke-

tones, 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

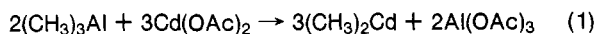
Although not chronologically the first method attempted for preparation of organocadmium reagents, the interaction of an organometallic reagent and a cadmium salt has become the standard route to their synthesis. It was first reported in 1917 by Krause,⁵ who prepared dimethyl- and diethylcadmium by distillation 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 generalization¹⁸ that the equilibrium involving two organome-

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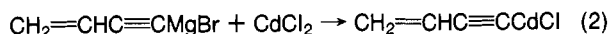
tallics lies on the side of the less reactive partner. Limitations and variations in the method as a general route to organometallics were noted in the ensuing years. It was found, for example, that alkyl bromides were superior to chlorides or iodides and that dibutyl ether was inferior to diethyl ether 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 aryl²¹ 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

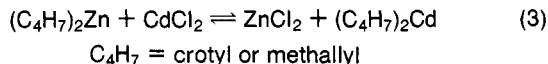


Exchange between aluminum alkyls and cadmium halides has been patented as a synthetic method.²³

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



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.



Difunctional organocadmium reagents from $\text{X}(\text{CH}_2)_n\text{X}$ 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 $\text{X}(\text{CH}_2)_6\text{X}$ with 2 equiv of CdX_2 affords final products (from acid chloride, aldehyde, or ketone) in considerably lower yield.²⁹

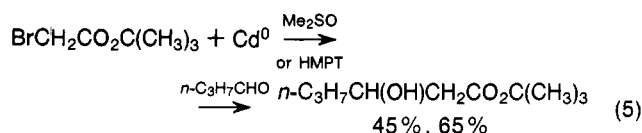
A methylene insertion into CdCl_2 with diazomethane leads to bis(chloromethyl)cadmium, but the yield is only 11%.³⁰



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 dimethylformamide³¹ 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.).



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

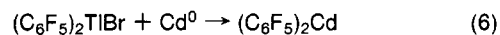
Although the best conversions were accomplished with diglyme (83%) and dioxane (74%), it is noteworthy that organometallic formation took place even in hexane (61%) and toluene (55%). Attempts to obtain purified diethylcadmium, however, failed.

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 pentafluoriodobenzene and cadmium turnings in dimethylformamide, dimethyl sulfoxide, or hexamethylphosphoramide afforded brown solutions, whose ¹⁹F NMR spectra indicated the presence of both Ar_2Cd and ArCdI .³⁶

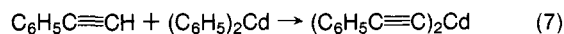
3. Reaction of an Organometallic Compound with Cadmium Metal

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

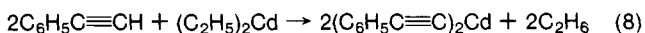


4. Metalation

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.

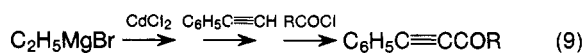


By contrast it was reported from another laboratory that diethylcadmium (unspecified nature) failed to react appreciably with phenylacetylene in ether at 20 °C under argon.⁴¹ Solvent had a profound effect on the rate of metalation. The half-life for phenylacetylene (as determined by evolution of ethane)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



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

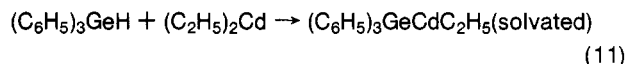
by way of the ethylcadmium reagent, as a general route to ketones.^{42,43} The solvent was ether-benzene, but there was no indication of other conditions required for effecting the metalation.



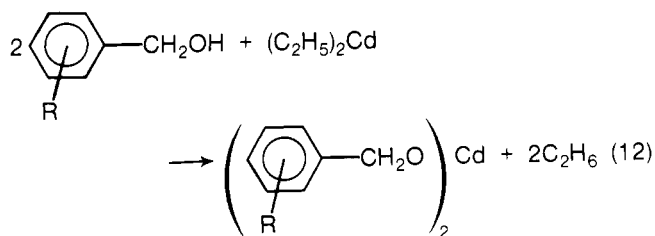
Metalation of tris(pentafluorophenyl)germane with diethylcadmium (unspecified) required heating in toluene at 100 °C for 2 h.⁴⁴



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



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.

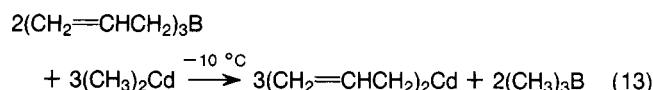


The half-lives, measured by evolution of ethane, at 35 °C for abstraction of hydrogen by halide-free diethylcadmium varied from 80 min (*p*-CF₃) to 36 min (*p*-OCH₃).⁴⁷ These results have been correlated with kinetics, isotope effect, and the Hammett relationship.⁴⁸

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 (ZnCl₂, AlCl₃, MgBr₂). This behavior is the opposite of that observed with Grignard reagents.⁴⁶

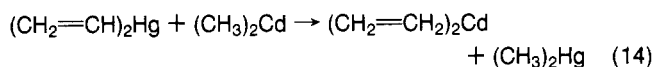
5. Redistribution

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

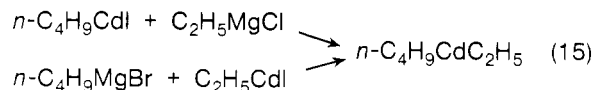


Diallyl-, dimethylallyl-, and dicrotylcadmium were obtained in the form of solids, the residual trimethylboron by-product (a gas) being removed in vacuo. This is the method of choice for preparation of allyl compounds, for solutions or mixtures from allylic Grignard or lithium compounds and cadmium salts 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.

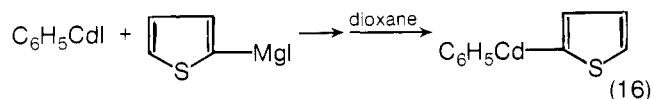
Divinylcadmium has been prepared by the redistribution between divinylmercury and dimethylcadmium, an exchange which is much slower than that for allylic compounds. The two components were heated at 60 °C in a sealed container for 5 days. After the dimethylmercury had been removed in vacuo, the residual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



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

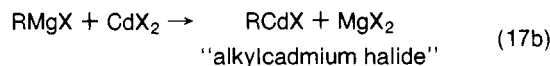
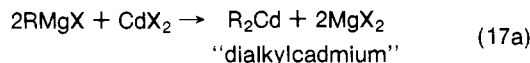


It was reported that 2-thienylphenylcadmium, in the form of a hemidioxanate, was obtained from equimolar amounts of phenylcadmium iodide and thienylmagnesium iodide; the magnesium iodide was precipitated by dioxane.⁵¹



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.



"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*-butylcadmium⁵² 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*-tolylcadmium⁵³ and dicyclohexylcadmium⁵⁴ 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 Thiele²⁶ 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 Kollonitsch¹¹⁻¹³ that their properties may be markedly different, and this situation has been confirmed by many other workers.

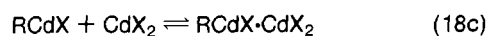
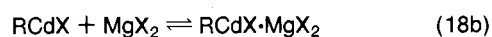
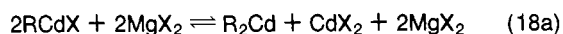
Relatively few investigations into the composition and structure of organocadmium reagents have been carried out. The use of spectroscopy to deduce structures is complicated by the many components in equilibrium in the in situ reagents, and information on purified compounds may be of limited use for 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 structure⁵⁸ and position of equilibrium⁵⁹ 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 infrared⁶¹ 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 ¹³C 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 ¹¹³Cd FT NMR spectroscopy for studying redistribution reactions is discussed in part VIII.

Garrett and co-workers⁶⁹ suggested that the chief component formed by mixing purified diethylcadmium and cadmium bromide in THF is (C₂H₅)₂Cd·CdBr₂, a conclusion based on molecular weight determination and exchange experiments with radioactive ¹¹⁵Cd. More recently Sanders and Ashby⁵² have made an extensive study of various in situ reagents in ether derived from *n*-C₄H₉MgX and CdX₂ 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:CdX₂ ratio of 2:1, it seems to consist only of R₂Cd + MgX₂. In a 1:1 ratio the reaction seems to afford MgX₂ and an equilibrium mixture of R₂Cd and CdX₂. Cooling the solution from the 1:1 reaction mixture caused precipitation of solids, whose analyses were consistent with the structure RCdX·MgX₂. 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:CdX₂) ratio, can be depicted in solution as R₂Cd + MgX₂ ⇌ R₂Cd·MgX₂. "Alkylcadmium halide", from a 1:1 ratio, is more complicated. The following additional equilibria are probably involved, with R₂Cd being the dominant organocadmium component.



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

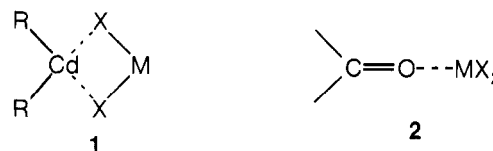
III. Reactions with Aldehydes and Ketones

A. The Reagent: In Situ vs. Purified

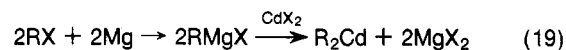
Contrary to widespread belief⁷⁵⁻⁷⁷ organocadmium reagents, prepared in ether or benzene solvent, add rapidly and efficiently to simple carbonyl compounds—aldehydes and ketones—under mild conditions, provided the in situ reagent is employed. The misconception that cadmium reagents are inert toward simple 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 Cason⁷ 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 Nelson⁶ 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 R₂Cd (represented by 1) or coordinates with the carbonyl group as in 2, thus enhancing the nucleophilicity of R₂Cd in the first case



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, lithium⁸⁵ 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:

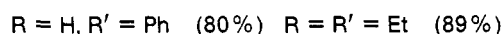
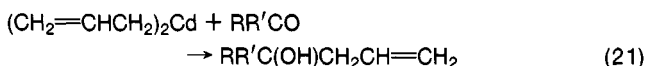
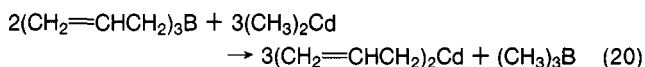


is most effective when X = I throughout. Comparable reconstituted reagents can be prepared by the addition of 2 molar equiv of MgI₂ to purified R₂Cd.

In the special case of ethoxymethylcadmium reagent, (C₂H₅OCH₂)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

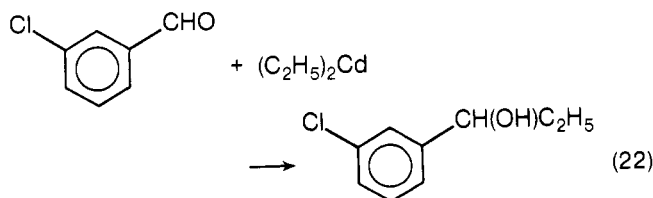
It is remarkable that allylic cadmium reagents, prepared *free of metal halide* by way of organoboron compounds,²⁶ are highly reactive toward aldehydes and ketones¹⁰²⁻¹⁰⁴ as evident in the following syntheses of secondary and tertiary alcohols.¹⁰²



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

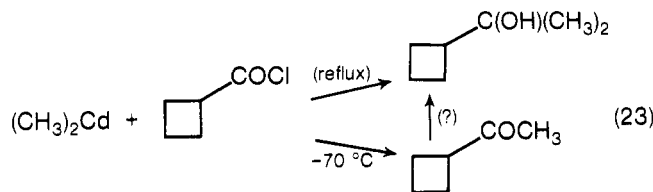


extent of only 20%. *p*-Chlorobenzaldehyde is likewise readily attacked, whereas *p*-tolualdehyde, containing an electron-rich group, is even less reactive than benzaldehyde.⁸³

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



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**,

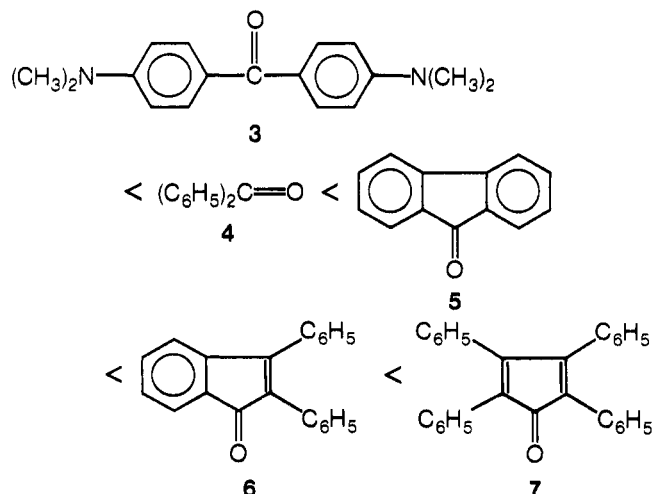


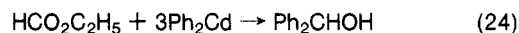
TABLE I. Solvent Effect in the Reaction of Purified Diethylcadmium with Benzaldehyde

$$\text{C}_6\text{H}_5\text{CHO} + (\text{C}_2\text{H}_5)_2\text{Cd} \xrightarrow{63^\circ\text{C}} \text{C}_6\text{H}_5\text{CH(OH)C}_2\text{H}_5$$

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

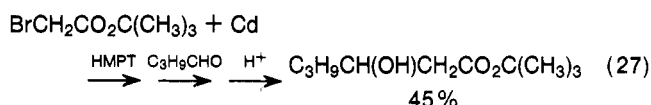
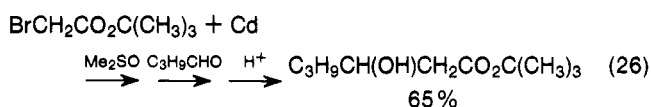
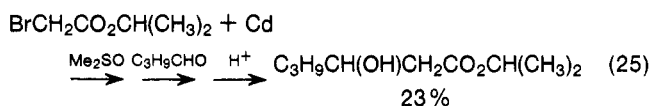
respectively.⁹⁰ Ketone **7**, in fact, undergoes addition in about 85% yield with purified halide-free ethyl reagent whereas **5** is inert under the same conditions.^{90,106}

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



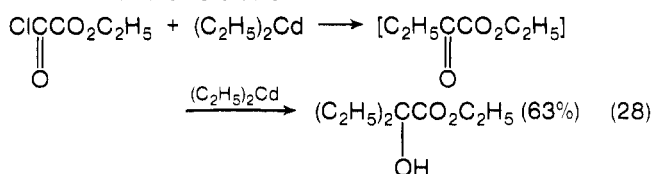
The dramatic change in the reactivity of cadmium reagents in polar, aprotic solvents has been noted. Purified reagents (halide-free) are greatly activated by use of the solvents tetramethylethylenediamine (TMED) or hexamethylphosphortri- amide (HMPT).⁸³ A comparison of the yields of alcohol in the familiar 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.



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

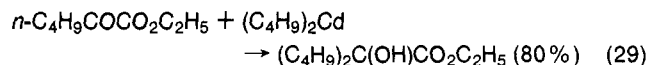
The fact that organocadmium reagents will add to "activated" carbonyl compounds—those in α -diketones, α -keto esters, etc.—was probably first realized by Gilman and Nelson,⁶ who observed that ethyl chlorooxalate formed not the expected ethyl α -ketobutyrate with ethylcadmium reagent, but the hydroxy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



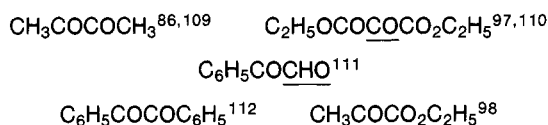
It was later shown that α -keto esters do indeed undergo addition readily.^{98,108} An example is the reaction of ethyl 2-oxohexanoate with in situ *n*-butylcadmium reagent at 0°C .¹⁰⁸

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

organometallic (ether)	% Z	% E	Z:E
CH ₃ MgBr	68	32	2.2
CH ₃ MgI	62	38	1.6
2CH ₃ MgBr + CdCl ₂	50	50	1.0
2CH ₃ MgI + CdCl ₂	42	52	0.74



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.



D. Stereochemistry of Additions to Aldehydes and Ketones

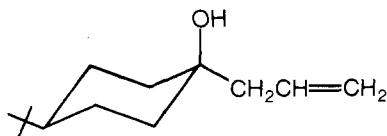
The limited stereochemical studies of additions to simple carbonyls have been carried out with a view to comparing the selectivity of various organometallic reagents, notably the magnesium, lithium, aluminum, cadmium, and zinc compounds. This subject was thoroughly reviewed in 1975,¹¹³ and so only the 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 ($\geq 95\%$).

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.

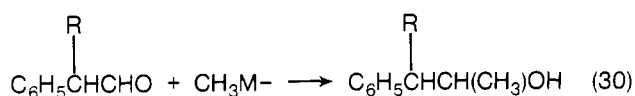
The halide-free allylcadmium reagent, on the other hand,

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

metal temp. (°C)	% "threo" (normalized)			
	R = C ₂ H ₅	n-C ₃ H ₇	(CH ₃) ₂ CH	(CH ₃) ₃ C
Mg (+35)	52	51	58	75
Zn (+35)	45	46	70	84
Cd (-20)	50	51	80	86

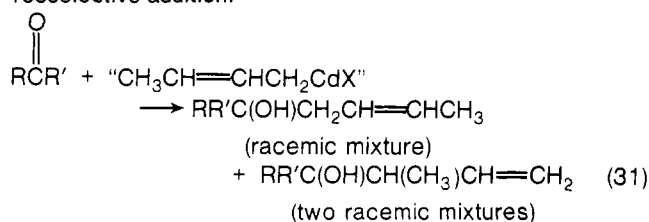
exhibits even a higher preference for equatorial attack, the *Z* alcohol constituting 78% of the mixture of diastereomers.¹⁰⁴

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

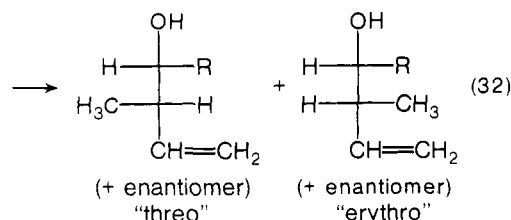


While in the cases where erythro is favored, the cadmium reagent is less stereoselective than the magnesium compound, the cadmium is *more stereoselective* (greater fraction of threo) when R = isopropyl.

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.

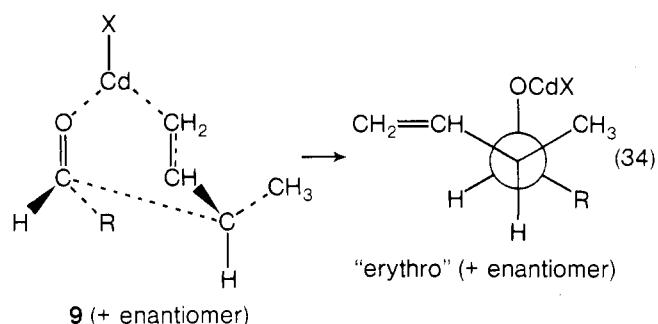
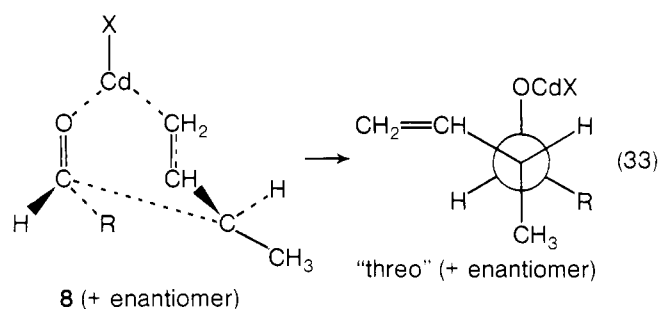


Remarkably, the "crotyl" reagent, prepared in situ from crotyl bromide by way of the Grignard reagent, affords exclusively the methylallyl adducts.^{103,120} Addition to aldehydes thus constitutes an interesting situation where two chiral centers are generated simultaneously. Four cases were examined (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.



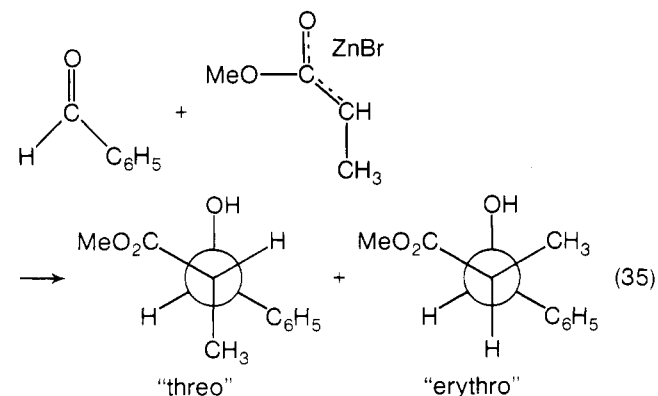
If one assumes the crotyl reagent adds in a concerted, allylic rearrangement (an S_E' process), two contrasting transition states **8** and **9** can be drawn as shown (alternative arrangements, leading to other conformers, are, of course, possible).

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



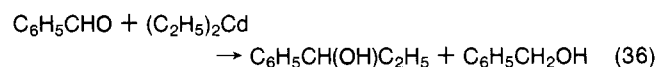
The results are consistent with this picture, for the stereoselectivity increases as the size of "R" increases. It is of interest that this interpretation holds only if one considers methyl "large" and vinyl "medium" at the organometallic site.

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**.

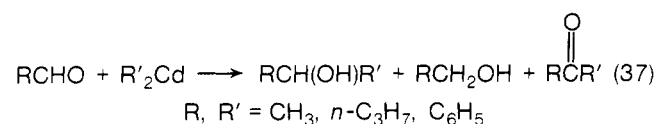


E. Side Reactions

It was noted by Tatibouët and Freon⁷⁸ 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.

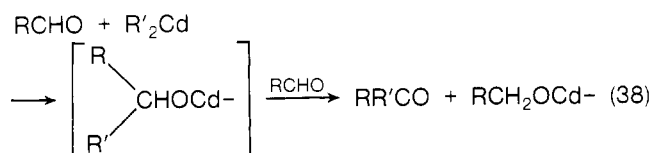


The possible formation of reduction products accompanying additions to aldehydes was subsequently investigated by Soussan in the same laboratory.

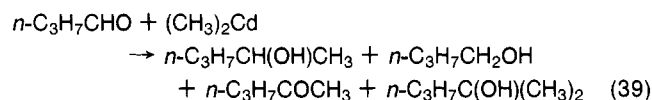


Products from the reactions of acetaldehyde, butyraldehyde, and benzaldehyde with in situ methyl-, *n*-propyl-, and phenylcadmium

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-Ponndorf-Verley (M-P-V) reduction (Oppenauer oxidation) route.

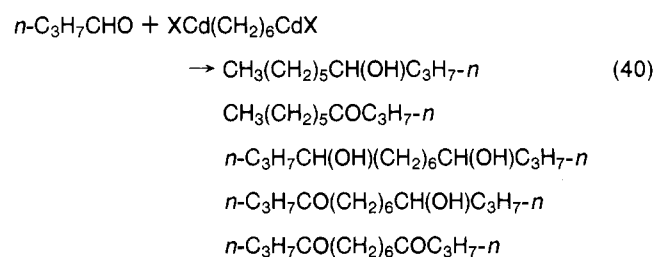


In some instances the tertiary alcohol, resulting from further addition of cadmium reagent to the ketone, was also detected in trace amounts. An example is the reaction of butyraldehyde with the methylcadmium reagent.

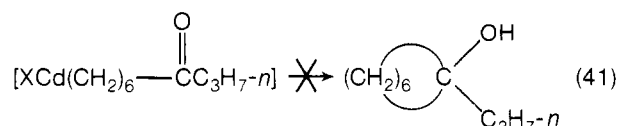


In a more detailed examination of the reaction of butyraldehyde with the *n*-propylcadmium reagent, it was shown that the amount of oxidation-reduction products increased with an excess of the cadmium reagent.

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.



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.

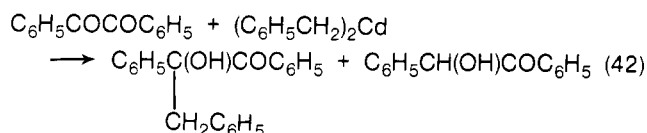


An even more complex sequence of reactions has been noted when the "addition" reaction of benzaldehyde and ethylcadmium reagent is carried out in ether in the presence of a variety of metal halides (MgCl₂, MgBr₂, MgI₂, ZnBr₂, LiBr, AlCl₃).

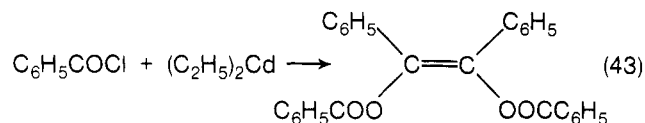
Not only were the oxidation-reduction products noted earlier found, but benzyl benzoate (Tischenko reaction), ethylphenylcarbinyl benzoate (Cannizzaro?), and benzalpropiofenone and ethylidenepropiofenone (aldol condensation) were detected in minimal amounts.⁸² The side reactions (in particular the M-P-V 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 CdBr₂ 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

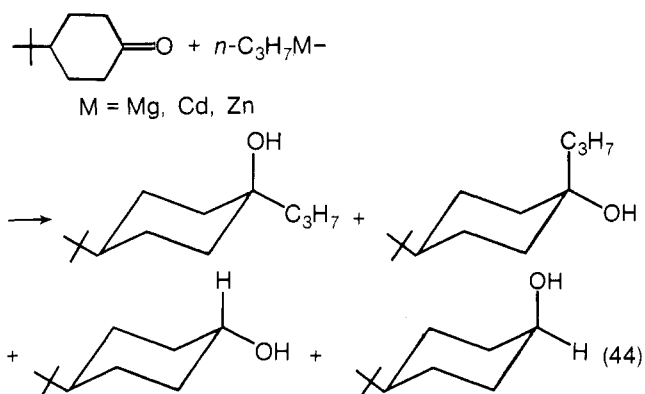
products, analyzed by column chromatography and NMR, does not change when oxygen is excluded. Furthermore, no trace of benzaldehyde could be detected.



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



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-

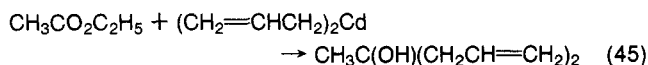


ganometallics, it has been found in two different laboratories^{89,116} that the ratio of addition:reduction decreases in the order Cd, Mg, Zn. Stereoselectivity in the reduction decreases in the order Mg, Cd, Zn. In one instance, in fact, the propylzinc reagent (from propylmagnesium bromide and ZnBr_2)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

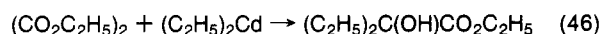
IV. Reactions with Other Unsaturated Functional Groups

A. Esters and Lactones

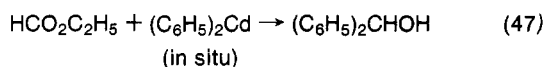
There are very few instances recorded in which an ester reacts by addition of an organocadmium reagent at the carbonyl group. (It has already been pointed out that propiolactone is attacked at the β carbon.¹²³) Halide-free allylic cadmium reagents seem to be exceptional, for they add to ethyl acetate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



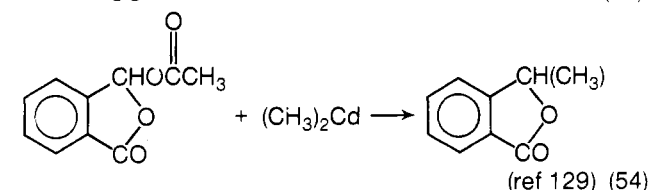
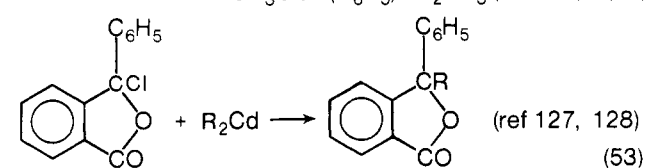
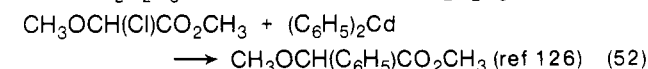
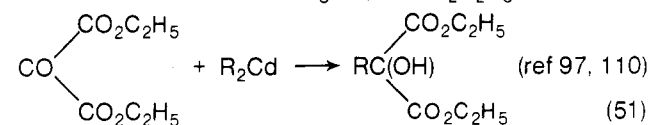
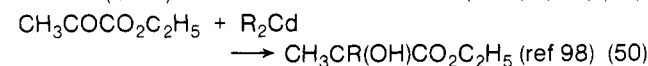
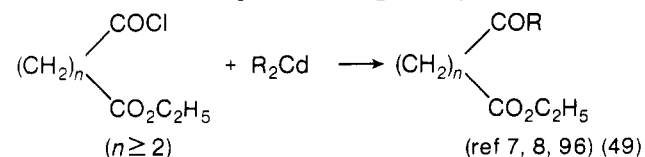
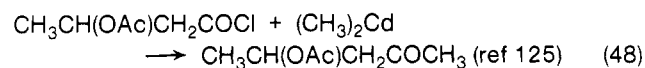
Reaction with other in situ organocadmium compounds is limited to "activated" esters^{6,85,86,88} such as diethyl oxalate.



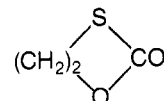
Even in these cases, addition occurs at only one ester function. The reaction fails with halide-free reagents.⁸⁸ The fact that ethyl formate undergoes addition is consistent with the tendency for aldehydes to react readily.⁸⁶



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.



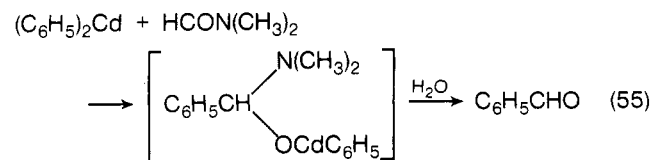
Recent interest in the use of diethylcadmium as a catalyst for the polymerization of ethylene monothiocarbonate



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

B. Amides, Lactams, and Nitriles

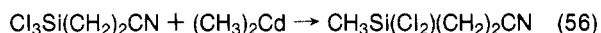
The generalization made in 1963⁷⁸ that amides and nitriles are unreactive toward organocadmium compounds has not been disputed. The only exception is the case of dimethylformamide, which was reported to be converted in 40% yield to benzaldehyde with an excess of the in situ phenylcadmium reagent.⁸⁶



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.

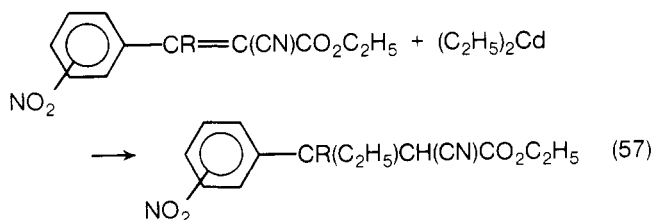
Presumably lactams, unless highly strained, would likewise be inert toward cadmium reagents. There are apparently no examples of ring openings of β -lactams.

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

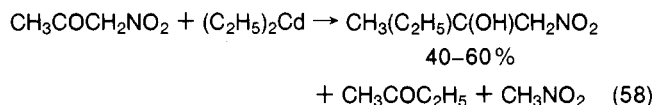


C. Nitro Compounds

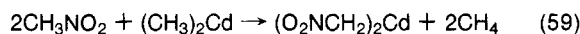
Nitroethylenes react with organocadmium compounds in the conjugate manner exclusively,^{86,88,132} the nitro group remaining intact. Likewise, cadmium reagents add in the conjugate manner to ethyl nitrocinnamates without affecting the nitro function.¹³³



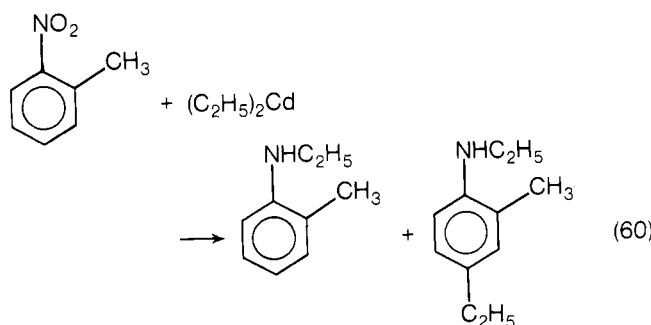
Although α -nitro ketones may lead to a complex mixture with cadmium reagents, in all of the products the nitro group is still present. An example is the addition of the ethylcadmium reagent to nitroacetone.⁹⁴



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



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, nitro-mesitylene, and *m*- and *p*-nitrotoluene.

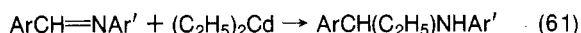


Because the reaction conditions for these reductive alkylations are extreme, it is reasonable to assume that nitro groups in general will survive treatment of a multifunctional compound with cadmium reagent under more usual conditions.

D. Miscellaneous Nitrogen Compounds

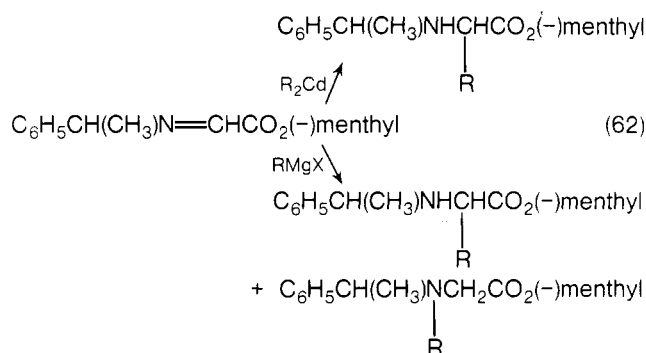
1. Imines

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



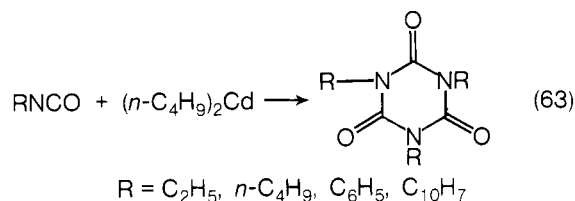
A study was made of the effect of substituents (*p*-OMe, *p*-Me, *p*-Cl, *m*-Cl) in both rings on the rate of addition,^{138,139} which appears to have little or no nucleophilic character, for the Hammett ρ values, although small (0.4–1.4), are negative. Thus, electron-withdrawing substituents slightly 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

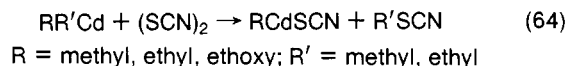
In contrast to the case with Grignard reagents, isocyanates do not undergo simple addition with in situ alkylcadmium reagents but rather trimerize.¹⁴²



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 $(\text{SCN})_2$ 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



4. Nitric Oxide

Nesmeyanov and Markarova reported formation of " $\text{C}_6\text{H}_5\text{N}=\text{NNO}_3$ " 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

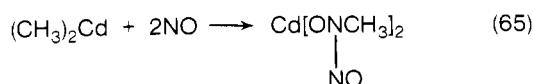


TABLE IV. Conjugate Addition of In Situ Cadmium Reagents to Unsaturated Compounds

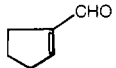
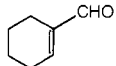
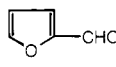
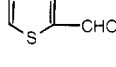
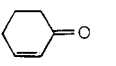
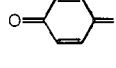
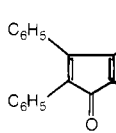
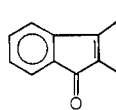
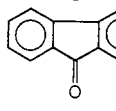
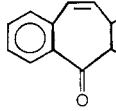
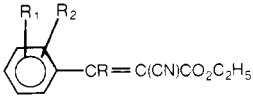
	unsatd compd	Cd reagent (R =)	1,2- addition	1,4- addition	ref
I. Aldehydes					
1.	$\text{CH}_2=\text{CHCHO}$	C_2H_5	10	0(25) ^a	149, 150
2.	$\text{CH}_2=\text{CHCHO}$	C_6H_5	45	0(33) ^a	149, 150
3.	$\text{CH}_3\text{CH}=\text{CHCHO}$	CH_3	14	<1	150
		C_2H_5	58	2	150
		<i>n</i> - C_4H_9	40	2	150
4.	$\text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$	CH_3	72	6	150
		CH_3	3	22	150
5.		C_2H_5	51	49	150
		<i>n</i> - C_4H_9	59	41	150
		CH_3	30	5 (starting material recovered, 43%)	150
6.		C_2H_5	56	16	150
		CH_3	82	0	150
7.		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.	$\text{CH}_2=\text{CHCOCH}_3$	CH_3	trace	5	106
10.	$\text{CH}_2=\text{CHCOCH}_3$	C_2H_5	≈ 1	3, 7 (10) ^a	106, 149
11.	$\text{CH}_3\text{CH}=\text{CHCOCH}_3$	CH_3	trace	5 (83, 89) ^a	106, 149
12.	$\text{CH}_3\text{CH}=\text{CHCOCH}_3$	C_2H_5	<1	6 (44, 50) ^a	106, 149
13.	$\text{CH}_3\text{CH}=\text{CHCOCH}_3$	iso- C_4H_9	<1	4 (44) ^a	149
14.	$(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3^b$	C_2H_5	40	0	106
15.	$(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)\text{COCH}_3^b$	C_2H_5	10	0	106
16.	$\text{CH}_3\text{CH}=\text{C}(\text{COCH}_3)_2$	C_2H_5	0	95	106
17.	$\text{C}_6\text{H}_5\text{CH}=\text{CHCOC}_6\text{H}_5$	C_6H_5	0	100	151
18.	$\text{C}_6\text{H}_5(\text{COCH}_3)=\text{C}(\text{C}_6\text{H}_5)\text{COCH}_3$	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
		<i>n</i> - C_4H_9	100	0	106
		C_6H_5	100	0	106
23.		C_2H_5	91	0	106
		<i>n</i> - C_4H_9	93	0	106
		C_6H_5	93	0	106
24.		C_2H_5	86	0	106
		C_2H_5 (purified)	0-1	0	106
		<i>n</i> - 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.	$\text{CH}_3\text{CH}=\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2$	$\alpha\text{-C}_{10}\text{H}_7$	0	60 ^c	153
27.	$\text{CH}_3\text{CH}_2\text{CH}=\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2$	$\alpha\text{-C}_{10}\text{H}_7$	0	65 ^c	153
28.	$(\text{CH}_3)_2\text{C}=\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2$	<i>n</i> - C_4H_9	0	28 (diethyl isopropylmalonate, 34%)	156
29.	$(\text{CH}_3)_2\text{CHCH}=\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2$	$\alpha\text{-C}_{10}\text{H}_7$	0	77 ^c	153
30.	$\text{CH}_3\text{CH}=\text{C}(\text{COCH}_3)\text{CO}_2\text{C}_2\text{H}_5$	C_2H_5	0	85	106
31.	$(\text{CH}_3)_2\text{CHCH}=\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2$	$\alpha\text{-C}_{10}\text{H}_7$	0	33	154
32.	$(\text{CH}_3)_2\text{C}=\text{C}(\text{CN})_2$ $\text{CO}(\text{CH}_2)_2\text{CO}_2\text{C}_2\text{H}_5$	<i>n</i> - C_4H_9	0	5 (isopropyl malononitrile, 39%)	156

TABLE V. (Cont)

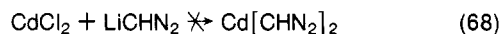
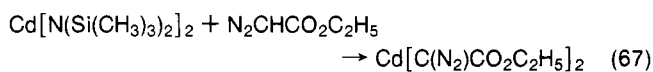
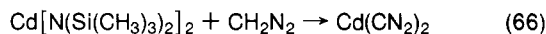
	unsatd compd	Cd reagent (R =)	1,2- addition	1,4- addition	ref
33.	(CH ₃) ₂ C=C(CN)CO ₂ C ₂ H ₅	<i>n</i> -C ₄ H ₉	0	15 (saturated cyano ester, 23%)	156
		C ₆ H ₅	0	12	156
		C ₆ H ₅ CH ₂	0	92	156
34.	C ₂ H ₅ C(CH ₃)=C(CN)CO ₂ C ₂ H ₅	<i>n</i> -C ₃ H ₇	0	12 (saturated cyano ester, 59%)	155
		C ₆ H ₅	0	26	155
		C ₆ H ₅ CH ₂	0	93	155
35.		C ₂ H ₅	0	8 (various adducts obtained; no yields recorded)	133
36.	CH ₃ CH=CHNO ₂	C ₂ H ₅	0	60	132
		<i>n</i> -C ₄ H ₉	0	55	132
		C ₆ H ₅	0	55	132
37.	C ₂ H ₅ CH=CHNO ₂	C ₂ H ₅	0	55	132
		<i>n</i> -C ₄ H ₉	0	60	132
		C ₆ H ₅	0	50	132
38.	(CH ₃) ₂ CHCH=CHNO ₂	C ₂ H ₅	0	55	132
		<i>n</i> -C ₄ H ₉	0	60	132
		C ₆ H ₅	0	50	132
39.	C ₆ H ₅ CH=CHNO ₂	C ₂ H ₅	0	76	132
		<i>n</i> -C ₄ H ₉	0	70	86, 132
		C ₆ H 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).

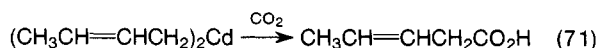
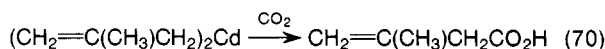
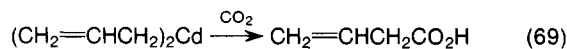


Although the diazo-containing cadmium compounds decompose readily (cadmium diazomethane is explosive), their formation illustrates the indifferent reactivity of the diazo group (as well as esters) toward organocadmium compounds.

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 CO₂.¹⁴⁴

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



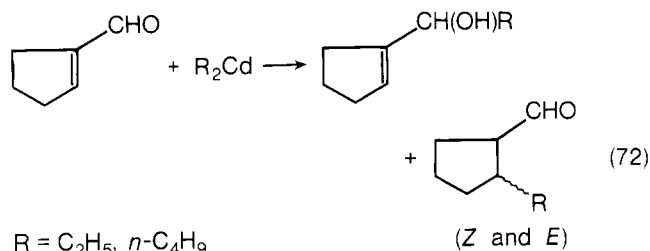
The lack of investigation in this area can be attributed to the fact that it offers no synthetic advantage over the carbonation of Grignard or lithium reagents.

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}

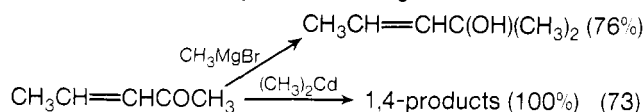
For the cases of crotonaldehyde with *n*-butylcadmium and of cyclopentene-1-carboxaldehyde with methylcadmium, it was shown that the tendency for 1,4-addition was enhanced by the presence of cuprous iodide and suppressed by increasing the Cd/aldehyde ratio.^{149,150} Only with cyclopentene-1-carboxaldehyde, 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



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

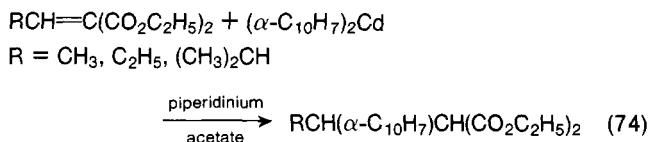


products from the latter case was the result entirely of a sequence of 1,4-additions.

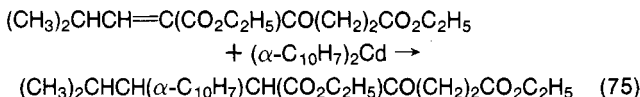
Benzalacetophenone gave the 1,4-adduct with phenylcadmium reagent in quantitative yield;¹⁵¹ although the phenyl Grignard reagent is known to produce predominantly the same product, there is, nevertheless, some 1,2-adduct as well.¹⁵²

2,3:6,7-Dibenzotropone is recovered unchanged after treatment under forcing conditions with the ethylcadmium reagent. Fluorenone⁸⁵ and other highly conjugated cyclanones react extensively in the 1,2 manner under milder conditions.¹⁰⁶

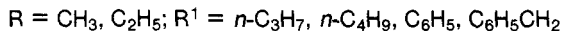
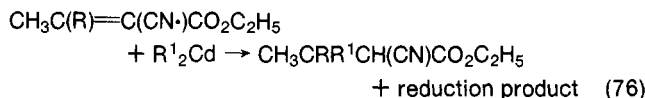
An early report by Riegel¹⁵³ indicated that the enhanced 1,4-addition with cadmium over magnesium reagents also prevailed with alkylidenemalonate esters. The saturated malonic esters from α -naphthyl reagent were isolated in higher yields from the cadmium compound in each case. It was noted, however, that piperidinium acetate facilitated the cadmium reaction, and so this salt was added to the reaction mixtures.



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

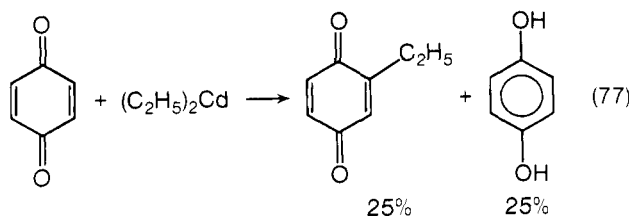


It was noted by Prout^{155,156} that alkylidene cyanoacetic esters behaved in the contrary way: 1,4-addition was higher with Grignard than with cadmium reagents, the examples being the propyl, butyl, and phenyl organometallics. Only in the case of the benzyl reagents did the cadmium compound afford the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



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

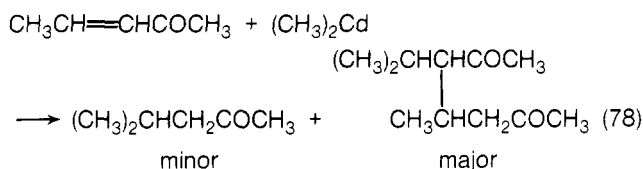
The 1,2- and 1,4-additions in conjugated compounds are likely to be accompanied by side reactions. If the cadmium reagent contains β hydrogens, it might be expected that reduction would occur. This is particularly the case with benzoquinone,^{92,93} where hydroquinone accounts for one-half the product.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



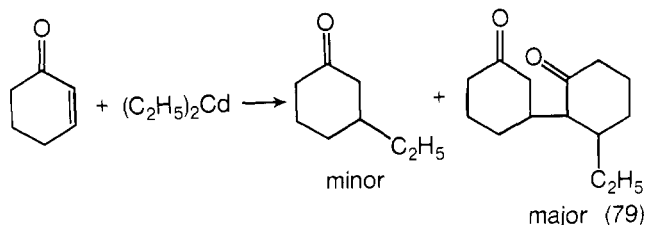
with the phenylcadmium reagent as well points to other pathways to reduction.⁹²

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

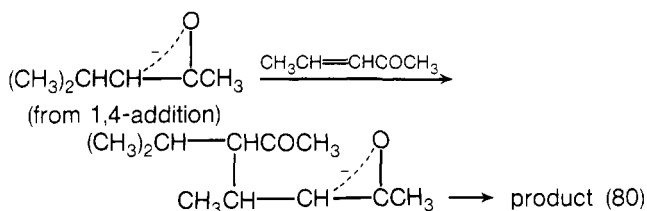
"Simple" 1,4-addition is followed by further Michael condensations with some conjugated ketones; in fact, this sequence accounts for all or most of the final products in some cases. For example, of the 1,4-addition product between 3-penten-2-one and methylcadmium reagent, all but 5% of it is the bimolecular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



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



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.



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 1,4-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 Fessenden¹⁵⁸ reported that some secondary and tertiary halides (2-iodooctane, 2-bromobutane, *tert*-butyl chloride, *tri-n*-propylcarbonyl chloride) were either inert toward *in situ*

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

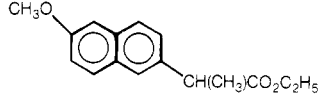
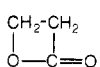
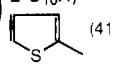
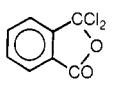
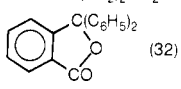
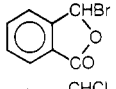
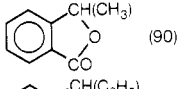
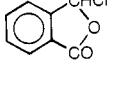
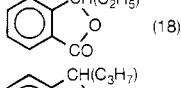
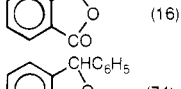
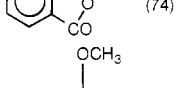
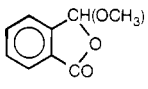
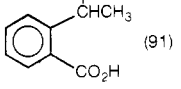
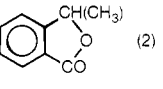
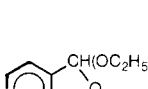
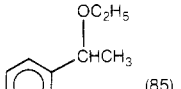
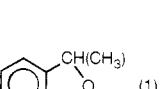
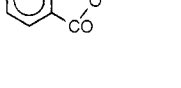
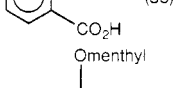
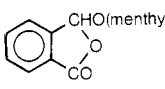
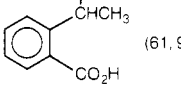
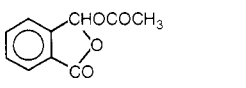
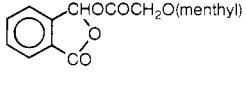
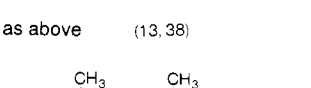
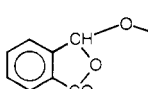
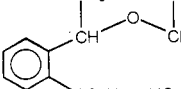
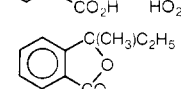
	Reactant	Cd reagent (R =)	product(s) (yield, %)	ref
1.	$C_6H_5COOCH(Cl)C_6H_5$	C_6H_5	$C_6H_5COOCH(C_6H_5)_2$ (29)	a
2.	$(C_6H_5COO)_2CHC_6H_5$	C_6H_5	$C_6H_5COOCH(C_6H_5)_2$ (13)	a
3.	$C_6H_5CO_2CH(Cl)CH=CHC_6H_5$	C_6H_5	$(C_6H_5)_2CHCH=CHC_6H_5$ (25)	a
4.	$BrCH_2CO_2C_2H_5$	C_6H_5	$C_6H_5CH_2CO_2C_2H_5$ (11, 26, 46, 53)	174
5.	$BrCH_2CO_2C_2H_5$	$\alpha-C_{10}H_7$	$\alpha-C_{10}H_7CH_2CO_2C_2H_5$ (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.	$CH_3CH(Br)CO_2C_2H_5$	$\alpha-C_{10}H_7$	$CH_3CH(\alpha-C_{10}H_7)CO_2C_2H_5$ (55)	179
9.	$CH_3CH(Br)CO_2C_2H_5$	6-(CH_3O)-2- $C_{10}H_8$		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)		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)

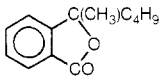
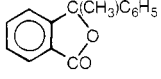
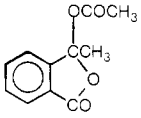
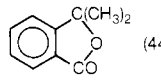
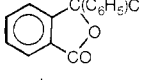
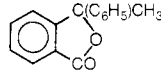
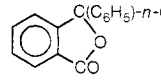
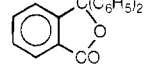
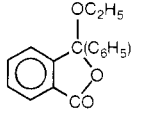
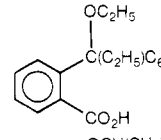
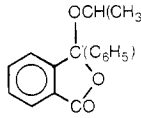
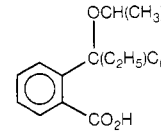
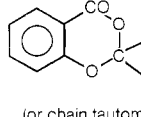
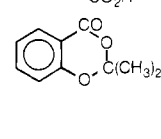
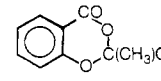
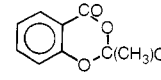
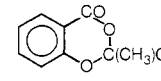
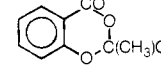
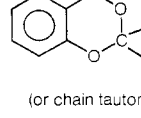
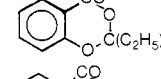
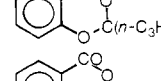
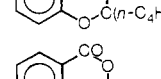
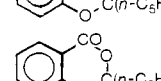
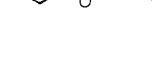
	Reactant	Cd reagent (R =)	product(s) (yield, %)	ref
28.	as above	C ₄ H ₉	 (60)	175
29.	as above	C ₆ H ₅	 (42)	175
30.		CH ₃	 (44)	128
31.		CH ₃	 (80)	175
32.	as above	CH ₃	as above (88)	127
33.	as above	<i>n</i> -C ₄ H ₉	 (80)	127
34.	as above	C ₆ H ₅	 (70)	127
35.	as above	C ₆ H ₅	as above (45)	175
36.		C ₂ H ₅	 (87)	a
37.		C ₂ H ₅	 (19)	a
38.	 (or chain tautomer)	CH ₃	 (98, crude)	c
39.	as above	C ₂ H ₅	 (60, 75)	d
40.	as above	C ₃ H ₇	 (62)	d
41.	as above	C ₄ H ₉	 (63)	d
42.	as above	+ C ₆ H ₅	 (73)	d
43.	 (or chain tautomer)	CH ₃	as above (64)	e
44.	as above	C ₂ H ₅	 (26)	e
45.	as above	<i>n</i> -C ₃ H ₇	 (43)	e
46.	as above	<i>n</i> -C ₄ H ₉	 (55)	e
47.	as above	<i>n</i> -C ₅ H ₁₁	 (57)	e
48.	as above	<i>n</i> -C ₆ H ₁₃	 (41)	e

TABLE V. (Cont)

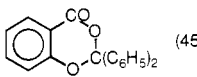
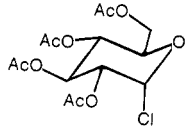
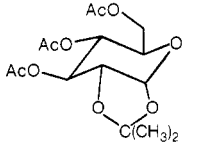
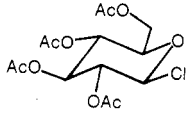
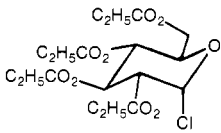
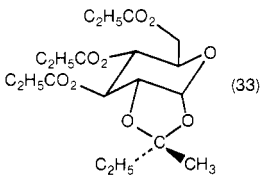
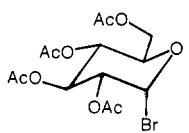
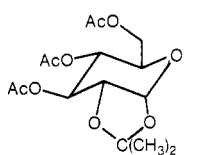
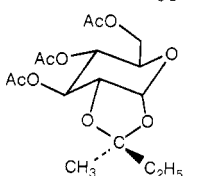
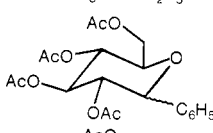
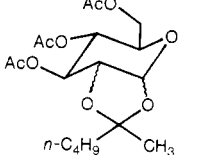
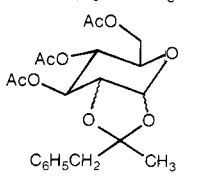
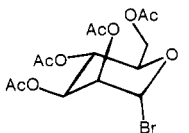
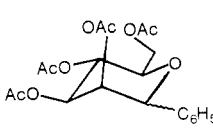
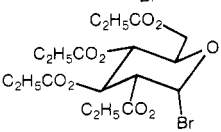
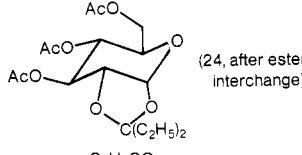
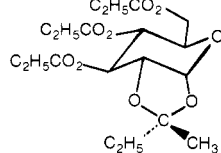
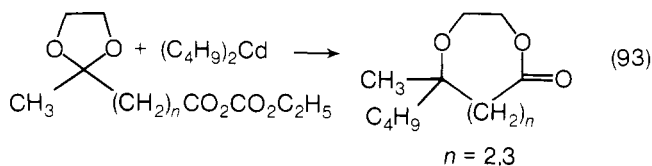
	Reactant	Cd reagent (R =)	product(s) (yield, %)	ref
49.	as above	C ₆ H ₅	 (45)	e
50.		CH ₃	 (33)	f
51.		CH ₃	as above (57)	f
52.		CH ₃	 (33)	f
53.		CH ₃	 (40)	f
54.	as above	C ₂ H ₅	 (36)	f
55.	as above	C ₆ H ₅	 (23)	177
56.	as above	n-C ₄ H ₉	 (57)	177
57.	as above	C ₆ H ₅ CH ₂	 (-)	177
58.		C ₆ H ₅	 (29)	177
59.		C ₂ H ₅	 (24, after ester interchange)	f
60.	as above	CH ₃	 (39)	f

TABLE V. (Cont)

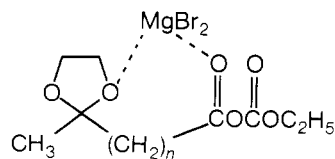
	Reactant	Cd reagent (R =)	product(s) (yield, %)	ref
61.		C_6H_5		(after saponification) 178
62.	as above			g
63.	as above			h
64.				h

^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. Zieliński, and C. Pillar, *ibid.*, **10**, 320 (1967).

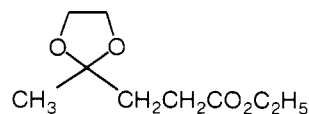
It was proposed by LeMahieu¹⁷⁰ that this interesting formation of eight- and nine-membered lactones depends upon coordi-



nation of $MgBr_2$ between the ketal oxygen and the carbonyl group, as depicted below. Support for this explanation is the

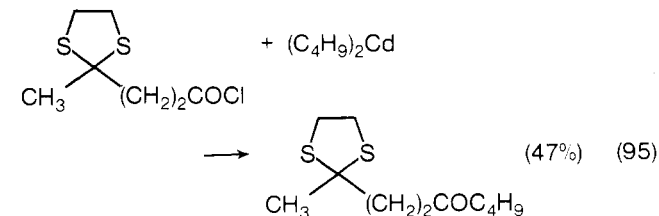
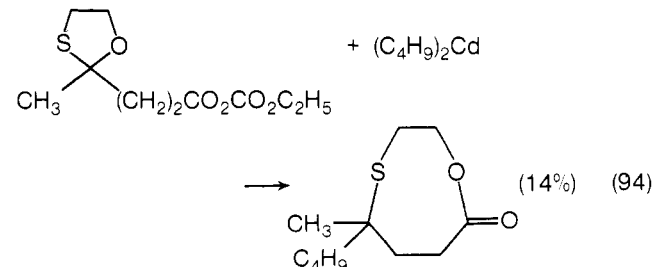


observation that purified dimethylcadmium results, not in cleavage of the dioxalane ring, but in generation of the ester. This

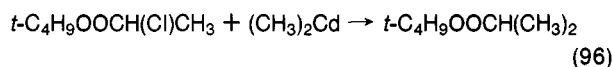


ethyl ester presumably forms as a result of cleavage of solvent ether, for which there is ample precedent,⁷ or from ethoxide originating from the mixed anhydride.

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

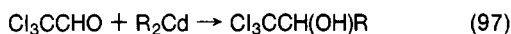


tert-Butyl 1-chloroethyl peroxide reacted with dimethylcadmium to afford the displacement product, *tert*-butyl isopropyl peroxide, in 50% yield.

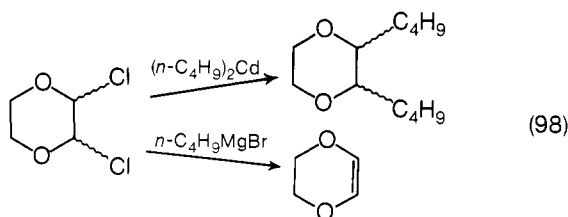


With lithium reagents the halo peroxide tended to undergo α -elimination instead.¹⁷²

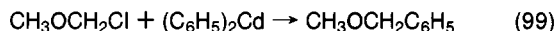
It was reported in 1963 that polychlorinated aliphatic aldehydes and ketones (of unspecified structure) for the most part undergo addition at the carbonyl, rather than displacement of halogen, with in situ cadmium reagents.⁷⁸ Chloral, for example, was reported to afford the secondary alcohol in 45–70%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



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.

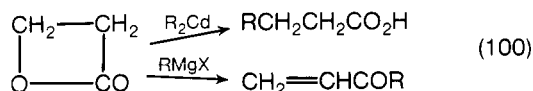


In an analogous manner, chloromethyl methyl ether formed benzyl methyl ether (34%) with the phenylcadmium reagent.¹⁶⁴

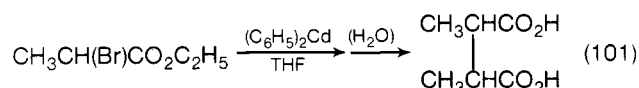


In general, esters and lactones are not attacked by addition under conditions where cadmium reagents cause displacement at saturated carbon. All the known instances of this preferential displacement over addition are assembled in Table V. Although the number of examples is limited, certain generalizations 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 $\text{Br}, \text{Cl} > \text{OCOR} > \text{OR}$. 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

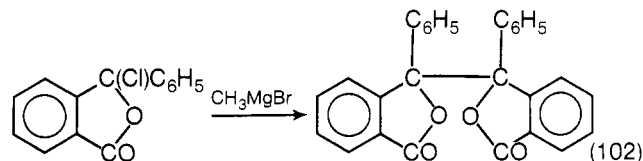
Propiolactone is reactive with some organocadmium reagents, probably because of the strain relieved when the ring opens. It is of interest that ring opening proceeds by attack at the *saturated* carbon (displacement), not by addition at the carbonyl. Most Grignard reagents (except benzylic and allylic)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



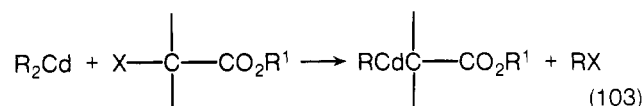
It has been noted in some instances that symmetrical coupling accompanies displacement in multifunctional compounds. For example, 2,3-dimethylsuccinic acid was isolated after hydrolytic workup from the reaction mixture from ethyl α -bromopropionate



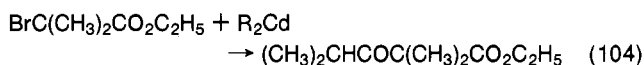
and phenylcadmium reagent in THF.¹⁷⁴ Similar coupling products were detected from α -bromoisobutyrate and α -bromoisovalerate esters.¹⁶⁴ There is some indication that symmetrical coupling is less prevalent with cadmium reagents than it is with Grignard reagents. Thus, whereas 3-chloro-3-phenylphthalide (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



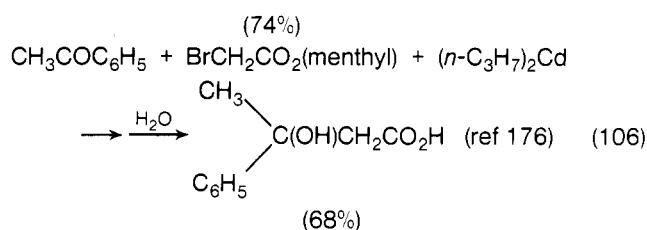
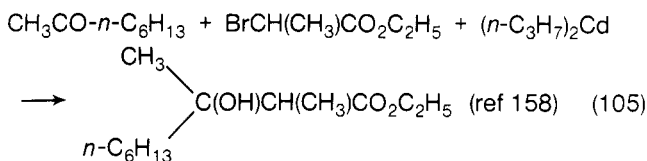
An alternative course of the reaction with α -halo esters and cadmium reagents is dehalogenative enolization.



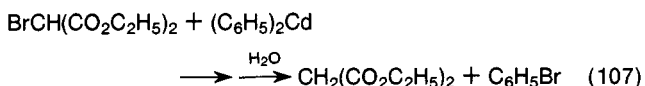
Cason and Fessenden reported formation of the β -keto ester product from ethyl α -bromoisobutyrate in the presence of *n*-butylcadmium or *n*-dodecylcadmium reagent.¹⁵⁸ It seems most plausible that the β -keto ester is a Claisen condensation product from the enolate.



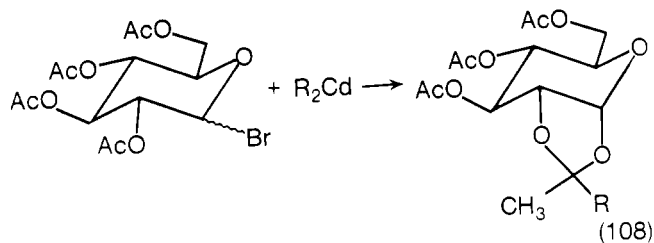
The enolate, resembling the classical Reformatsky reagent, is probably the intermediate in the condensation between α -bromo esters and ketones, induced by cadmium reagents.



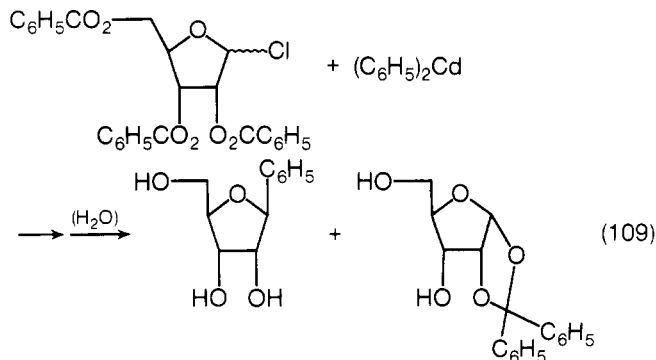
Similar Claisen products were not found in cases where the phenylcadmium reagent was employed with simple α -halo esters,^{164,174} but the dehalogenative enolization with bromomalonate was extensive¹⁷⁴ and bromobenzene was shown to be produced in equimolar amount.¹⁷⁴ Presumably the cadmium enolate $\text{C}_6\text{H}_5\text{CdCH}(\text{CO}_2\text{C}_2\text{H}_5)_2$ is generated, along with bromobenzene, before the hydrolytic step.



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 bromide¹⁷⁷ (entries 55 and 56). Although Hurd and Holysz observed that neighboring group participation occurred with butyl- and benzylcadmium reagents and not the phenyl re-



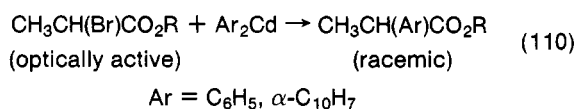
agent,¹⁷⁷ it has subsequently been shown that similar products can be formed in the ribose series with the phenyl reagent as well. An example is the behavior of the benzoyl-protected ribofuranosyl chloride¹⁷⁸ (entry 61).



D. Mechanism

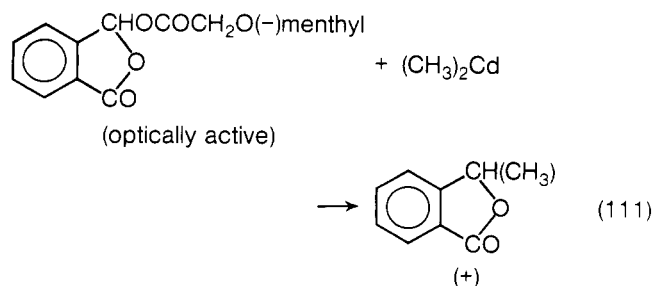
Very little information is available which can be used in support of one or more mechanisms for displacement at saturated carbon. The order of ease of leaving group displacement—Cl, Br > OCOR > OR—is in line with a nucleophilic process. On the other hand, there is evidence from ESR spectroscopy for the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

Both stereoselective and nonstereoselective displacements have been recorded. Optically active α -bromopropionate esters react with phenyl¹⁶⁴ and α -naphthyl¹⁷⁹ cadmium reagents to afford racemic α -arylpropionate esters.



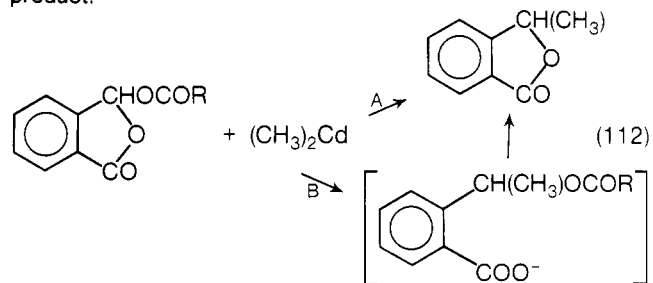
It was shown that both the starting ester^{164,179} and product¹⁷⁹ were optically stable under the reaction conditions. Consistent with this finding is the fact that the reaction with phenylcadmium reagent generates free radicals, so an electron-transfer process¹⁶⁴ is a plausible pathway for this conversion.

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

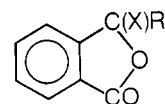


Although the absolute configuration of the 3-methylphthalide is known to be *R*,¹⁸¹ it is not known whether the displacement proceeded with net retention or inversion, inasmuch as the configuration and optical purity of the starting material could not be determined.

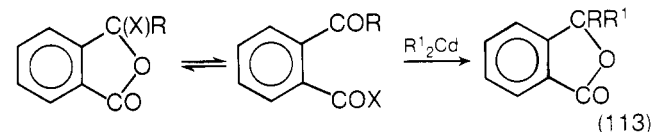
The formation of 3-methylphthalide could occur "directly", as represented in path A (eq 112), or "indirectly" by sequential displacement of endocyclic and exocyclic acyloxy groups, as represented in path B. In either case, the steps must be concerted to account for retention of optical activity in the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



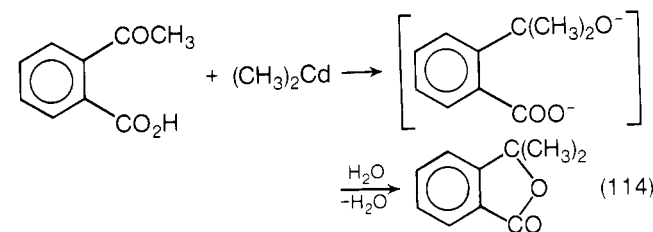
Other phthalide compounds with a potential leaving group "X" in the 3 position:



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.



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-} ".



VII. Rearrangements

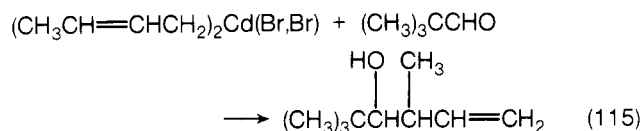
Rearrangement in the alkyl or aryl moiety of the cadmium reagent seems to be an area which has received little attention.

A. Allylic Compounds

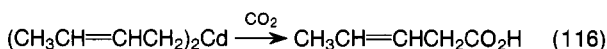
Of the few rearrangements which have been reported, most have been observed in allylic structures. From recent reviews of allylic organometallics,^{124,183-185} it is evident that rearrangements are known to occur more widely in allylic compounds of lithium, sodium, magnesium, and even zinc, than in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

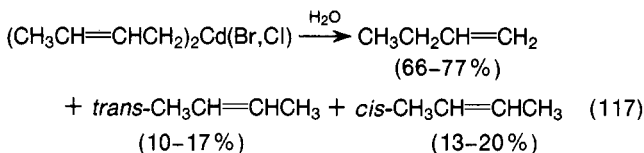
spectral analysis. As an example, the in situ crotylcadmium reagent is reported to afford 2,2,4-trimethyl-5-hexen-3-ol with pivalaldehyde.^{103,120} Other carbonyl compounds which give the "rearranged" alcohols are methyl ethyl ketone, diethyl ketone, butyraldehyde, and benzaldehyde.



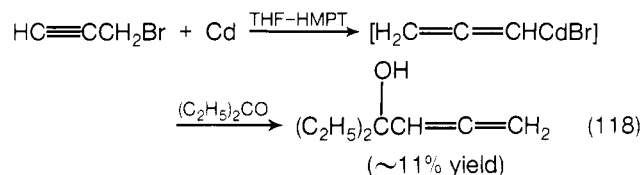
The crotylzinc reagent, halide-free, prepared from the boron compound, is reported^{102,105} to decompose with deposition of metallic cadmium under comparable reaction conditions. Subjected to air oxidation, it affords a mixture of *Z* and *E* crotyl alcohols, but-1-en-3-ol, and C_8 coupling products.¹⁸⁶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



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

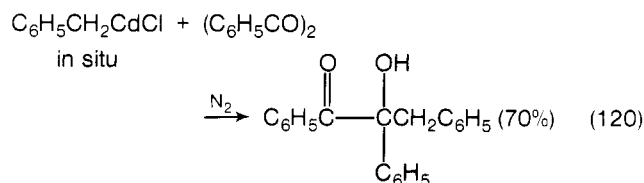
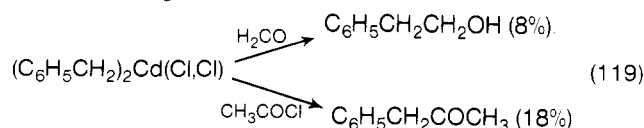


Propargyl bromide and metallic cadmium in THF-HMPT give rise to a solution whose infrared spectrum exhibits a significant band at 1903 cm^{-1} , which was interpreted by Moreau and



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

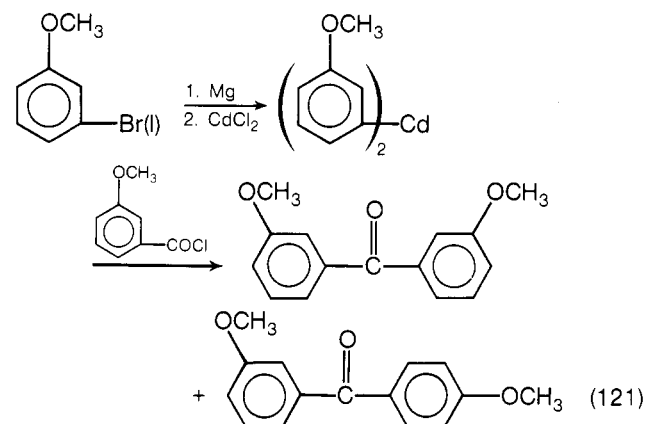
Although benzylcadmium reagents have received only cursory attention, they appear to give unrearranged (benzyl) products, in contrast to the benzyl Grignard reagents. As early as 1939, Gilman and Nelson reported formation in low yield of "normal" products from in situ benzylcadmium with formaldehyde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



B. Aryl Compounds

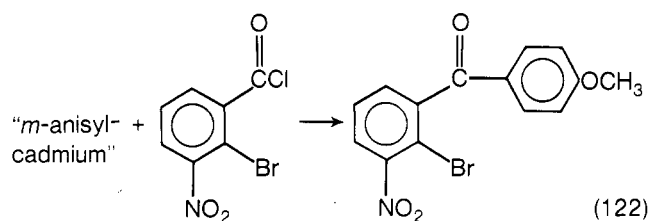
A rearrangement in the aryl moiety of an in situ arylcadmium compound was first reported by Klemm, Mann, and Lind in

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.



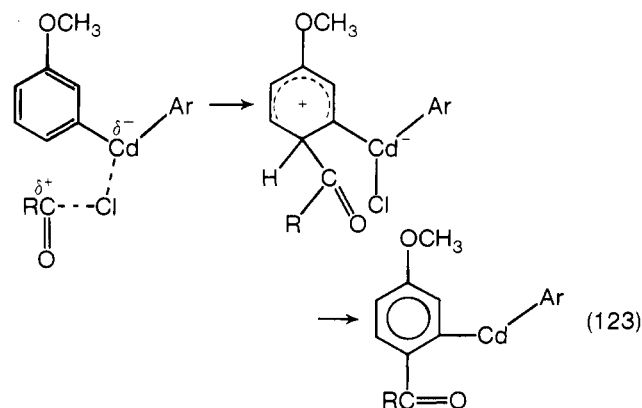
Dauben and Collette¹⁹⁰ observed the same peculiar behavior of the "*m*-anisyl" cadmium reagent. Rearranged, *p*-anisyl products were identified in reactions with 1-cyclohexenecarbonyl chloride, acetyl chloride, β -carbomethoxypropionyl chloride, and acetic anhydride, but only "normal" products could 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-

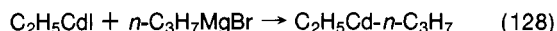


trophthalic anhydride.¹⁹¹ The reactions of *m*-anisylcadmium reagent are summarized in Table VI.

Clearly, the coreactant with the cadmium reagent plays a role in this curious rearrangement. Klemm, Mann, and Lind¹⁸⁹ and Dauben and Collette¹⁹⁰ 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:

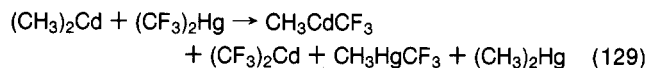


ganometallics was found to be: $\text{Me}_2\text{Cd} > \text{Me}_2\text{Zn} > \text{Me}_2\text{Mg}$. The preexchange lifetime for a 1:1 mixture of dimethylmagnesium and dimethylcadmium in THF, for example, was estimated to be less than 0.007 s at 28 °C.²⁰⁰ Apparently a rapid exchange occurs between " $\text{C}_2\text{H}_5\text{CdI}$ " (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



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 dialkylcadmium 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 $(\text{CH}_3)_3\text{Ga}$ being somewhat faster than that for $(\text{CH}_3)_3\text{In}$.²¹¹

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



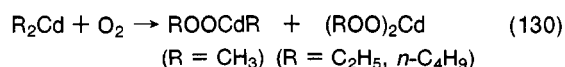
Equilibrium was established "rather quickly" at 34 °C. By noting the change in composition of the four products with varying amounts of initial cadmium and mercury compounds, it was concluded that CH_3CdCF_3 exchanges more slowly than dimethylcadmium. The rapid exchange with the perfluorinated mercury 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

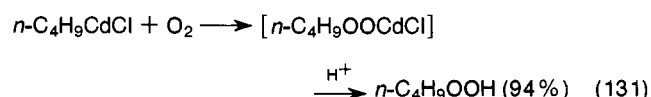
A. Reactions with Oxygen and Peroxides

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" $(\text{C}_2\text{H}_5)_2\text{Cd} \cdot 2\text{O}_2$ 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 diethyl- and di-*n*-butylcadmium are converted to diperoxy derivatives.^{134,217} The fact that peroxide formation was inhibited by galvinoxyl sug-

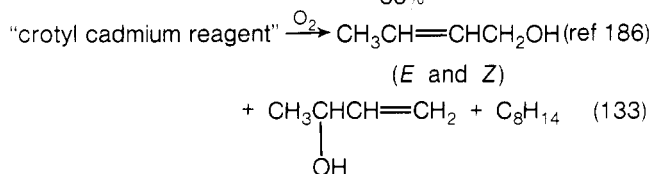
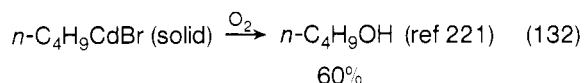


gested that the reaction could be formulated as a free-radical chain mechanism not involving a long-lived oxygen complex.²¹⁸ Hydroperoxides have been synthesized by controlled oxidation of organocadmium reagents with oxygen and hydrolysis of the resulting peroxide.^{219,220} The reaction, illustrated with *n*-butylcadmium chloride²¹⁹

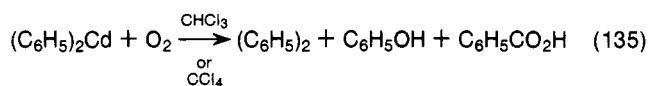
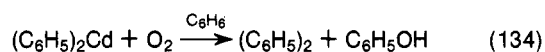


was also carried out with dibutylcadmium (95%), octylcadmium chloride (90%), and benzylcadmium chloride (86%). It was noted

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.

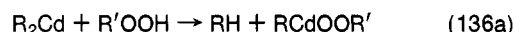


There seems to be very little information about the behavior of arylcadmium reagents toward oxygen. Diphenylcadmium in benzene gave some phenol but mainly biphenyl, which was shown from labeling studies to come from radical attack on benzene.²²² Oxidation of diphenylcadmium in chloroform or carbon tetrachloride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



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

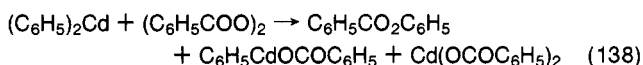
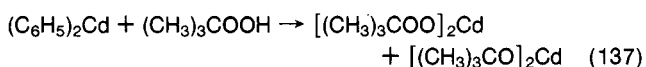
An alternative route to peroxy cadmium compounds is the reaction of purified alkylcadmium reagents with hydroperoxides, which might be visualized as a nucleophilic displacement by the cadmium reagent on hydrogen.²¹⁷



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



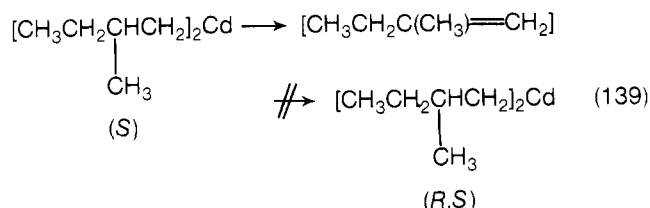
Dimethylcadmium and *tert*-butylperoxy radicals, generated thermally from di-*tert*-butyl hyponitrite, react to form methyl radicals, which are detected by ESR spectroscopy.²²⁵

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

B. Thermal Reactions

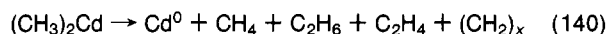
Diethylcadmium decomposes at 250–290 °C to deposit

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.

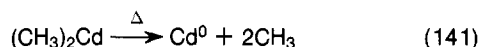


Thermal decomposition of diphenylcadmium in ¹⁴C-labeled benzene at 215–220 °C for about 80 h afforded, after removal of solvent and hydrolysis, benzene (50%) and biphenyl (50%), each containing a small amount of radioactive label.²²⁹

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



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}



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

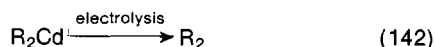
C. Photolysis

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 ¹⁴C-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}



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

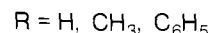
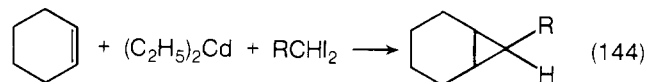
alkanes. Dotriacontane and hexatriacontane, for example, are produced in higher yield by coupling of the hexadecyl and octadecylcadmium reagents, respectively, than from other organometallics.²⁴¹ Several terpene derivatives were coupled, including farnesyl halide, which afforded squalene, albeit in only 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

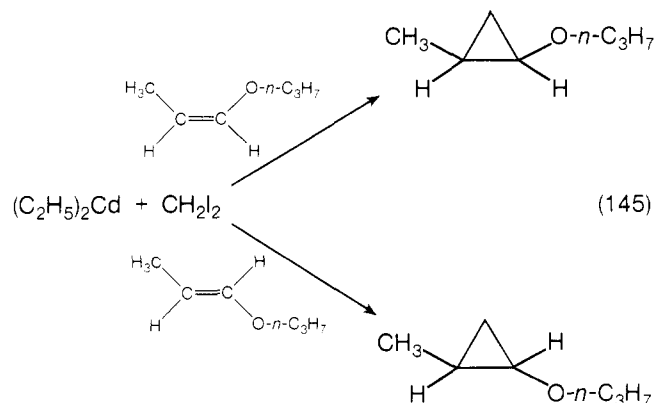
The interaction of diethylcadmium (and zinc) with carbon tetrachloride and chloroform leads to dichlorocarbene formation, the evidence for the divalent intermediate being the trapping product with cyclohexene and 1-chloropropene, presumed to form by an insertion of dichlorocarbene into the carbon–cadmium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

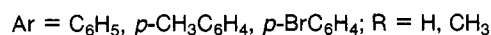
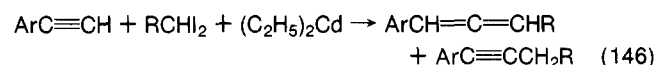


The addition of substituted carbenoids to cyclohexene (R = methyl, phenyl) is less stereoselective in favor of the syn isomer than is the corresponding zinc carbenoid; in fact, the anti isomer predominates slightly in the product from 1,1-diodoethane (R = CH₃).

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



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

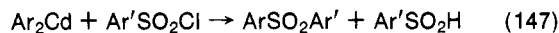


F. Reactions with Sulfur-Containing Functional Groups

1. Sulfonyl Chlorides

Gilman and Nelson first noted that the in situ phenylcadmium reagent (from bromide-free Ar₂Mg) and benzenesulfonyl chloride

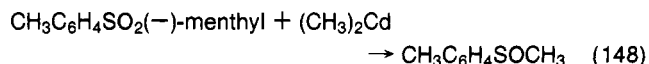
led to formation of diphenyl sulfone (15%), benzenesulfonic acid, and chlorobenzene (15%).⁶ This reaction was apparently not investigated further until 1957, when Henze and Artman explored its utility as a synthetic route to sulfones.²⁴³ The yields of diaryl sulfones from a variety of arenesulfonyl chlorides generally ranged from 30 to 46%, although in one case (*p*-chlorophenyl cadmium reagent and benzenesulfonyl chloride) it was as high as 61%. Arenesulfonic 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.



Quite recently these general results have been confirmed;²⁴⁴⁻²⁴⁶ that is, sulfones are obtained in moderate to low yield along with arenesulfonic 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.

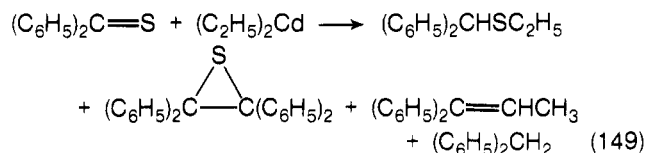
2. Sulfinate Esters

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.



3. Thioketones

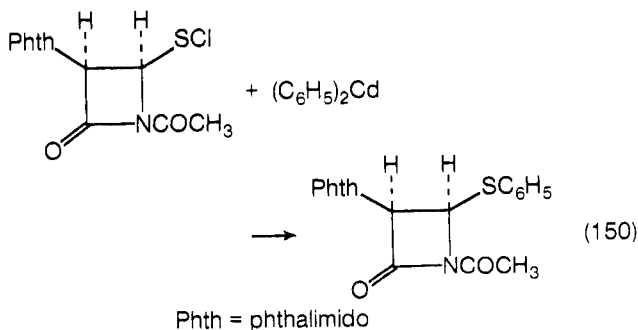
Thiobenzophenone is converted to a variety of products with the ethylcadmium reagent in THF, and about one-half the starting material is recovered.²⁴⁸ Similar products are formed with the *n*-propylcadmium reagent.



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

4. Sulfonyl Chlorides

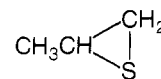
A displacement with diphenylcadmium in THF at a sulfonyl chloride was used to generate a sulfide in a penicillin synthesis. The selectivity for reaction at the sulfonyl chloride over that at any of the imide functions is difficult to assess, however, inasmuch as the yield was only 3%.²⁴⁹



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-CH₃COSH combination, which is superior to diethylcadmium combined with alcohol, mercaptan, or carboxylic acid.²⁵⁴

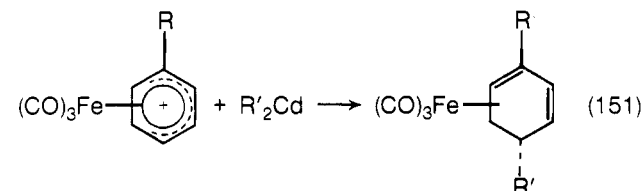
Cadmium alkoxides (ROCdC₂H₅), from optically active alcohols and diethylcadmium, have been used in initiating vinyl polymerizations.²⁵⁵

H. Other

Decaborane (B₁₀H₁₄) is metalated with diethylcadmium in ether to form CdB₁₀H₁₂·2Et₂O, 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.



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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