

THE REACTION OF ORGANOZING COMPOUND
WITH CARBON MONOXIDE

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
TSENWHEI HELEN YU

1970

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ABSTRACT

THE REACTION OF ORGANOZINC COMPOUND WITH CARBON MONOXIDE

by Tsenwhei Helen Yu

Organozinc compounds can be activated to react with carbon monoxide with the use of a proper catalyst. The reaction produces an acyloin. Using potassium tert-butoxide as catalyst, carbon monoxide reacts with di-n-butyl zinc to yield n-valeroïn; with diisopropyl zinc to yield isobutyroïn; with diphenyl zinc, no definite products are isolated. The reaction yield depends on temperature, solvent and catalyst. The conditions for optimum yield are to run the reaction at -15°C with diglyme as solvent and with potassium tert-butoxide as catalyst.

THE REACTION OF ORGANOZINC COMPOUND WITH CARBON MONOXIDE

By

Tsenwhei Helen Yu

A THESIS

Submitted to
Michigan State University
In partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemistry

1970

G 651411
1-15-71

ACKNOWLEDGMENTS

The author wishes to express her deep gratitude to Dr. M. W. Rathke for his patience and continuous guidance through the course of this research. Thanks are also due to her committee members, Dr. W. H. Reusch and Dr. J. B. Hamilton, for their time and interest in this work.

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INTRODUCTION

The reaction of carbon monoxide with organometallic compounds has been extensively studied by many workers. The results of these studies have provided convenient, high yield syntheses for a variety of novel products. Certain organometallics, such as organoboron, organomagnesium and organomercury compounds have been found to react directly with carbon monoxide. On the other hand, certain organometallics, such as organoaluminium, organogallium and organoindium compounds are inert to carbon monoxide. In many cases, the addition of small quantities of a catalyst to the reaction mixture promotes a reaction between carbon monoxide and organometallic compounds. In this thesis emphasis is focused on the reaction of carbon monoxide with zinc organometallic compounds. Such studies seem desirable in view of the fact that very little has been published on the reaction of zinc organometallic compounds with carbon monoxide. In order to provide a background for the explanations and discussions developed in later chapters, a brief review of related work is first presented.

LITERATURE REVIEW

(A) The reaction of carbon monoxide with the Grignard reagent

The reaction of carbon monoxide with the Grignard reagent was first studied in the early nineteenth century by several investigators. With reference to his unpublished works, Grignard stated that carbon monoxide might be expected to react with organomagnesium halides to yield aldehyde derivatives and secondary alcohols.¹ Vinay² reported that carbon monoxide reacts with Grignard reagents of the types R_2CHMgX and R_3CMgX to yield tertiary alcohols. Jegorawa³ reported the reaction of carbon monoxide with isopropylmagnesium bromide, tert-butylmagnesium chloride and tert-amylmagnesium chloride; however, no reaction took place between carbon monoxide and methylmagnesium iodide, phenylmagnesium bromide, t-heptylmagnesium bromide, or triphenylmethylmagnesium chloride.^{1,4}

Carbon monoxide also reacted freely with certain Grignard reagents when the reaction solution was activated by a small amount of nickel carbonyl.¹ Zelinski⁵ reported the formation of aldehydes and ketones by the action of nickel carbonyl on propylmagnesium iodide. From the reaction products of phenylmagnesium iodide and nickel carbonyl, H. O. Jones⁶ was able to isolate biphenyl and benzoin.

In a similar experimental study of the reaction

between nickel carbonyl, carbon monoxide and Grignard reagents, Gilliland and Blanchard⁷ found that the reaction was initiated by adding slowly a clear ethereal solution of nickel carbonyl to an ether solution of phenylmagnesium bromide, and was maintained by passing carbon monoxide into the reaction mixture. In this process, the nickel carbonyl was continuously regenerated from the liberated nickel and fresh carbon monoxide. After hydrolysis and evaporation of the ether layer, the reaction products (crystalline products in a yellow oil) were vacuum distilled. The isolated substances included: (1) triphenylmethane, (2) triphenylvinyl alcohol, (3) pentaphenylethane and (4) tetraphenylethylene. In most cases, these identified substances constituted only a small part of the total products, while unidentified substances remained in a tarry residue. The yield of the identified substances was found to depend strongly on the rate of carbon monoxide absorption. When carbon monoxide absorption was slow, triphenylmethane was the predominant product. On the other hand, when carbon monoxide absorption was rapid and accompanied by violent stirring, triphenylvinyl alcohol was found more abundantly in the product. In contrast to Jones's finding, Gilliland and Blanchard were unable to isolate benzoin from the reaction product.

Using chromium chloride (CrCl_3) as the activation agent in an ethereal solution of phenylmagnesium bromide,

Job and Cassal⁸ found that the reaction mixture absorbed carbon monoxide at temperatures between -15°C and the boiling point of ether. From the crude reaction product they were able to isolate and identify the following substances: biphenyl, benzophenone, benzhydrol, triphenylvinyl alcohol, β -benzopinacolone, benzoin, benzil, triphenylmethane and traces of benzaldehyde, phenol and chromium carbonyl. These substances accounted for approximately 50 percent of the Grignard reagent used.

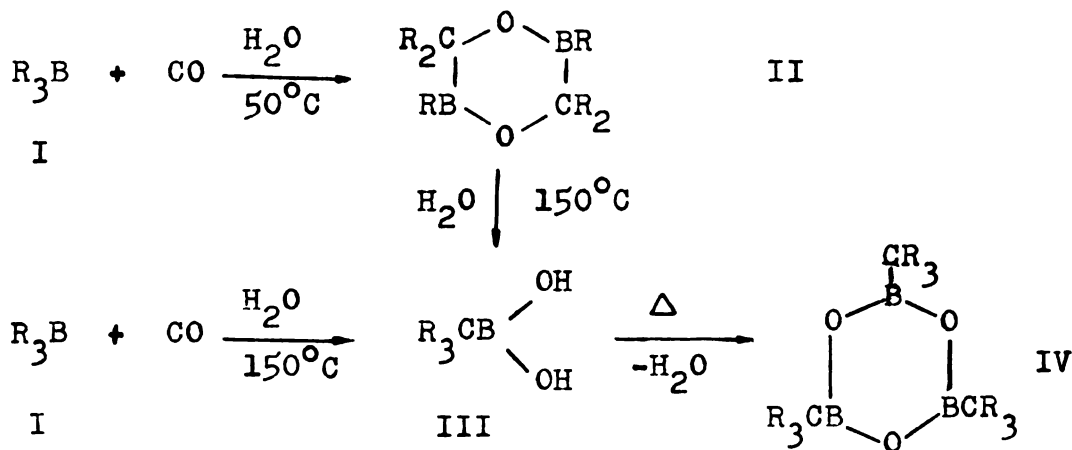
Fischer and Stoffers⁹ investigated reactions of carbon monoxide with Grignard reagents under carbon monoxide pressures from 50 to 180 atmospheres and at temperatures from 60°C to 160°C . They observed that carbon monoxide absorption was much faster when a small amount of halomagnesium alcoholates was present in the system. The alcoholates, which do not react with carbon monoxide themselves, were generated either by oxidation of the Grignard reagent or by addition of alcohol. Their work raised the question of whether or not there is in fact any uncatalyzed reaction of carbon monoxide with Grignard reagents.

Eidus et al¹⁰ reported that carbon monoxide under pressure reacted with n-butyilmagnesium bromide (also with n-butyilmagnesium chloride) to yield 4-nonene, and with isoamyilmagnesium bromide (also with isoamyilmagnesium chloride) to yield 2,8-dimethyl 4-nonene. In contrast

to the organomagnesium compounds, no calcium or beryllium organometallic compound has been found to react with carbon monoxide.

(B) Reaction of carbon monoxide with trialkylboranes

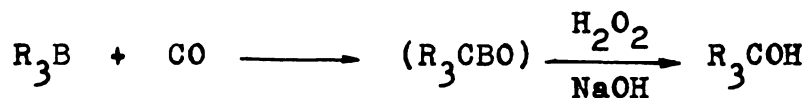
Of all the elements (i.e. B, Al, Ga, In and Tl) in the IIIA group in the periodic table, only boron organometallic compounds have been shown to react with carbon monoxide. In particular, the reaction of carbon monoxide with trialkylboranes has received the most attention. Hillman¹¹ reported that carbon monoxide reacted exothermally with trialkylboranes (I) to yield a variety of products which depend on the reaction temperature and solvent. Carbonylation of trialkylboranes in excess water at 25°C and 75°C yielded 2,3,3,5,6,6-hexaalkyl-2,5-dibora-1,4-dioxanes (II), whereas the same reaction at temperatures between 140°C and 175°C produced only the trialkylcarbonyl boronic acids (III). Vacuum distillation of the boronic acids gave boronic anhydrides (IV) which were oxidized to produce trialkylcarbinols.



This synthesis of trialkylcarbinols gave quantitative yields at high carbon monoxide pressure (in excess of 500 atmospheres); however, at atmospheric pressure, the reaction produced only low yields of alcohols (less than 40% after 24 hours reaction).

In an attempt to find a monomeric derivative of the boronic acid (II), Hillman prepared cyclic esters of trialkylcarbiny boronic acids having 5-7 atoms in the ring.¹² Similar studies with the hexaalkyl-2,5-diboradioxanes led to the following discovery: the reaction of trialkylboranes with carbon monoxide and aldehydes gave substituted 4-bora-1,3-dioxolanes.¹³

Recently, H. C. Brown and M. W. Rathke¹⁴ reported that carbon monoxide at atmospheric pressure readily reacts at 100°C-125°C with trialkylboranes, synthesized in situ in diglyme solution, to provide a convenient route to the corresponding trialkylcarbinols.

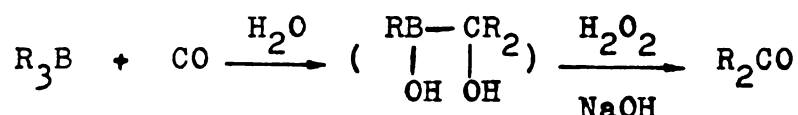


Carbon monoxide absorption was extremely slow at lower temperature (25°C). Approximately 1 mole of carbon monoxide was absorbed per mole of trialkylborane.

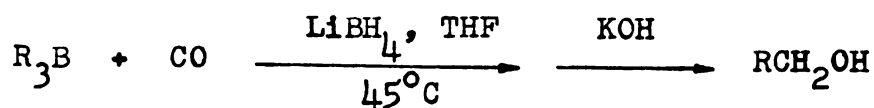
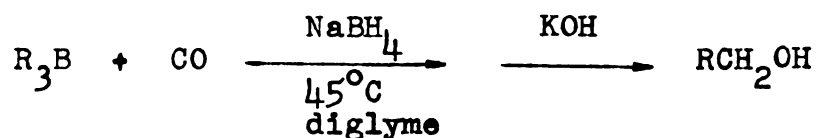
Complete absorption of gas requires a few days; however, the rate of absorption increased with increasing temperature, so that at high temperatures (100°C-125°C) complete carbonylation could be achieved within a few

hours. The reaction mixture obtained in the carbonylation was oxidized with alkaline hydrogen peroxide, producing high yields (90%) of trialkylcarbinols.

Brown and Rathke¹⁵ also reported that adding water to the reaction mixture inhibits the migration of the third alkyl group from boron to carbon. As a result, oxidation of the organoboron intermediate obtained in the presence of water produces the corresponding dialkyl ketone. instead of the trialkylcarbinol as realized in the reaction in the absence of water.



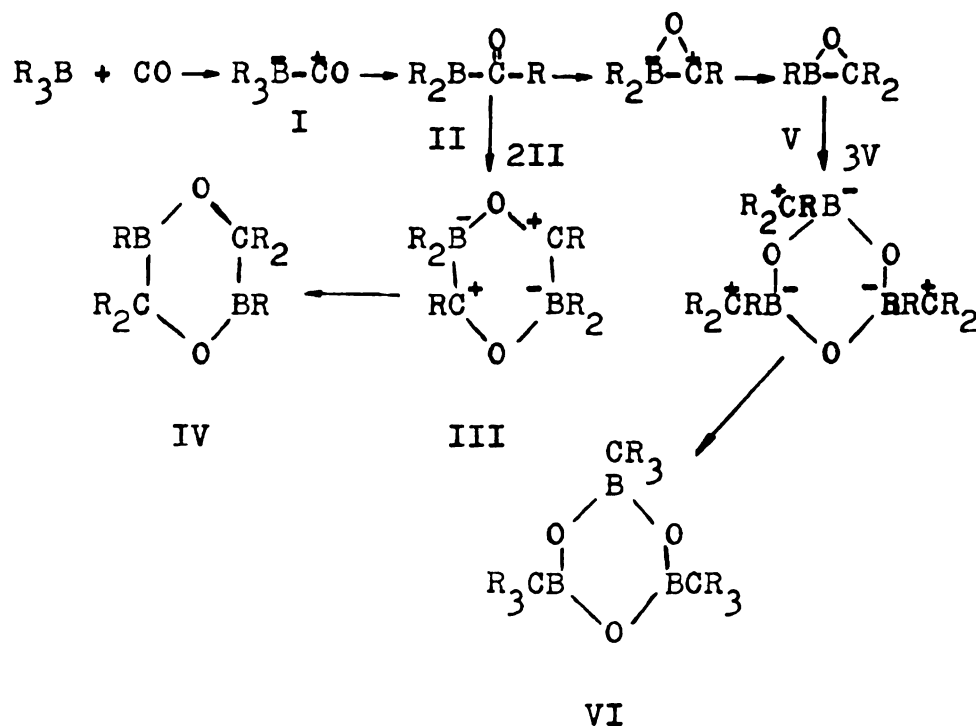
Finally, Brown and Rathke¹⁶ found that both sodium and lithium borohydride markedly catalyzed the rate of absorption of carbon monoxide at atmospheric pressure by trialkylboranes in ether solvent. Hydrolysis of the reaction intermediate with ethanolic potassium hydroxide produces the homologated alcohol (i.e. monoalkylmethanols).



The completion of carbon monoxide absorption required one hour at 45°C in the presence of alkali metal borohydrides (compared to 100°C-125°C with no catalyst in 3 hours).

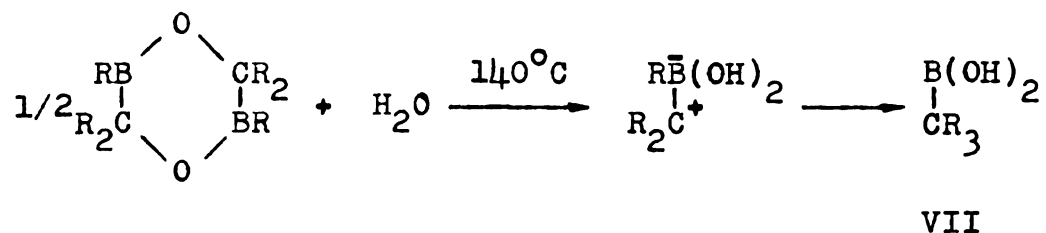
Mechanisms.

The mechanism proposed by Hillman¹¹ involves three migrations in which the alkyl group migrates with its bonding electrons from negative boron to positively charged carbon

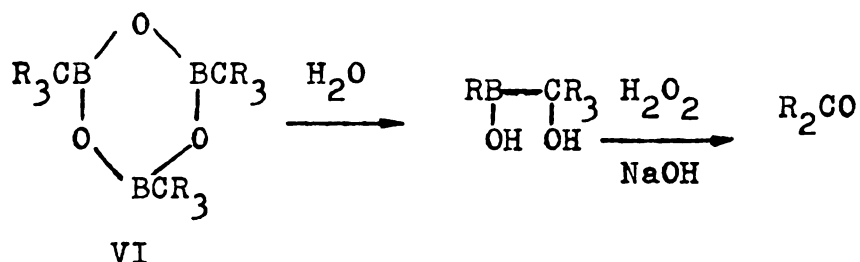


According to Hillman, the trialkylborane-carbonyl (I) could not be isolated. Furthermore, there was no trace of the postulated intermediate (II) in the reaction products after one alkyl migration. Hillman proposed that the intermediate (II) dimerizes to (III), which rearranges to (IV). The hexaalkyldiboradionane (IV),

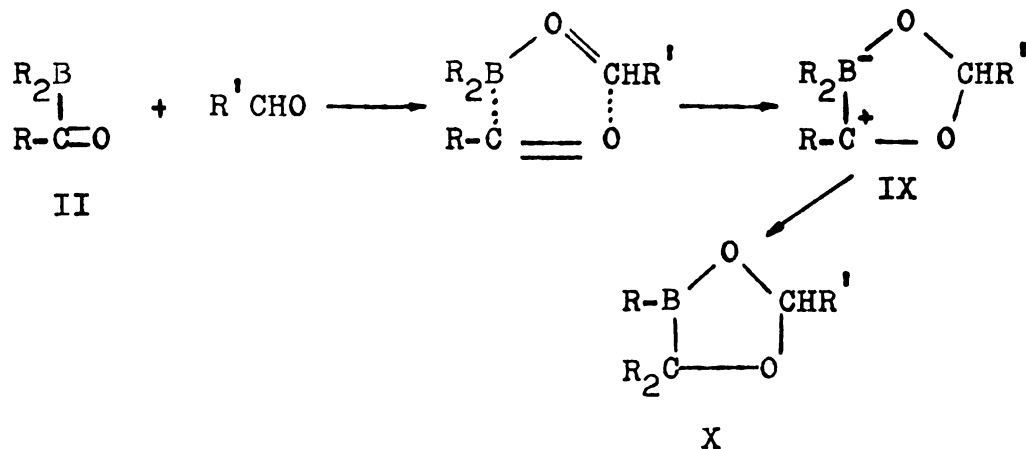
which was stable in water at 80°C, was completely isomerized to the boronic acid (VII) at 140°C.



In the presence of water, the boronic anhydrides (boroxines) (VI) were presumed to be converted into hydrate (VIII). Oxidation of (VIII) produced the ketone.¹⁵



Hillman¹³ also outlined a possible mechanism for the carbonylation of organoboranes in the presence of aldehydes as follow



He assumed that the dialkylacylborane (II) undergoes a 1,3-dipolar addition reaction with the aldehyde to give an unstable charged intermediate (IX) which rearranges to the 4-bora-1,3-dioxolane (X).

(C) The reaction of lithium, sodium and potassium organometallic compounds with carbon monoxide.

There have been very few published works on the reaction of potassium organometallic compounds with carbon monoxide. Thus, very little is known about this reaction. The reaction of sodium organometallics with carbon monoxide was investigated by Ryang and Tsutsum.¹⁷ They reported that NaPh reacted with CO at -10°C to yield Ph_2 , Ph_2CO , Ph_3COH , BzOH and PhOH . The carbon monoxide was added in the amount of 0.5 liter per two hours.

According to Ryang, Rhee and Tsutsum,¹⁸ the reaction of iron pentacarbonyl with aryllithium at -50°C to -60°C yielded the following aromatic aldehydes: 2,6-dimethylbenzaldehyde (36.4%); 2,4-dimethylbenzaldehyde (15.4%); p-tert-butylbenzaldehyde (47%); o-tert-butylbenzaldehyde (54.3%); p-methoxybenzaldehyde (24.2%) and 2,4,6-trimethylbenzaldehyde (60.5%). In the presence of Et_2O or petroleum ether, organolithium compounds react with carbon monoxide to yield ketones and polymers. The order of reactivity of the lithium compounds with CO is C_4H_9 , o-, m-, and p-toyl at 70°C > benzyl at -40°C - -70°C > vinyl at -40°C to -65°C > diphenyl at 30°C - 60°C >

triphenyl at 230°C (120 atm.), LiC_6H_5 , $\text{LiC}\equiv\text{CC}_2\text{H}_5$ (no reaction). The following compounds were obtained at -70°C : $(\text{C}_6\text{H}_5)_2\text{C}=\text{O}$, 55%; $(\text{o-CH}_3\text{C}_6\text{H}_4)_2\text{C}=\text{O}$, 48%; $(\text{p-CH}_3\text{C}_6\text{H}_4)_2\text{C}=\text{O}$ 50%; $(\text{n-C}_5\text{H}_{11})_2\text{C}=\text{O}$, 28%; $(\text{C}_4\text{H}_9)_2\text{C}=\text{O}$, 30%; and $(\text{iso-C}_3\text{H}_7)_2\text{C}=\text{O}$, 30%.¹⁹

Organolithium compounds also react with $\text{Fe}(\text{CO})_5$ at -50°C to form the complex, $\text{Li}[\text{RFe}(\text{CO})_5]$, which decomposes to form ketone when R is alkyl, but is stable when R is aryl, the latter reacting with H_2O to form aldehydes and acyloins. Reaction with $\text{Ni}(\text{CO})_4$ at -70°C gave mono and diketones through decomposition of the complexes at room temperature. The complex reacted with styrene to give an R-substituted styrene.²⁰

To conclude, relatively little study has been done on the reactions of the organolithium, organosodium and organopotassium compounds with CO; however, the ones studied had rapid reactions with CO at -70°C . In particular, when the compound was a lithium alkyl, the corresponding reaction provided a useful synthesis of symmetrical ketones.

(D) The reactions of Cu, Ag, Au, Cd, Zn and Hg, organo-metallic compounds with carbon monoxide

Of the six transition elements Cu, Ag, Au, Cd, Zn and Hg, only mercury organometallic compounds have been reported to react with carbon monoxide. According to Barlow and Davidson,²¹ arylmercury (II) ions reacted

with carbon monoxide at high pressure to yield derivatives of the corresponding carboxylic acids. In particular phenylmercury (II) basic nitrate reacted with carbon monoxide at 100°C (247 atm.) in benzene solution. The reaction was accompanied by precipitation of mercury and crystallization of the crude reaction mixture. The final products consisted of principally phenylmercury (II) benzoate, carboxylic acid anhydride and some free acid. The reaction was inhibited by anions such as Cl^- and CH_3CO_2^- which form covalent bonds with Hg(II) . Thus arylmercury (II) compounds generally undergo electrophilic attack at the carbon adjacent to mercury.

Recently, Davison²² reported that carboxylic acid and esters could be prepared from carbon monoxide and alkylnitratomercury (II) complexes. For example, the n-butyl- and 2-methoxyethyl-nitratomercury (II) complexes reacted with carbon monoxide at 75°C in 10% solutions in benzene, water or methanol under pressures of 25-250 atmospheres. In the first two solvents, carboxylic acids were formed (10-50% yield), while in MeOH corresponding esters were obtained (35-50% yield). The major by products were 1-nitrobutane and 1-methoxy-2-nitroethane. Formation of an intermediate carbonyl-complex, which decomposed to give nitroalkane or carboxylic acid derivative, was considered possible. The process thus involved nucleophilic attack at the α -carbon

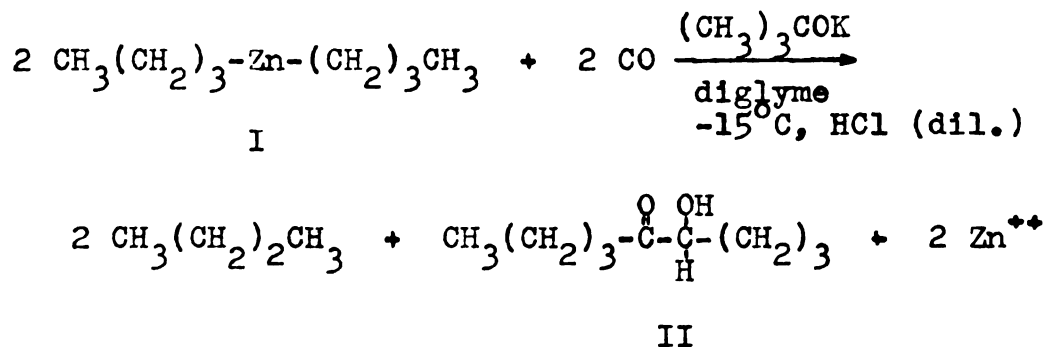
atom in contrast to electrophilic attack as in the case of arylmercury (II) compounds.

Since no published work concerning the reaction of zinc organometallic compounds with carbon monoxide has been found, nothing is known about this reaction. In this thesis, the reaction of dialkylzinc and diarylzinc compounds with carbon monoxide have been studied. Detailed discussions of the experimental results are presented below.

RESULTS AND DISCUSSION

(1) Reaction of di-n-butyl zinc with carbon monoxide

When carbon monoxide is reacted with di-n-butyl zinc (I) in diglyme solution, n-valeroic acid (II) (33% on the basis of di-n-butyl zinc) is isolated, and butane (99% of the theoretical amount) is measured. The reaction is run at a temperature of -15°C with potassium tert-butoxide as catalyst.



In some cases, carbon monoxide does not react with zinc organometallic compounds. The addition of a base catalyst is sometimes essential in order for the reaction to take place. Di-n-butyl zinc is found to react with carbon monoxide only in the presence of a base catalyst. However, it is found that n-butylzinc bromide does not react with carbon monoxide under any circumstance (i.e. with or without catalyst).

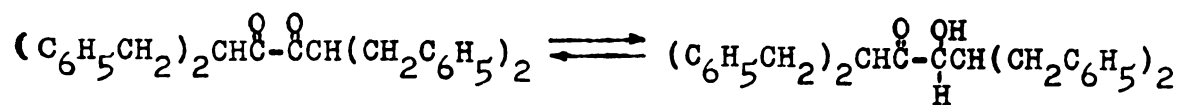
The yield of the final product is found to depend on the following four factors: (1) temperature, (2) base catalyst, (3) solvent and (4) speed of stirring.

If the temperature is too high (above 35°C), the reaction mixture generates gas instead of absorbing carbon monoxide. On the other hand, if the temperature is too low (below -35°C) the reaction solution solidifies, and stirring becomes difficult. In fact, stirring is stopped at a temperature of -65°C . In practice, the reaction should be run at temperatures from -15°C to 25°C . The highest yield is obtained at a temperature of approximately -15°C . The speed of stirring also has marked effect on the yield. Experimental results indicate that the yield increases with increasing speed.

Different combinations of solvent and base catalyst were used in an attempt to optimize the yield. No uptake of carbon monoxide is observed when reactions are run in the presence of either diglyme or benzene with any of the following catalysts: triethylamine, 4-picoline, 2,2'-bipyridine, sodium iodide, piperidine, 2-pyrrolidinone, benzil, pyridine, HMPA, and sodium acetate. With diglyme as solvent and with sodium benzoate, sodium methoxide or sodium amide as catalyst, slight uptake of carbon monoxide is observed. However, no final product could be isolated with these reactions. The highest yield is achieved by running the reaction around -15°C with potassium tert-butoxide as catalyst and diglyme as solvent. In this case, potassium tert-butoxide and diglyme are found to be the most effective

catalyst and solvent respectively since they account for a large uptake of carbon monoxide as well as the highest yield (33%). Results corresponding to different experimental conditions are tabulated in Table 1 below. The reaction curve showing the absorption of carbon monoxide as a function of time is shown in Figure 1.

At the end of the reaction, the isolated product obtained by distillation is a slightly yellow solution. When the product solution is placed in the dark for several days, the color of the solution gradually changes to deep yellow. However the pale yellow color returns after exposing the deep yellow solution to light. A previous experimental study of aliphatic acyloins by Corson, Benson and Goodwin,²³ showed that acyloins prepared by distillation always contained a small amount of diketones.²⁴ Although the diketones are characterized by their deep yellow color, the depth of color of the acyloin solution changes significantly for different degrees of exposure to light. Scheibler²⁵ also observed the extreme light sensitivity of an aromatic substituted aliphatic diketone, tetrabenzylldiacetyl, and found that the photo-reaction was to some extent reversible.



Table

10 mmole of di-n-butyl zinc reacted with carbon monoxide
using potassium tert-butoxide as catalyst under different
conditions

Quantities of Base	Absorption of CO	Reaction Time	Solvent	n-valeroic % yield	Temp.
20 mmole	9.92 mmole	1 hr. 6 min.	diglyme	0	25°C
10 mmole	8.48 mmole	3 hr. 5 min.	diglyme	19.58%	25°C
5 mmole	3.55 mmole	45 min.	diglyme	0.898%	25°C
1½ mmole	1.4 mmole	1 hr.	diglyme	trace	25°C
1 mmole	0.28 mmole	22 hr. 40 min.	diglyme	0	25°C
10 mmole	8.2 mmole	3 hr.	diglyme	28.95%	0°C
10 mmole	8.2 mmole	3 hr. 15 min.	diglyme	32.9%	-15°C
10 mmole	—	—	diglyme	absorption too slow	-35°C
10 mmole	—	—	diglyme	can't be stirred	-65°C

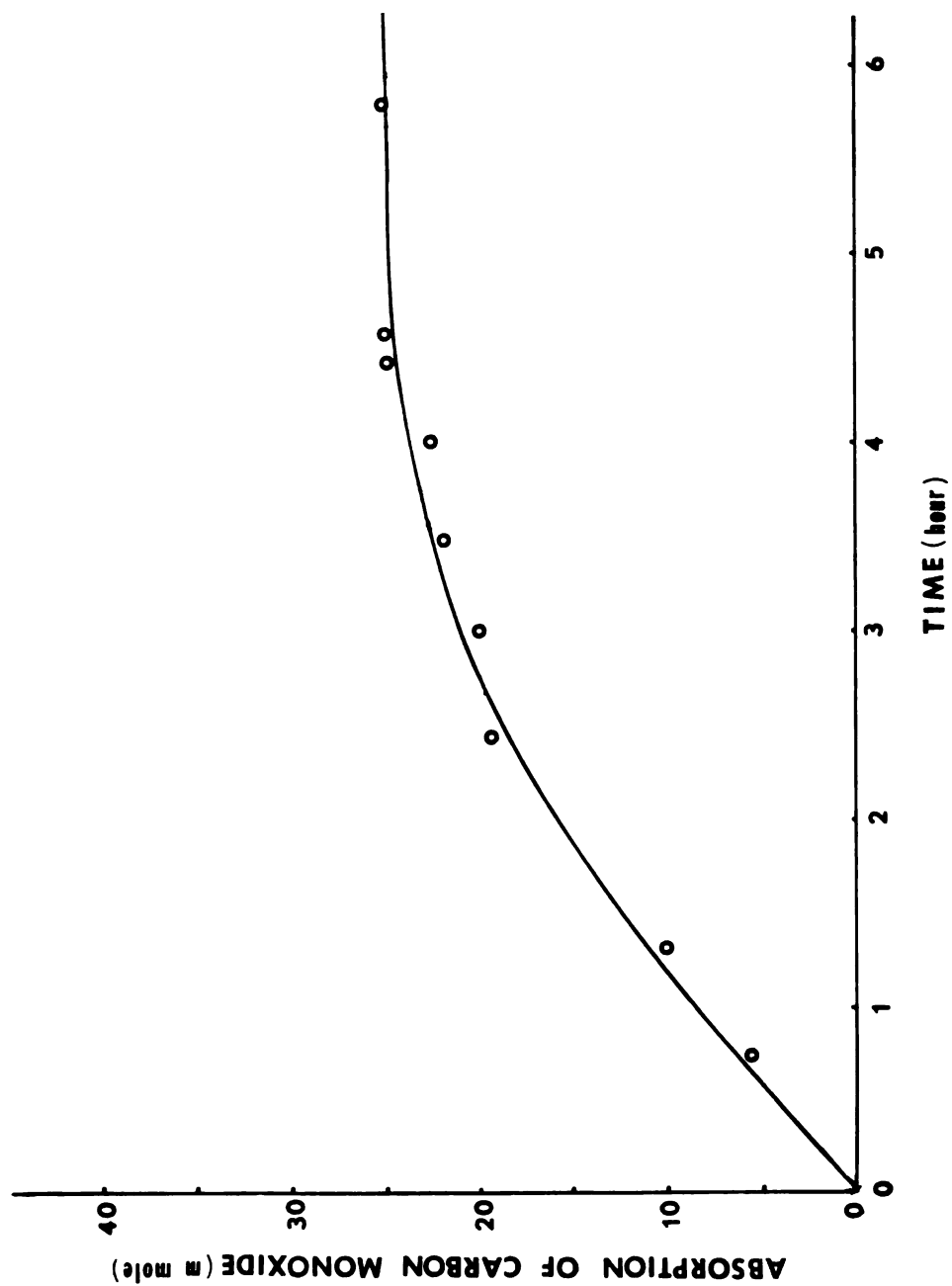


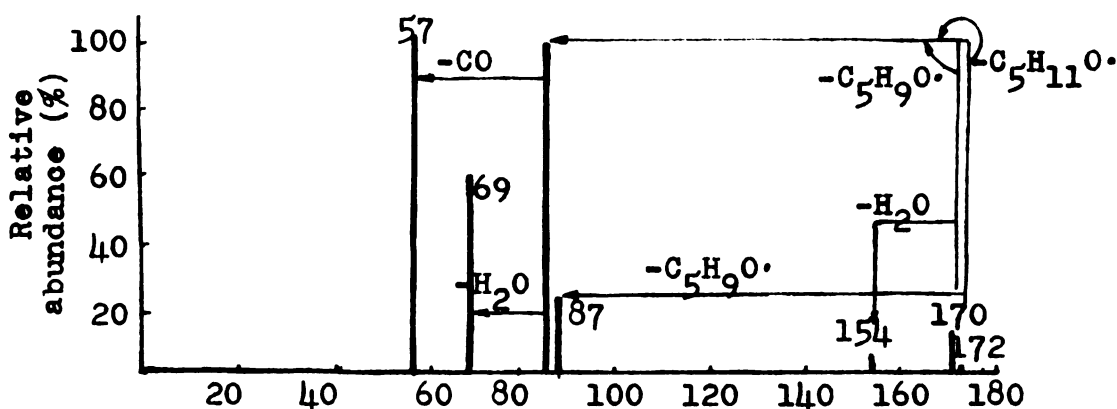
Figure 1 Reaction of di-n-butyl zinc (30 mmole) and potassium tert-butoxide (30 mmole) in diglyme solution at -15°C with carbon monoxide

The reversible color change is due to the reduction-oxidation of the diketone-hydroxyketone system.

Since exposure of the isolated product to light has never been avoided, it seems that the isolated product as obtained by vacuum distillation is always a mixture of n-valeroïn and the corresponding 1,2-diketone. This conclusion is based upon the following experimental evidence:

- (1) The yellow color, probably due to the presence of the corresponding yellow diketone.
- (2) The proton NMR spectrum does not give the correct ratio of protons. This tends to confirm that the isolated product is a mixture.
- (3) When using carbon tetrachloride as solvent, the proton NMR spectrum exhibits a peak at 6.0τ , a triplet at 7.5τ and two broad highly complex series of peaks centered at 8.6τ and 9.1τ respectively. However, when using DMSO as solvent, a multiplet at 6.0τ as well as a doublet at a lower position of 5.2τ appear. The multiplet corresponds to the proton attached to the carbon atom bearing the hydroxyl, while the doublet corresponds to the hydroxyl proton.
- (4) In the IR spectrum, two peaks appear at 1700cm^{-1} and 3450cm^{-1} . These peaks correspond to those of the carbonyl and hydroxy groups.

- (5) As shown below, the mass spectrum displays a parent peak at 170 and another small peak at 172. The former corresponds to the parent peak of diketone, while the latter is believed to result from a hydroxy compound. This belief is supported by the presence of the peak at 154 which agrees with the spectral line of the hydroxy ketone minus one water. Since the parent peak of an alcohol is normally quite small and sometimes obscure, the parent peak of the hydroxy compound is thus much smaller in comparison to the diketone.



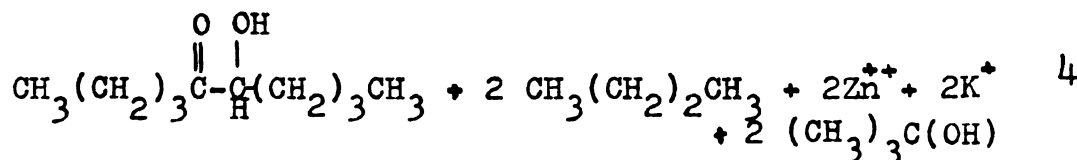
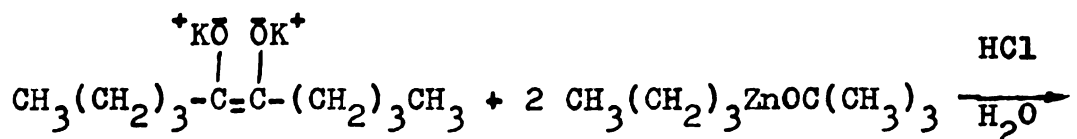
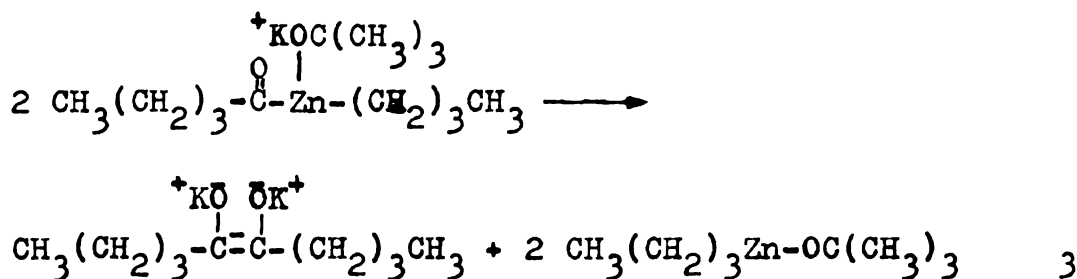
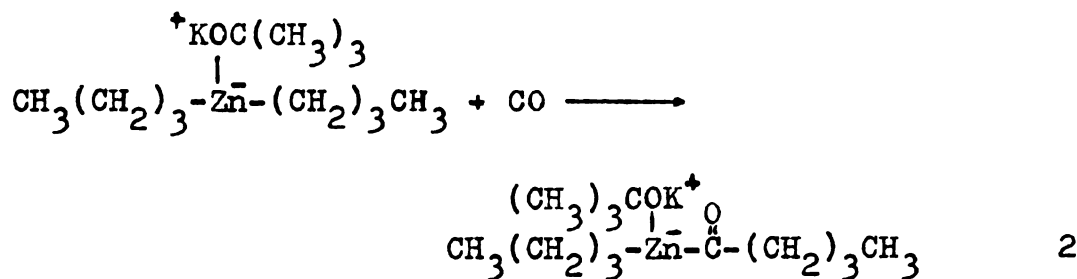
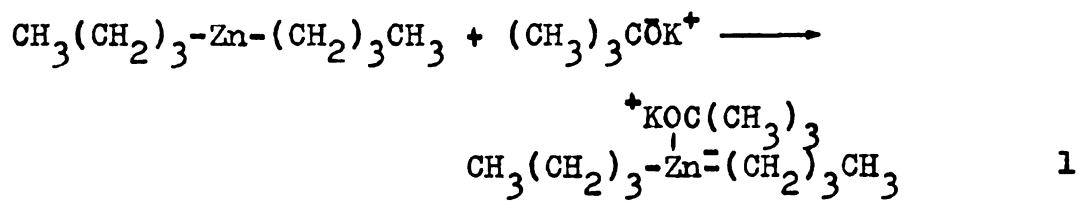
The mass spectrum of $\text{CH}_3(\text{CH}_2)_3\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\overset{\text{OH}}{\text{C}}-(\text{CH}_2)_3\text{CH}_3$

- (6) The derivative of the isolated product prepared from 2,4-dinitrophenylhydrazine is an orange-yellow solid. The melting point of the derivative found to be 222°C-223°C. The phenylosazone, pre-

pared from n-valeroïn and phenylhydrazine, is in the form of white needles with a melting point of 126.5-127.5°C. (lit., mp 127°C).²⁶ The unrecrystallized phenylosazone melts at 124-125°C. Finally, the refractive index of n-valeroïn is $n_D^{24.2^\circ\text{C}} = 1.4312$ (lit., $n_D^{26.6^\circ\text{C}} = 1.4298$).²³

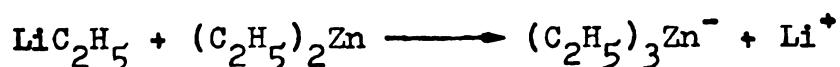
Mechanism:

A possible mechanism consists of the sequence of steps shown in equations 1-4:



Equation 1 describes a base catalyzed (potassium tert-butoxide) reaction in which the electron rich base attaches to the electron poor zinc. In equation 2, the coordination of the potassium tert-butoxide to di-n-butyl zinc causes an insertion of carbon monoxide. The cleavage of the compound on the left-hand side of equation 3, produces the dipotassium salt of the enediol and butylzinc tert-butoxide. The latter is inert to carbon monoxide either with or without a base catalyst. In equation 4, the injection of hydrochloric acid produces n-valeroïn and butane. No intermediate has been isolated in the experiment.

Being a strong base, potassium tert-butoxide coordinates with zinc (equation 1) to result in a partially negatively charged butyl group. This may make the butyl group more reactive, allowing reaction with carbon monoxide to take place. Thus the absorption of carbon monoxide in the reaction becomes possible. The establishment of equation 1 is further supported by the following well-known reaction.²⁷



As for other bases which fail to catalyze the reaction, two explanations are possible: (1) The base is too weak to coordinate with the zinc, (2) Two bases

coordinate together with the zinc.

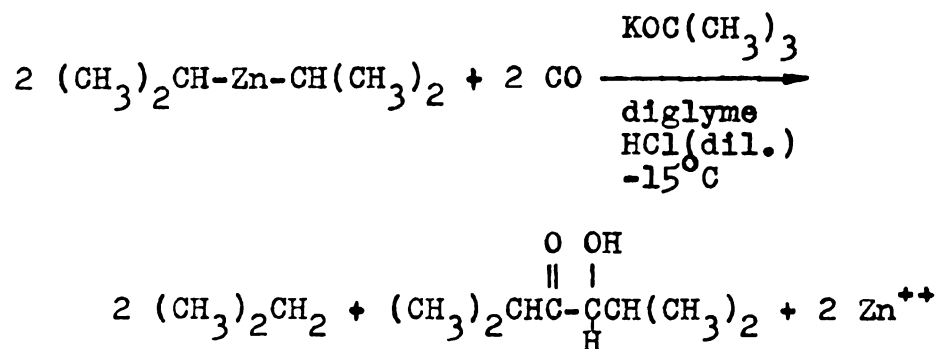
From the above discussion, the highest yield obtained is only 33%. This yield can be explained from the stoichiometry predicted by the mechanism. According to equation 4, one mole of the final product requires two moles of carbon monoxide and one mole of di-n-butyl zinc. However, from equation 3, the hydrochloric acid cleavage of the intermediates converts one mole of the di-n-butyl zinc into butane in the final product. Consequently, the theoretical yield can at most be 50%.

From Table 1, the absorption of carbon monoxide by 10 mmole of di-n-butyl zinc is about 8 mmole instead of the calculated 10 mmole. This decrease in the amount of carbon monoxide absorption lowers the theoretical yield.

Based on a 10 mmole scale of di-n-butyl zinc, the mechanism predicts a theoretical yield of 10 mmole butane. The results agree with this prediction. More than 9 mmole of butane was measured in the experiment.

(2) Reaction of diisopropyl zinc with carbon monoxide

Diisopropyl zinc reacts with carbon monoxide to yield isobutyroin (29% yield on the basis of diisopropyl zinc). and propane (99% of the theoretical amount).



The reaction is run at -15°C with diglyme as solvent and potassium tert-butoxide as catalyst. As mentioned above, these experimental conditions result in the highest yield for the reaction of di-n-butyl zinc. The absorption of carbon monoxide in this reaction is faster than that in the reaction of di-n-butyl zinc. The rate of absorption of carbon monoxide is shown in Figure 2. When the reaction is run in the absence of a catalyst, no uptake of carbon monoxide is observed.

To identify the product, the IR, NMR and mass spectra were obtained. A typical mass spectrum of this product is provided below.

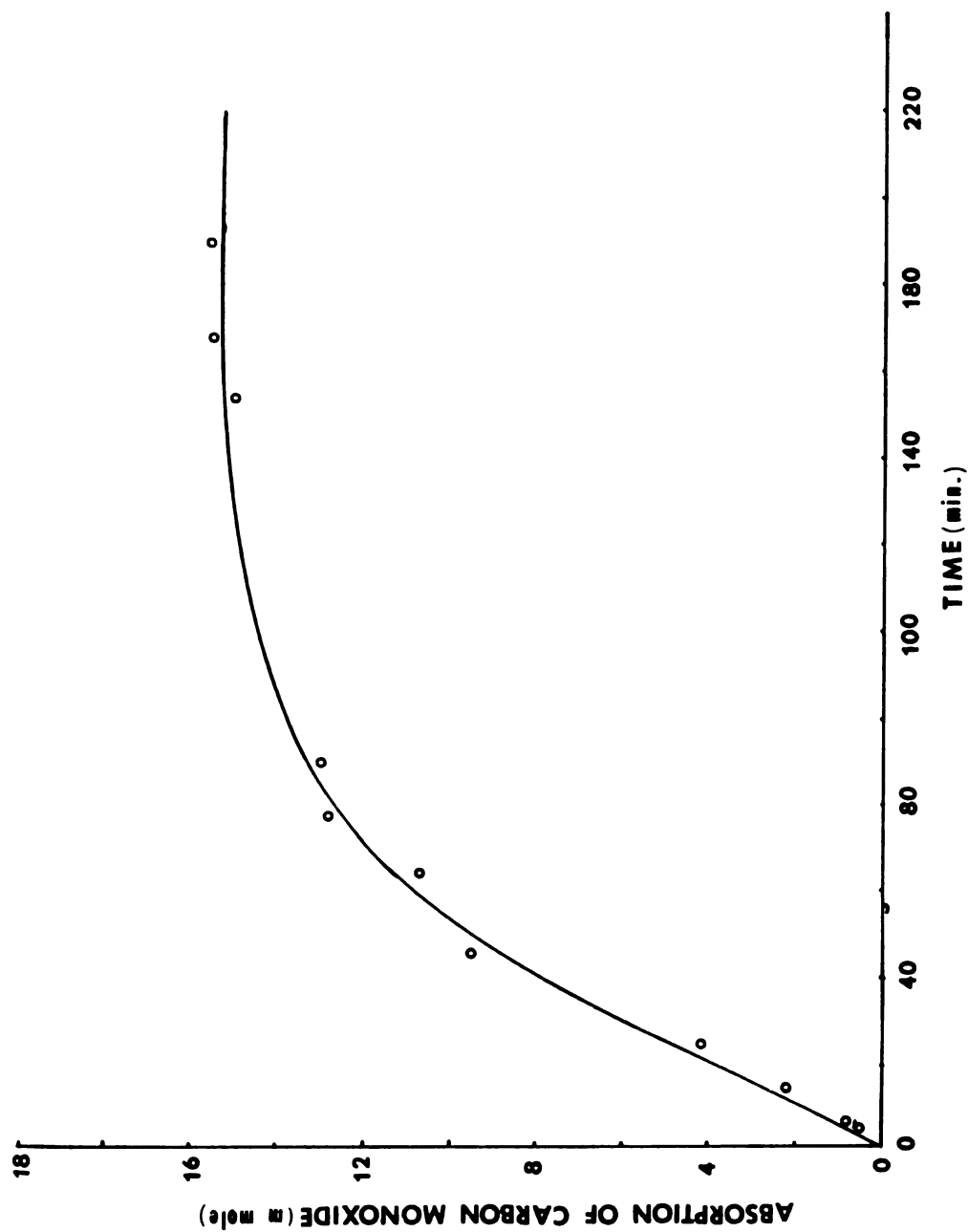
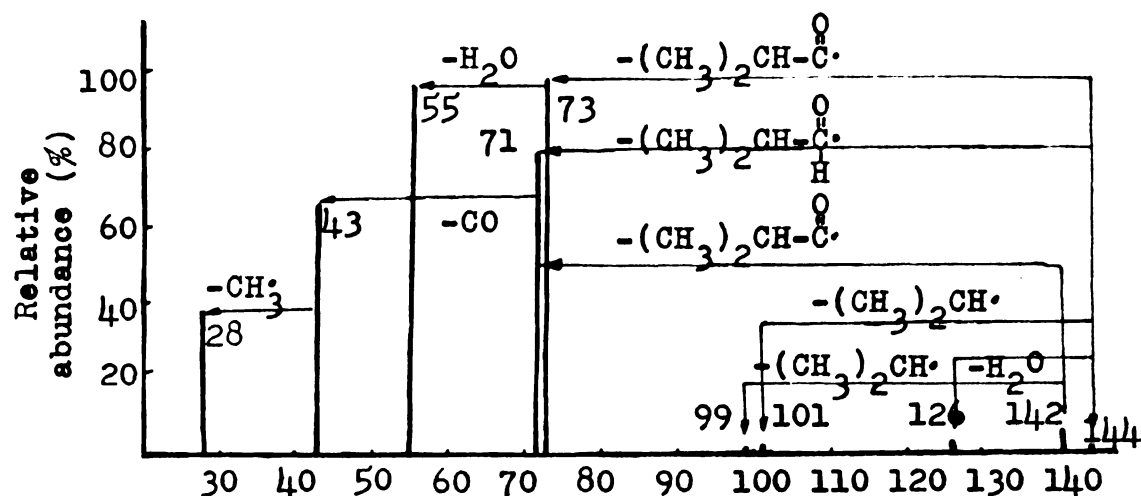


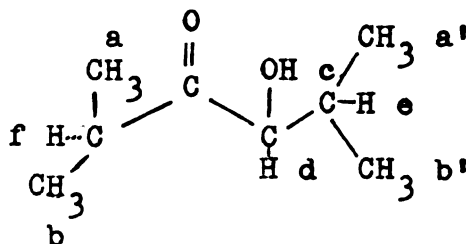
Figure 2 Reaction of diisopropyl zinc (16.5 mmole) and potassium tert-butoxide (16.5 mmole) in diglyme solution at -15°C with carbon monoxide



The mass spectrum of $(\text{CH}_3)_2\text{CH}-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}=\overset{\text{O}}{\text{C}}-\text{CH}(\text{OH})-\text{CH}(\text{CH}_3)_2$

Clearly, the mass spectrum displays two parent peaks. The parent peak at 142 corresponds to that of diketone, while the peak at 144 results from the hydroxy compound. This conclusion is further supported by the peak at 126 which is consistent with the peak of the hydroxy ketone minus one water. The similarity between the mass spectrum of this product and that of di-n-butyl zinc is quite expected, since these two compounds are closely related.

The structure of isobutyroin is as given below.



The NMR displays four doublets at 9.25 τ , 8.92 τ , 8.81 τ and 5.78 τ . The doublets at 9.25 τ and 5.78 τ correspond to the protons of b' and d respectively, while the other doublets at 8.92 τ and 8.81 τ correspond to the protons of a, b and a'. In addition, two broad series of peaks appear in the NMR spectrum: one centered at 7.61 τ - 8.1 τ is due to the proton of e; another at 6.8 τ - 7.4 τ is due to the proton of f; a broad peak at 6.13 τ results from the hydroxy groups.

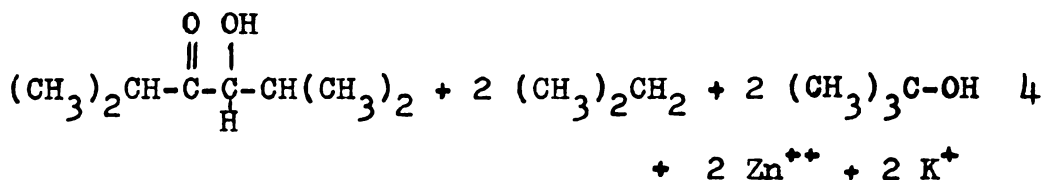
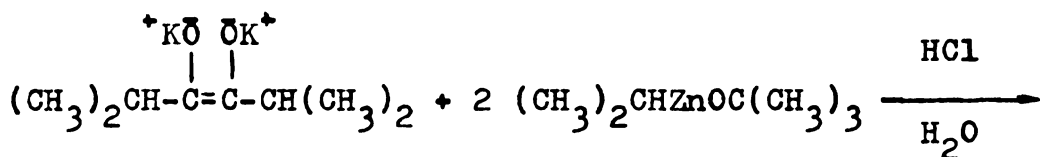
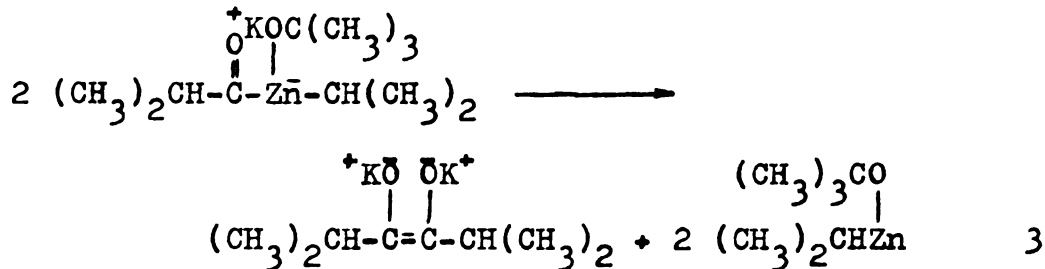
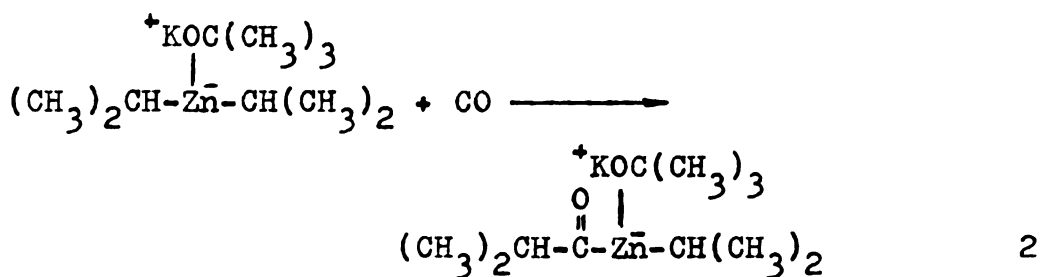
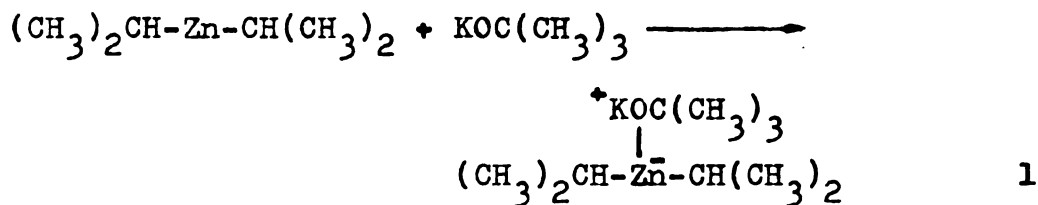
The IR spectrum exhibits two peaks at 1720cm⁻¹ and 3500cm⁻¹ respectively. The appearance of these peaks indicates the presence of carbonyl and hydroxy groups.

The derivative of isobutyroin from phenylhydrazine crystallizes in the form of colorless needles (phenylosazone) with a melting point of 136°C-137°C (lit., 139.5°C-140°C).²⁸ The unrecrystallized phenylosazone has a melting point of 124°C-126°C. The refractive index of isobutyroin is $n^{23.8^\circ\text{C}}_{\text{D}} = 1.4178$ (lit., $n^{26.6^\circ\text{C}}_{\text{D}} = 1.4159$).

Mechanism

The mechanism of this reaction is the same as that

proposed for the reaction of di-n-butyl zinc. Thus explanations for the former case can be applied here also. The following equations describe the sequence of steps involved in the reaction.



(3) Reaction of diphenyl zinc with carbon monoxide

Carbon monoxide reacts with diphenyl zinc using potassium tert-butoxide as catalyst. The reaction is run in diglyme solution at -15°C . From the reaction mixture, biphenyl and benzene are isolated.

Usually, the absorption of carbon monoxide in this reaction is considerably less in comparison with previous reactions (i.e. di-n-butyl zinc and diisopropyl zinc). For example, with 10 mmole of diphenyl zinc, the absorption of carbon monoxide is approximately 2.5 mmole (compared to about 8 mmole for the other reactions). Figure 3 shows the amount of carbon monoxide absorbed versus time.

At the end of the reaction, a nearly colorless solution with a pale yellow precipitate is obtained. The yellow precipitate crystallized from 95% ethanol in the form of white crystals. A small amount of the white crystals is dissolved in carbon tetrachloride, and then injected into G.C. The G.C. trace exhibits two peaks: one corresponding to carbon tetrachloride and the other corresponding to the unknown. By adding a small amount of biphenyl powder to the prepared solution of white crystals and carbon tetrachloride, the G.C. trace again exhibits the same two peaks except that there is an increase in the intensity of the unknown peak. The G.C. results thus indicate that the

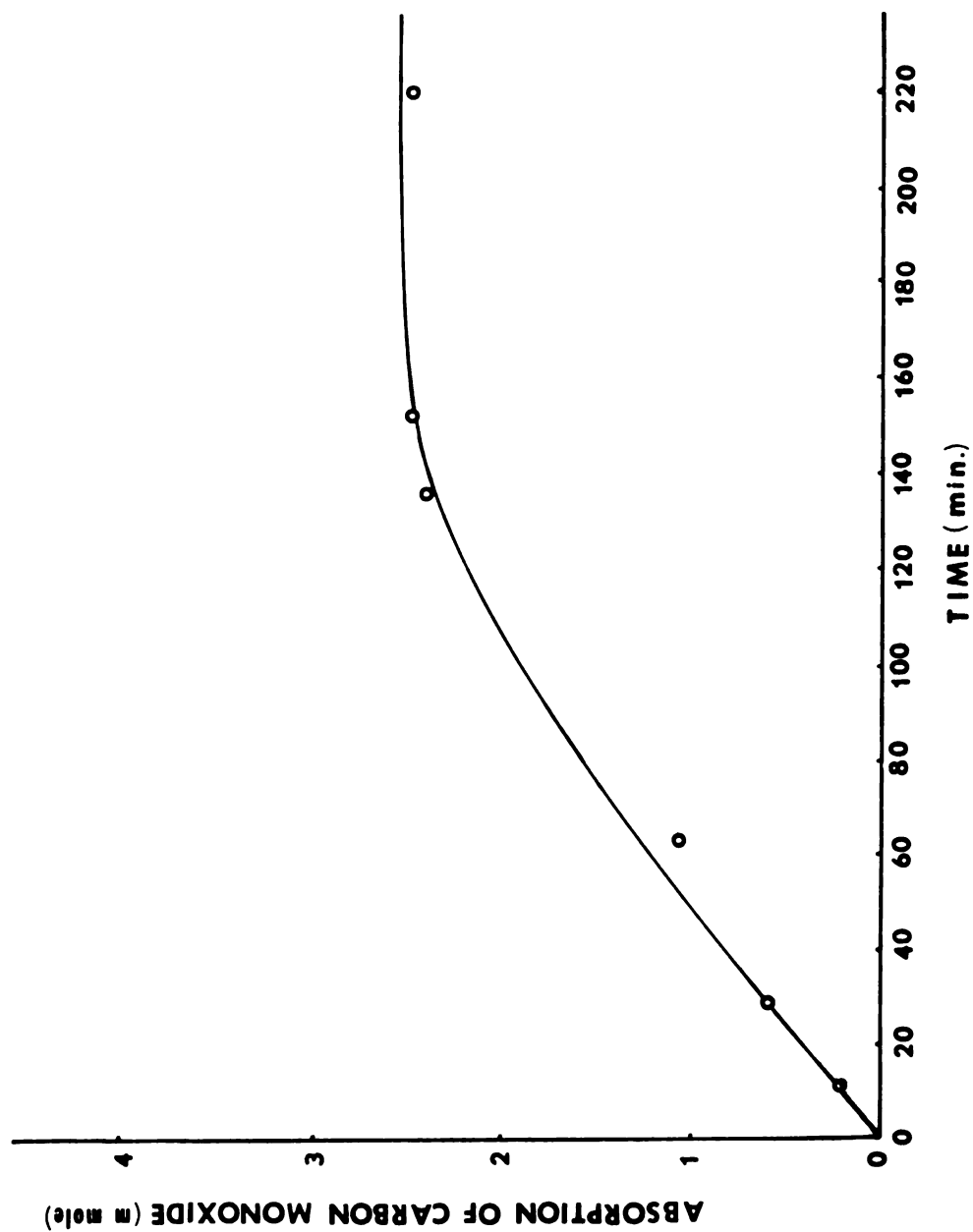


Figure 3 Reaction of diphenyl zinc (10 mmole) and potassium tert-butoxide (10 mmole) in diglyme solution at -15°C with carbon monoxide

unknown crystal is biphenyl. This identification is also confirmed by the analysis of the melting point and NMR spectrum. The melting point of the unknown crystal is found to be 68°C to 69°C. The NMR spectrum exhibits peaks near 2.4 τ -2.9 τ . Finally, the IR spectrum of the unknown crystal is identical with the IR spectrum of a known biphenyl compound.

After removing the water, ten μ l of extracts of the clear solution is injected into G.C. for identification. The peaks shown on the G.C. trace correspond to those of pentane, benzene, diglyme and biphenyl. Since all the peaks are very small in comparison with the peaks of solvent pentane, benzene and diglyme, no attempt is made to isolate the products.

Diphenyl zinc is known to be extremely sensitive to air and moisture.²⁹ It decomposes instantly with water into Zn(OH)₂ and benzene, and with dry air into ZnO and biphenyl. With the exception of benzene and biphenyl (31% yield on the basis of diphenyl zinc), all other compounds isolated from reaction products are of negligible amount. It is likely that benzene and biphenyl do not result from the interaction of carbon monoxide with diphenyl zinc, but rather from the decomposition of diphenyl zinc. The decomposition could possibly occur during the injection of hydrochloric acid or the disconnection of experimental apparatus.

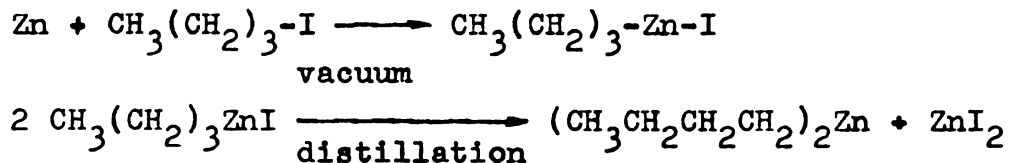
In the absence of base, diphenyl zinc does not react with carbon monoxide.

EXPERIMENTAL

(A) Reaction of di-n-butyl zinc with carbon monoxide

1. Preparation of di-n-butyl zinc

The procedure for preparing di-n-butyl zinc is as follow



First, zinc-copper couple³⁰ was prepared by adding 156.91 g. (2 moles plus 20% excess) of granular zinc (20 mesh) to a hot solution of cupric acetate monohydrate (2.15 g.) in 215 ml. of glacial acetic acid. The mixture was kept hot with a steam bath to prevent precipitation of zinc acetate. After shaking the mixture for 1 to 3 minutes, the acetic acid was poured out and the zinc-copper couple was rinsed with a 215 ml. portion of glacial acetic acid, then with three 215 ml. portions of ether.

The experimental system was a three-necked reaction flask connected to an air tight mechanical stirrer, a connecting tube and a reflux condenser. After placing two moles of the prepared zinc couple in the reaction flask under nitrogen, two moles of butyl iodide were added to mix with the zinc couple. The mixture was stirred at a slow rate, and heated gently for the reaction to start. The reaction flask was cooled with

ice water when necessary to maintain the temperature under 75°C throughout the experiment.³¹ When the reaction was completed (in approximately three hours), di-n-butyl zinc was vacuum distilled at a temperature of 81°C - 82°C and a pressure of 9 mm. The yield was approximately 75-80%. In order to minimize impurities in the final product, a distilled forerun of about 10 ml. was taken. The di-n-butyl zinc was distilled into a receiver in a 100 ml. round-bottom flask with a side-arm. Both a teflon stop-cock and a septum were used to seal out the air.

Although alkylzinc halide may be briefly exposed to air without danger, di-n-butyl zinc is extremely sensitive to moisture and ignites spontaneously in air. Thus, the product must be completely isolated from air with nitrogen.³²

2. Preparation of potassium tert-butoxide solution

A 250 ml. reaction flask which was attached to a connecting tube and a mercury bubbler was flame dried and thoroughly flushed with nitrogen. The flask was then allowed to cool to the room temperature. While still flushing with nitrogen, 25 g. of potassium tert-butoxide was quickly dropped into the flask through a funnel. At the same time, 120 ml. of distilled diglyme was injected. Stirring was started and continued until the solid was dissolved. After the solution

became clear with impurities deposited in the bottom of the flask, the solution was titrated with standard hydrochloric acid solution. Phenolphthalein was used as indicator. The concentration of the prepared potassium tert-butoxide solution was found to be about 1.44 M.

3. Reaction of di-n-butyl zinc with carbon monoxide

The experimental apparatus consisted of a 50 ml. reaction flask which was connected to a 250 ml. buret through a rubber tube. The top of the buret was attached to a carbon monoxide tank with three-way stopcock regulating the supply of carbon monoxide, while the bottom end of the buret was connected to a dropping funnel which was filled with diethylphthalate. After the system was flushed with nitrogen, 30 mmole (approximately 5.28 ml.) of di-n-butyl zinc was injected into the reaction flask. Then, 30 mmole potassium tert-butoxide solution (in diglyme) was added as catalyst. In order to eliminate the chances of exposing the solution to air, the base solution was freshly prepared for this purpose. The preparation of the base was discussed in the previous section.

The reaction flask was cooled to about -10°C to -15°C with dry ice and carbon tetrachloride, the system was then flushed with carbon monoxide. By properly adjusting the height of the dropping funnel, nitrogen

was forced out of the system through the mercury bubbler. The closed system was now entirely filled with carbon monoxide. The diethylphthalate level was set at the zero mark of the buret. The reaction solution, which initially appeared pale yellow, was rapidly stirred to initiate the reaction. The absorption of carbon monoxide by di-n-butyl zinc was indicated by the rising level of the diethylphthalate in the buret. The amount of carbon monoxide absorption was recorded as a function of time. The absorption of carbon monoxide changed the color of the reaction solution from pale yellow to deep green. After the absorption of carbon monoxide ceased, the mixture of dry ice and carbon tetrachloride was removed, and the reaction solution was allowed to warm to room temperature. To neutralize the base in the reaction solution, 12 ml. of concentrated hydrochloric acid solution in 3 ml. of water was injected slowly into the flask. The addition of the hydrochloric acid solution generated both heat and gas in the reaction solution. Thus, before the injection of the hydrochloric acid solution, the clamp on the rubber tube of the mercury bubbler was released to allow the escape of gas. Also a cool water bath was used to remove heat from the solution. After the addition of the hydrochloric acid solution, the reaction solution became clear. This clear solution was then

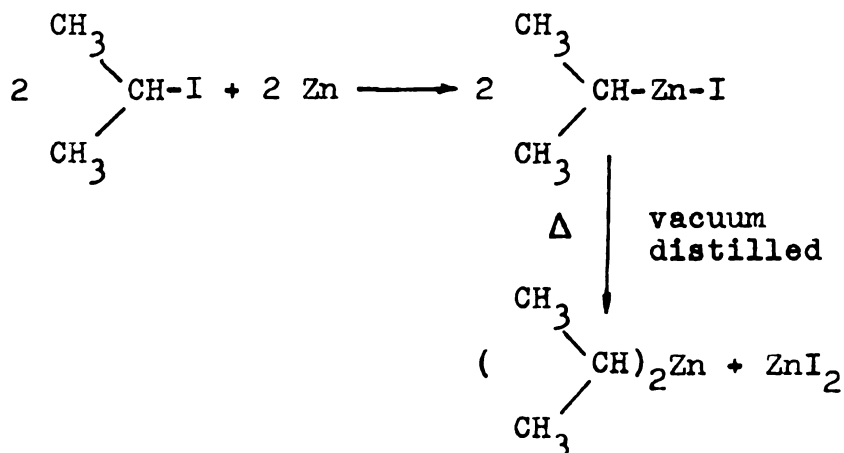
placed in a separatory funnel, and extracted three times with 20 ml. of pentane (or ether). The extract, which contained diglyme, pentane and the final product, was sealed in an Erlenmeyer flask, and saved for analysis using G.C. After first adding 30 ml. of pentane, the diglyme was extracted three times with 30 ml. of water. The solution after extraction of diglyme contains only pentane and the final product.

To obtain pure final product, a steam bath was used to remove pentane at a temperature of 35°C to 36°C. Pure final product was distilled under reduced pressure (.05 mm.) at a temperature of 60°C. A yield of 33% (1.77 g.) was achieved.

(B) Reaction of diisopropyl zinc with carbon monoxide

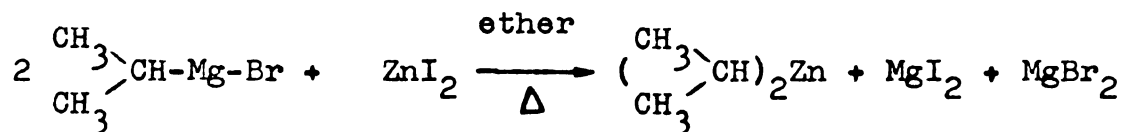
1. Preparation of diisopropyl zinc

Diisopropyl zinc may be prepared according to the procedure discussed in (A-1) above. The reaction involved can be described by the following equation:



This method of preparing diisopropyl zinc results in only poor yields (0-25%).³³ In the reaction, the secondary halides (such as isopropyl bromide) give chiefly gaseous products.³⁴ Thus, this method, which is successful for the primary zinc compound, has limited usefulness for the secondary zinc compound.

A higher yield of diisopropyl zinc (about 70-75%) can be achieved with the Grignard method³⁵ in which the Grignard reagent reacts with zinc iodide in ether solution.



The Grignard reagent and the zinc iodide were first prepared. A separate discussion of these preparations will be given later. To prepare the diisopropyl zinc, the Grignard reagent (150 mmole) was added to the reaction flask containing zinc iodide. The contents were then heated in an oil bath to a temperature of about 48°C at which distillation of ether occurred. After all the ether was distilled, the remaining reaction mixture which was composed of diisopropyl zinc and magnesium halide had a dark gray color. The diisopropyl zinc was distilled under reduced pressure directly from the reaction flask into a receiver which was immersed in a dry ice-acetone bath. The distillation

of diisopropyl zinc took place at a temperature of approximately 30°C , and at a pressure of about 15 mm.

2. The preparation of the Grignard reagent³⁶--isopropyl-magnesium bromide

The experimental apparatus consisted of a 1000 ml. three-necked flask which was connected to an air tight mechanical stirrer, a reflux condenser and a 125 ml. dropping funnel.

The reaction flask was heated to 100°C , then cooled to the room temperature under nitrogen. Into the flask was placed 30.0 g. (1.2 g. atoms) of magnesium turnings and 50 ml. of absolute ether. Then a solution of 93.9 ml. of isopropyl bromide (1.0 mole) in 300 ml. of absolute ether was prepared. 10 ml. of this solution was first added. This mixture was continuously stirred to allow reaction to take place.

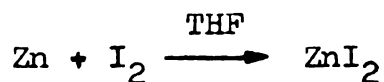
After reaction had started in the flask, the rest of the solution was then added at a slow rate to maintain the reflux. Stirring and refluxing were continued for about one hour after all of the solution were added.

The concentration of isopropylmagnesium bromide was determined through titration. In the process,³⁷ two ml. of Grignard solution and 150 ml. of water were placed in a 300 ml. flask. Sufficient standard acid was added so that about 10 ml. of standard base (0.098 N NaOH) was required in the back titration. Phenol-

phthalein was used as indicator.

3. The preparation of zinc iodide

The experimental system for the preparation of zinc iodide consisted of a 500 ml. round-bottom reaction flask which was connected to a mercury bubbler. After the system was thoroughly flushed with nitrogen, 30 ml. of THF and 75 mmole (19.05 g.) of iodine were placed in the reaction flask. While the mixture was being stirred, 100 mmole (6.358 g.) of zinc was added in four equal portions so that the reaction would not become too vigorous. An ice-water bath was used to remove heat generated by the exothermal reaction. At the start of the reaction, the solution appeared deep red. The reaction was allowed to run for about one hour, when the solution became colorless, and the reaction was completed. While the colorless solution was still being stirred, the THF was evaporated under nitrogen with a warm water bath. The final product (ZnI_2) was in the form of white powder. The reaction can be described by the following equation



The zinc iodide was prepared under nitrogen, since it absorbs water from air rapidly. The presence of water would destroy the organozinc compound.

4. Reaction of diisopropyl zinc with carbon monoxide

The experimental procedure of this reaction was the same as that previously described for the reaction of di-n-butyl zinc and carbon monoxide. In brief, about 10 mmole of diisopropyl zinc reacted with carbon monoxide at -15°C in the presence of 10 mmole of base catalyst (potassium tert-butoxide). During the absorption of carbon monoxide (about 9 mmole on the basis of diisopropyl zinc), the color of the reaction solution changed from pale yellow to deep green. After the solution was neutralized with 4 ml. of concentrated hydrochloric acid in 1 ml. of water, the color of the solution disappeared. This colorless solution was then extracted twice with 10 ml. of pentane. The extract, which now contained diglyme, pentane and the final product, was saved for analysis by the G.C. To purify the product, diglyme was extracted three times with 10 ml. of water. Then, pentane was removed with a steam bath. Pure final product was distilled under reduced pressure (14 mm.) at a temperature of 70°C to 75°C . The yield was found to be about 29% (0.44 g.).

(C) Reaction of diphenyl zinc with carbon monoxide

1. Preparation of diphenyl zinc

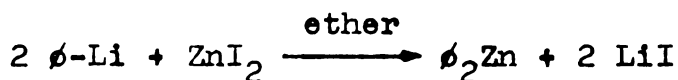
To prepare diphenyl zinc,³⁸ it is necessary to first prepare phenyl lithium and zinc iodide. The preparation of zinc iodide was already discussed above,

while the preparation of phenyl lithium will be discussed later. The experimental system consisted of a 500 ml. round-bottom reaction flask which was connected to a 50 ml. receiving flask and a vacuum pump through the inter-connections of a dropping funnel, a connecting tube and a distilling head.

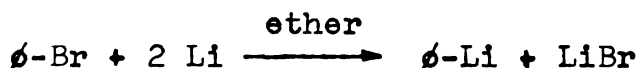
Into the flask was placed 75 mmole of the prepared zinc iodide. To this was added slowly 150 mmole of phenyl lithium in ether solution. The mixing of these two compounds generated heat in the solution. When necessary, a cold water bath was used to remove the excess heat. The reaction flask and part of the dropping funnel were then submersed in a heated oil bath. Ether was distilled first at about 36°C - 40°C under nitrogen. The mixture in the flask appeared pale brown. To obtain pure diphenyl zinc, vacuum sublimation was used. The temperature of the oil bath was slowly raised to a temperature of about 140°C by means of the magnetic heater. Simultaneously, the system was pumped down to a pressure of about 0.04 mm. Under these conditions, pure diphenyl zinc sublimed on the wall of the dropping funnel above the oil level in the form of white crystals. In order for sublimation to continue, the temperature of the oil bath must be raised slowly to about 160°C . However, if the temperature is increased to 165°C or above, decomposition take place. The contents then appeared grey in color.

The sublimation proceeded very slowly. The completion of sublimation required four days. Since diphenyl zinc is very sensitive to air and moisture, the removal of diphenyl zinc from the dropping funnel was achieved under a nitrogen atmosphere.

The reaction equation for the preparation of diphenyl zinc is given below

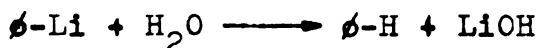


2. Preparation of phenyl lithium^{39,40}



The experimental apparatus consisted of a 250 ml. three-neck flask, a stirrer, a dropping funnel, a reflux condenser and a mercury bubbler. After flushing the system with nitrogen, about 50 ml. of ether was placed in the reaction flask. Then 2.94 g. (420 mmole) of lithium metal in small pieces was added.⁴¹ A solution of 200 mmole (20.95 ml.) of bromobenzene in 100 ml. of ether was separately prepared. A portion of the bromobenzene solution (approximately 10 ml.) was dropped slowly into the flask at room temperature until vigorous refluxing began. Addition of the remaining bromobenzene solution was regulated so that proper refluxing was maintained. In case the reaction became too vigorous, the

reaction flask was submerged in ice water to remove heat generated by exothermal reaction. However, the reaction mixture was not allowed to cool below the refluxing temperature. After all the prepared bromobenzene solution was added, stirring was continued until refluxing stopped. The completion of the reaction took approximately two hours. The solution became clear after it was cooled down with all the impurities deposited in the bottom of the flask. To determine the concentration of $\phi\text{-Li}$,⁴¹ one ml. of $\phi\text{-Li}$ was dissolved in 50 ml. of H_2O , and titrated with 0.0905 N HCl. That is,



phenolphthalein was used as indicator.

3. Reaction of diphenyl zinc with carbon monoxide

The reaction was run at -15°C with 10 mmole of the prepared diphenyl zinc mixing with 10 mmole of base catalyst (potassium tert-butoxide) under a carbon monoxide atmosphere. The experimental procedures as those of previously described reactions were followed. During the reaction about 2.5 mmole of carbon monoxide was absorbed. This absorption of carbon monoxide changed the color of the reaction solution from pale brown to deep brown. After neutralizing the base with 4 ml. of concentrated hydrochloric acid (in 2 ml. of water),

a nearly colorless solution with pale yellow precipitate was obtained. The precipitate was separated from the solution by mean of filtration. The filtrate was extracted twice with 20 ml. of pentane, and then twice with 20 ml. of water. Finally, an analysis of the extract by G.C. was performed to identify the product. After being recrystallized from 95% ethanol, the pale yellow precipitate gave white crystals. Then it was analyzed for identification by recording its melting point, IR spectrum and NMR spectrum.

CONCLUSION

The reaction of carbon monoxide with arylzinc compounds as well as alkylzinc compounds have been studied in a series of experiments. In particular, using potassium tert-butoxide as catalyst, carbon monoxide reacted with di-n-butyl zinc to yield n-valeroïn and the diketone (33% yield), and with diisopropyl zinc to yield isobutyroïn and the diketone (29% yield). However, carbon monoxide reacted to only a small extent with diphenyl zinc resulting in an unmeasurable amount of isolated products. In general, carbon monoxide does not ordinarily react with organozinc compounds. Uptake of carbon monoxide occurred only when the reaction was run in the presence of a proper catalyst. The reaction yield was found to depend strongly on the experimental conditions of temperature, solvent and catalyst. Experimental results indicated that the highest yield was obtained when the reaction was run at -15°C with diglyme as solvent, and with potassium tert-butoxide as catalyst.

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