



A study of the reactions of carbon monoxide with  $\beta$ -Dicarbonyl compounds and their derivatives [and] the synthesis of aldehydes by the reaction of formyl fluoride with organocadmium bromides  
by Jack R Gaines

A THESIS Submitted to the Graduate Committee in partial fulfillment of the requirements for the degree of Master of Science in Chemistry  
Montana State University  
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Abstract:

The reactions between carbon monoxide and the metal enolates of  $\beta$ -di-carbonyl compounds have been investigated. The catalysts used were nickel tetracarbonyl and dicobalt octacarbonyl. Hydrogen was used, in many cases, in addition to the carbon monoxide. Reactions were also run with the free  $\beta$ -dicarbonyl compounds.

No apparent reaction was found to take place between carbon monoxide and these compounds under the conditions which were used. The reaction of O-acetylacetoacetic ester with carbon monoxide and hydrogen in the presence of dicobalt octacarbonyl, however, led to the synthesis of an aldehyde. The identity of this aldehyde has not yet been determined.

Experimental details are given on the preparation of formyl fluoride and the synthesis of 2-methyl-1-butanal by the reaction of formyl fluoride with secondary-butylcadmium bromide. The synthesis of other aldehydes by using formyl fluoride and organocadmium compounds is mentioned.

A STUDY OF THE REACTIONS OF CARBON MONOXIDE WITH  
 $\beta$ -DICARBONYL COMPOUNDS AND THEIR DERIVATIVES.

THE SYNTHESIS OF ALDEHYDES BY THE REACTION OF  
FORMYL FLUORIDE WITH ORGANOCADMIUM BROMIDES.

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Jack R. Gaines

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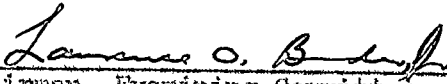
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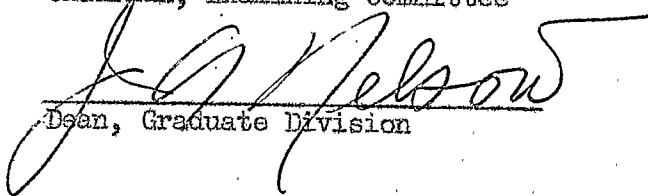
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Head of Major Department

  
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TABLE OF CONTENTS

	Pg.
I. ABSTRACT . . . . .	4
II. INTRODUCTION . . . . .	5
III. THEORETICAL DISCUSSION . . . . .	7
IV. EXPERIMENTAL . . . . .	11
Materials . . . . .	11
Apparatus . . . . .	11
Dicobalt octacarbonyl . . . . .	11
Sodium acetoacetic ester . . . . .	12
Sodium acetylacetone . . . . .	13
Copper acetoacetic ester . . . . .	13
Copper acetylacetone . . . . .	13
Zinc acetylacetone . . . . .	14
O-Acetylacetoacetic ester . . . . .	14
Reaction of acetoacetic ester with carbon monoxide and hydrogen . . . . .	15
Reaction of acetylacetone with carbon monoxide . . . . .	15
Reaction of acetylacetone with carbon monoxide and hydrogen . . . . .	15
Reaction of sodium acetoacetic ester with carbon monoxide . . . . .	15
Reaction of sodium acetylacetone with carbon monoxide . . . . .	17
Reaction of zinc and copper acetylacetone with carbon monoxide and hydrogen . . . . .	17
Reaction of O-acetylacetoacetic ester with carbon monoxide and hydrogen . . . . .	17

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(Table of Contents)

	<u>PG.</u>
Preparation of formyl fluoride . . . . .	19
Secondary-butylmagnesium bromide . . . . .	20
Secondary-butylcadmium bromide . . . . .	20
Synthesis of 2-methylbutanal-1 . . . . .	21
Reactions of formyl fluoride with other organocadmium bromides . . . . .	22
V. DISCUSSION OF EXPERIMENTAL RESULTS . . . . .	23
VI. SUMMARY . . . . .	24
VII. ACKNOWLEDGMENT . . . . .	25
VIII. LITERATURE CITED AND CONSULTED . . . . .	26

I. ABSTRACT

The reactions between carbon monoxide and the metal enolates of  $\beta$ -dicarbonyl compounds have been investigated. The catalysts used were nickel tetracarbonyl and dicobalt octacarbonyl. Hydrogen was used, in many cases, in addition to the carbon monoxide. Reactions were also run with the free  $\beta$ -dicarbonyl compounds.

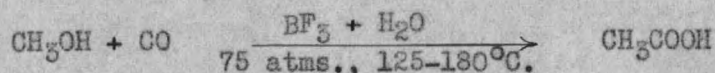
No apparent reaction was found to take place between carbon monoxide and these compounds under the conditions which were used. The reaction of O-acetylacetoacetic ester with carbon monoxide and hydrogen in the presence of dicobalt octacarbonyl, however, led to the synthesis of an aldehyde. The identity of this aldehyde has not yet been determined.

Experimental details are given on the preparation of formyl fluoride and the synthesis of 2-methyl-1-butanal by the reaction of formyl fluoride with secondary-butylcadmium bromide. The synthesis of other aldehydes by using formyl fluoride and organocadmium compounds is mentioned.

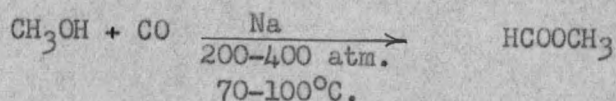
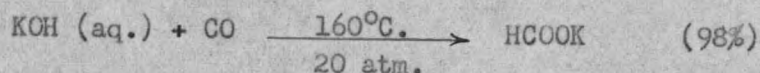
## II. INTRODUCTION

The use of carbon monoxide as an addition reagent in organic syntheses has become of great technical importance. The number of types of compounds which may be synthesized by the use of carbon monoxide have been greatly increased within the past few years.

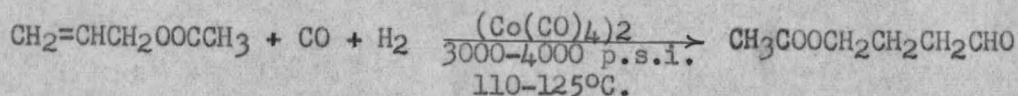
The synthesis of methyl alcohol and higher alcohols from carbon monoxide and hydrogen (14) is carried out on a commercial scale. Both laboratory and industrial reactions are known for the preparation of aldehydes, aliphatic and substituted aliphatic acids. The commercial production of acetic acid and its higher homologs by E.I. du Pont de Nemours (4) is accomplished by the following reaction:



A similar reaction between ethylene and carbon monoxide yields propionic acid (32). By using various starting materials, hydroxy-acids (35)(36), amino-acids (35), and polycarboxylic-acids (5) have been produced by du Pont. Gattermann and Koch (11) have shown that aromatic aldehydes can be prepared by the reaction of aromatic hydrocarbons with carbon monoxide and dry hydrogen chloride in the presence of anhydrous aluminum chloride and a small amount of cuprous chloride. Guthke (30) has reported the synthesis of benzaldehyde by the reaction of benzene and carbon monoxide in the presence of anhydrous aluminum chloride and titanium tetrachloride at high pressures. Both inorganic (10) and organic bases (6)(10) will react with carbon monoxide, under pressure, to yield formates or other addition compounds. Two such reactions are:



Aldehydes have been synthesized industrially by reactions between carbon monoxide, hydrogen and olefins in the presence of cobalt catalysts and under conditions of high pressure (29) (31). This process is known as the "oxo" process. Adkins and Krsek (2) (3) have studied laboratory conditions under which certain unsaturated compounds will add carbon monoxide and hydrogen in the presence of dicobalt octacarbonyl. These reactions yield, in nearly all cases, a high percentage of a single addition product. An illustrative example is given with allyl acetate:



The increasing importance of carbon monoxide as an addition reagent in organic syntheses was one of the reasons for the investigations considered in this paper. One of the original purposes of this investigation was the synthesis of aldehydes through the reaction of carbon monoxide and hydrogen with  $\beta$ -dicarbonyl compounds or their derivatives.

Formyl fluoride (21) is the only acid halide derivative of formic acid which has been isolated. It has been postulated that the hypothetical formyl chloride is formed as an intermediate in the Gattermann-Koch synthesis of aromatic aldehydes (11).

Gilman and Nelson (13) have shown that organocadmium compounds will react with acid chlorides to form ketones. Thus experiments were carried

out to determine the possibility of preparing aldehydes through the reaction of formyl fluoride with organocadmium compounds.

### III. THEORETICAL DISCUSSION

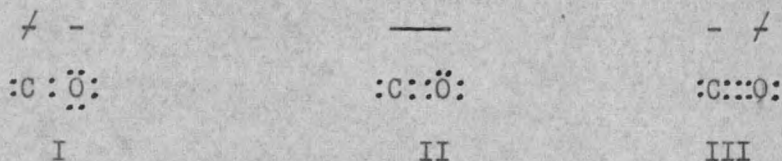
No work, up to the present time, has been reported involving reactions of carbon monoxide and  $\beta$ -dicarbonyl compounds or their metal enolates. Most of the work dealing with the reaction of an organic salt of any type with carbon monoxide, is that of sodium ethoxide and carbon monoxide.

Stahler (26) has reported that alcohol free sodium ethoxide will react with carbon monoxide at high pressures to form the addition product  $\text{NaCOOC}_2\text{H}_5$ . Scheibler and Frikell (25), however, report the formation of a bevalent carbon derivative  $\text{C}(\text{ONa})\text{OC}_2\text{H}_5$ , using the same conditions. Adickes, Simson and Peckelhoff (1) state that both the carbon monoxide and the sodium ethoxide used by Scheibler and Frickell were impure, and that there is no reaction between pure carbon monoxide and pure sodium ethoxide, even after 86 hours. Thus there is no substantial proof that an addition product of any kind is formed when sodium ethoxide is treated with carbon monoxide at high pressures. It has, however, been definitely shown by Burrell (6) and other investigators (34) that a small amount of sodium or sodium ethoxide will catalyze the reaction between ethyl alcohol and carbon monoxide. The reaction results in the formation of ethyl formate in a nearly quantitative yield. This would indicate that the addition of the carbon monoxide proceeds through an ionic mechanism, quite possibly involving the ethoxide ion.

The addition of carbon monoxide to a carbanion would require that the carbon atom in the carbon monoxide molecule carry a positive charge. From the work of Pauling and Sherman (22)(23) it has been concluded that the



carbon monoxide molecule consists of three resonating structures:

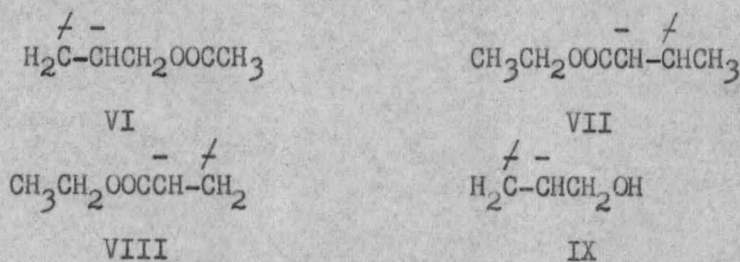


All three structures make about equal contributions to the stability of the molecule. Thus, it seems logical that the type of structure taking part in an addition reaction depends upon the charge of the ion to which the addition is being made and to the stability of the product.

Whitmore (37) has postulated that olefins exist in an activated state under certain conditions. Formulas IV and V represent the normal and activated ethylene molecule respectively:



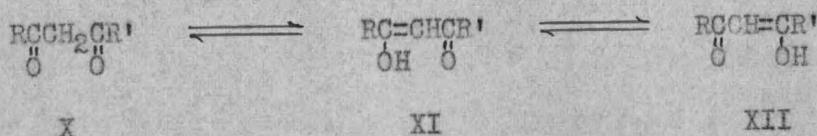
The existence of the activated form V has been fairly well verified by the work of numerous investigators. As previously mentioned, carbon monoxide and hydrogen have been found to add to unsaturated compounds in the presence of dicobalt octacarbonyl (2) (3). Allyl acetate, ethyl crotonate, ethyl acrylate, and allyl alcohol are four compounds which were found to undergo this reaction. A probable polarized or activated form of each compound is given below.



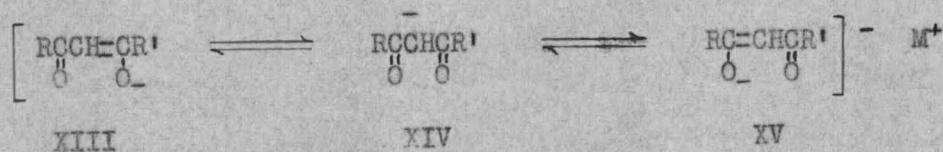
The respective products obtained by Adkins and Krsek were  $\gamma$ -acetoxy-

butyraldehyde, ethyl  $\beta$ -formylbutyrate,  $\beta$ -carbethoxypropionaldehyde, and  $\gamma$ -hydroxybutyraldehyde. If the products are compared with the proposed polarized molecules, it is seen that the addition of the carbon monoxide takes place on the carbon atom carrying the partial positive charge.

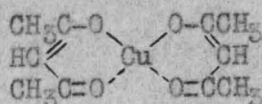
$\beta$ -dicarbonyl compounds<sup>(37)</sup> exhibit tautomerism:



The monovalent salts of  $\beta$ -dicarbonyl compounds<sup>(15)</sup> possess a resonating structure:



A divalent salt, such as copper acetylaceton<sup>(37)</sup>, exists in a chelate ring:

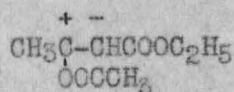


XVI

Structures XIII, XIV, and XV are true anions, while VI, VII, VIII, and IX possess only partial positive and negative charges. Although it appears that the preferential addition of carbon monoxide to unsaturated compounds is on the carbon atom carrying a partial positive charge, it is still likely, due to the resonance structure of carbon monoxide, that an addition to the anion XIV is possible. The structure of the divalent salts such as XVI and the structure of the enols X and XII resemble the ethylenic structure of the unsaturated compounds more so than the

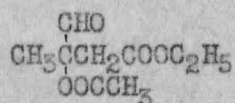
monovalent salts. The unsaturation in XVI is, to a certain degree, fixed due to the presence of chelation.

O-acetylacetoacetic ester is a true ethylenic compound, its activated form is postulated as:



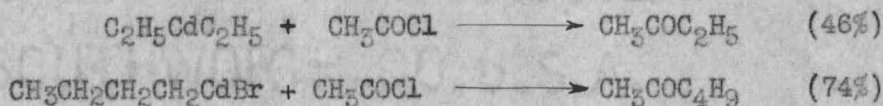
XVIII

This derivative of acetoacetic ester should form the following addition compound with carbon monoxide and hydrogen:

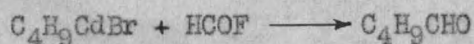


XIX

Gilman and Nelson<sup>(13)</sup> have shown that acid chlorides will react with organocadmium compounds to form good yields of ketones. Two such reactions are:



Grignard reagents, on the other hand, form alcohols with acid chlorides<sup>(37)</sup>. The formation of the ketones with the organocadmium compounds is attributed to the slow rate of reaction of these compounds with the carbonyl group<sup>(13)</sup>. It is logical, therefore, to assume that formyl fluoride should react with organocadmium compounds to form aldehydes. The proposed reaction of secondary-butylcadmium bromide with formyl fluoride is:



#### IV. EXPERIMENTAL

##### Materials

The acetoacetic ester and acetylacetone were Eastman's pure or practical grade. They were properly dried (when necessary) and distilled before use. The inorganic and other organic reagents were of C.P. grade and were used, in most cases, without further purification. The nickel carbonyl, carbon monoxide, and hydrogen were purchased from the Matheson Co. and were used without further purification.

##### Apparatus

Nearly all of the high pressure reactions were carried out in a stainless steel, micro reaction vessel, manufactured by the American Instrument Co. The bomb had a total volume of 183 ml. When larger volumes of reactants were used, a 500 ml Parr bomb was employed. Each bomb was provided with a heating jacket which was mounted in an oscillating mechanism. The oscillating mechanism was powered by a 1/6 H.P. geared head motor, which ran the contents of the bomb from end to end at the rate of 36 cycles per minute. The reaction temperature was controlled by means of a Brown millivoltmeter pyrometer. The thermocouple was inserted through the end of the heating jacket into the rear portion of the bomb. The high pressures, necessary for the reactions, were obtained by means of an Aminco gas booster pump. The booster pump gives a maximum cold pressure of 6000 p.s.i.

##### Dicobalt Octacarbonyl Catalyst

The preparation of the active Raney cobalt was carried out according to the procedure given by Pavlic and Adkins <sup>(24)</sup> for the preparation of

Raney nickel. The "Raney Cobalt Aluminum Catalyst Powder" was purchased from the Gilman Paint and Varnish Co. The procedure followed for the preparation of dicobalt octacarbonyl, was that given by Adkins and Krsek <sup>(2)</sup>.

About 6 g of Raney cobalt was placed in 120 ml of ether and pressured with carbon monoxide to 3400 p.s.i. The mixture was heated with shaking for 6 hours at 150°C. After the bomb had cooled to room temperature, the pressure was 2600 p.s.i., a drop of 800 p.s.i. The dark reddish brown clear solution was separated from unreacted cobalt by centrifugation and decantation. The carbonyl was always used in solution. It was found that the use of cyclohexane as the solvent, resulted in an increased formation of the cobalt carbonyl.

#### Sodium Acetoacetic Ester (20)

A one-liter three-necked flask was mounted in an ice bath and fitted with a reflux condenser, a separatory funnel, and a mercury-sealed stirrer. 300 ml of absolute ethyl alcohol was poured into the flask and to this was added 23 g (1 mole) of sodium wire. As the rate of the reaction became slower, the ice bath was replaced with a steam bath. After the reaction was complete, the solution was cooled to room temperature with constant stirring. 130 ml (1 mole) of ethyl acetoacetate was slowly added through the separatory funnel (about .5 of an hour). The reflux condenser was then replaced by a short still head, and the alcohol was removed by distillation at 35-40°C., under the partial vacuum provided by an aspirator. When most of the alcohol had been removed, the pressure was reduced (1-2 mm) and the remainder of the alcohol was driven off with a steam bath. The flask was allowed to cool to room temperature under the reduced pres-

sure. The yield was 150 g or 96%.

#### Sodium Acetylacetone

A 500 ml, three-necked flask was mounted in an ice bath and fitted with a reflux condenser, a glass stopper, and a mercury-sealed stirrer. In the flask was placed 150 ml of absolute ethyl alcohol and to this was added 12.5 g (0.5 mole) of sodium wire. As the reaction began to slow down, the ice bath was replaced with a steam bath. After the reaction was complete, the sodium ethoxide solution was cooled to room temperature and 50.0 g (0.5 mole) of acetylacetone was slowly added through a separatory funnel. The precipitated enolate was removed by suction filtration and allowed to air dry for 24 hours. The yield was 58 g or 95%.

#### Copper Acetoacetic Ester (38)

A solution of 130 g (1 mole) of acetoacetic ester, dissolved in 300 ml of ether, was thoroughly shaken with a solution of 99.8 g (0.5 mole) of copper acetate monohydrate dissolved in 800 ml of distilled water. The salt which precipitated out was filtered off. The filtrate was neutralized with dilute sodium hydroxide solution until it was only slightly acid. The additional precipitate which formed was filtered off and added to the first batch. The salt was washed until the filtrate gave no acid reaction. The yield was 110 g or 68%.

#### Copper Acetylacetone (8)

49.9 g (0.25 mole) of copper acetate monohydrate was dissolved in 400 ml of distilled water, heated to about 80°C., and filtered. A solution of 50.0 g (0.5 mole) of acetylacetone dissolved in 100 ml of water at 80°C. was added with stirring to the copper acetate solution. The salt which formed, was removed by filtration. The filtrate was treated with

dilute sodium hydroxide until it was just acid. The additional precipitate which formed was filtered off and added to the first batch. The combined salt was washed with water until the filtrate no longer gave an acid reaction and then dried for 12 hours at 80-85°C. The yield was 55 g or 85%.

Zinc Acetylacetonate (28)

To a mixture of 15.7 g (0.125 mole) of zinc carbonate and 25.0 g (0.25 mole) of acetylacetonate, in a 300 ml erlenmeyer flask, was added 200 ml of distilled water. The mixture was stirred for one hour and was allowed to stand for 12 hours. The salt was removed by filtration and dried at 90°C. The yield was 25 g or 75%.

O-Acetylacetoacetic Ester (9)

130 g (1.0 mole) of acetoacetic ester was mixed with 158 g (2.0 moles) of pyridine and 170 g (1.5 moles) of acetyl chloride was slowly added through a dropping funnel. (The acetoacetic ester was dried over calcium sulfate and distilled; the pyridine was dried over sodium hydroxide and distilled; the acetyl chloride was freshly distilled before using.) The mixture was vigorously stirred throughout the addition. At the end of the addition, the solution became nearly solid. The flask was tightly stoppered and allowed to sit for 2 days. 300 ml of ether was added and the pyridine hydrochloride was filtered off and washed several times with ether. The filtrate and ether washings were cooled to 0°C. and washed with a cold (0.5 C.) 1-N solution of sodium hydroxide until the ether layer no longer gave an enol test with ferric chloride. The ether solution was then shaken with cold water, then with cold dilute sulfuric acid, and finally with cold water. After drying over calcium chloride, the ether

was removed by distillation and the remaining oil was fractionated under reduced pressure. The acetylacetoacetic ester distilled over at 100-102° C. at 9 mm. The average yield obtained was 100-110 g or 58-64%.

Reaction of Acetoacetic Ester with Carbon Monoxide and Hydrogen

13.0 g (0.1 mole) of acetoacetic ester, 50 ml of benzene and 2 g of Raney-cobalt were placed in the bomb and pressured to 1630 p.s.i. with hydrogen and then to 3730 p.s.i. with carbon monoxide. The mixture was agitated for 4 hours at 150°C. A pressure drop of 310 p.s.i. was obtained. The resulting mixture contained benzene, acetoacetic ester, dicobalt octacarbonyl, and some unchanged cobalt.

Reaction of Acetylacetone with Carbon Monoxide

10.0 g (0.1 mole) of acetylacetone, 30 ml of ether and 15 ml of the dicobalt octacarbonyl-ether solution were placed in the bomb and pressured to 3830 p.s.i. with carbon monoxide. The final pressure was 3220 p.s.i., a drop of 610 p.s.i. The mixture was agitated at 100°C. for 3 hours. The resulting mixture contained ether, acetylacetone and cobalt acetylacetone.

Reaction of Acetylacetone with Carbon Monoxide and Hydrogen

20.0 g (0.2 mole) of acetylacetone, 28 ml of ether and 15 ml of the dicobalt octacarbonyl-ether solution were pressured to 1980 p.s.i. with hydrogen and then to 4200 p.s.i. with carbon monoxide. The mixture was agitated for 2 hours at 150 C. 20.0 g of acetylacetone was recovered.

Reaction of Sodium Acetoacetic Ester with Carbon Monoxide

15.2 g (0.1 mole) of the salt, 1 ml of nickel tetracarbonyl and 40 ml of cyclohexane were placed in the bomb liner. The bomb was pressured to



3290 p.s.i. with carbon monoxide. The reaction was run at 150°C. for two hours. The final pressure was 2770 p.s.i., a drop of 520 p.s.i. The solid was removed by filtration, washed with ether and allowed to air dry. The solid (4 g) was reddish-brown in color. Vacuum distillation of the filtrate yielded an additional 6 g of the brown solid.

A run using 0.05 mole of salt gave a pressure drop of 480 p.s.i.; 0.15 mole of salt gave 610 p.s.i. drop. Both runs had an initial pressure of 3280 p.s.i. and were carried out at 150°C. for two hours.

7.8 g of the brown solid was refluxed for 3 hours with 100 ml of 1-N sodium hydroxide solution. The solution was acidified with dilute hydrochloric acid and fractionated. The fraction collected under 60°C. was identified as acetone by the formation of its 2,4-dinitrophenylhydrazine derivative (m.p. 125°C. (16)).

A suspension of 21.5 g of the brown solid in 130 ml of anhydrous ether, was placed in a 200 ml three-necked flask. The flask was provided with an inlet tube, a mechanical stirrer and a condenser-outlet tube combination. The flask was cooled in an ice bath and dry hydrogen chloride was slowly passed into the stirred suspension for 3 hours. Dry air was then drawn through the inlet tube for about one hour. The mixture was filtered and fractionated under reduced pressure. 6.9 g of a colorless oil was obtained at 72-72°C. (12-13 mm). Beilstein lists the boiling point of acetoacetic ester at 12.5 mm as 71°C. 0.78 g (0.006 mole, based on the molecular weight of acetoacetic ester) of the oil and 0.62 g (0.006 mole) of phenylhydrazine were mixed in a small beaker and allowed to stand over night on a steam plate. The resulting viscous oil was stirred with ether;

this resulted in the formation of a white crystalline solid. The solid was removed by filtration, washed with ether and dried at 100°C. After recrystallization from alcohol, it melted at 127°C. Using the same procedure, ethyl acetoacetate forms 3-methyl-1-phenyl-5-pyrazolone (17)(27), which has a melting point of 127 C. By using an excess of phenylhydrazine, both the oil and acetoacetic ester (17)(18) yield a high melting, insoluble white solid. The oil was, therefore, acetoacetic ester.

Reaction of Sodium Acetylacetonate with Carbon Monoxide

12.2 g (0.1 mole) of the salt, 25 ml of ether and 15 ml of the dicobalt octacarbonyl-ether solution were placed in the bomb and pressured to 3730 p.s.i. with carbon monoxide. The mixture was agitated for 2 hours at 150° C. A drop of 360 p.s.i. was obtained. The solid was removed by filtration and washed twice with ether. 7.2 g of the solid was refluxed with 200 ml of distilled water for one hour. About one ml of acetone was obtained upon distillation. The residue consisted of a resinous material which could not be identified. 7.2 g of the original salt gave 2.5 ml of acetone when refluxed for 1 hour with 100 ml of distilled water. A drop of 350 p.s.i. was obtained when 40 ml of ether was subjected to the same conditions.

Reactions of Zinc and Copper Acetylacetonate with Carbon Monoxide and Hydrogen

Typical runs in the presence of both nickel tetracarbonyl and dicobalt octacarbonyl resulted in the reduction of the copper compound to metallic copper and acetylacetonate. The zinc salt, under the same conditions was recovered unchanged at the end of the reactions.

Reaction of O-Acetylacetoacetic Ester with Carbon Monoxide and Hydrogen

A description of a typical run is given as follows: 34.4 g (0.2 mole)

of acetylacetoacetic ester, 40 ml of benzene and 2 g of Raney cobalt catalyst were placed in the bomb. The mixture was pressured to 1500 p.s.i. and 3400 p.s.i. with hydrogen and carbon monoxide respectively. The mixture was agitated for 4 hours at 150°C. A pressure drop of 1750 p.s.i. was obtained. Fractionation of the product yielded the following fractions:

1. Benzene.
2. 16 ml of a clear, low boiling liquid.
3. 17 ml of a colorless oil (50-80°C., 12 mm).
4. 17 ml of a colorless oil (85-100°C., 12 mm).
5. 23 ml of a high boiling residue.

Fraction 2 contained 3.4 g of acetic acid, the remainder being benzene. Fractions 3 and 4 were redistilled to give 15 g of a colorless oil, X (b.p. 88-90°C. at 11 mm), 4.1 g of acetic acid, and some higher boiling material.

#### Identification of Oil X

The oil was insoluble in water and 5% NaHCO<sub>3</sub> solution; soluble in 5% NaOH, concentrated H<sub>2</sub>SO<sub>4</sub> and 85% H<sub>3</sub>PO<sub>4</sub>. With the sulfuric acid it gave a yellow colored solution. A small amount of H<sub>2</sub>SO<sub>4</sub> produced a brownish precipitate.

Its reaction with litmus was acid. It gave a silver mirror with Tollen's reagent and an immediate deep purple color with Schiff's reagent. Its 2,4-dinitrophenylhydrazine derivative melted at 49-50°C. A semi-carbazone derivative could not be obtained.

6 ml of the oil was refluxed for 24 hours with 100 ml of 20% HNO<sub>3</sub>. The solution was evaporated to dryness on a steam bath, with repeated additions of distilled water to remove the last traces of nitric acid. A

white, crystalline solid was formed. It was identified as succinic acid through its neutralization equivalent (obtained, 59.12; calculated, 59.05) and its p-toluidine derivative (m.p. obtained, 260°C.; literature value<sup>(16)</sup> 260°C.).

(The molecular weight of the oil was determined by the freezing point method, the solvent used was benzene. The value obtained by extrapolation to infinite dilution was 147. Investigation regarding the identity of this compound is being continued.

#### Preparation of Formyl Fluoride (21)

The apparatus which was used consisted of a 200 ml round bottom flask fitted with an efficient reflux condenser. The top of the condenser was connected to a series of two large U-tubes, 25-30 cm in height. The outlet of the second U-tube was connected to two calcium chloride tubes, the first contained sodium hydroxide pellets and the second contained fused calcium chloride. The apparatus was flushed with hot, dry nitrogen for 2 hours immediately before using. The anhydrous formic acid, used in the preparation, was prepared by refluxing commercial 98-100% formic acid with phthalic anhydride for 2-3 hours and then distilling the mixture.

19 ml (0.5 mole) of anhydrous formic acid, 57 ml (0.5 mole) of benzoyl chloride and 21 g (0.5 mole) of sodium fluoride were placed in the round bottom flask. The flask was then connected to the condenser, the temperature of which was held at 10-15°C. The first U-tube was surrounded by an ice-salt bath and the second U-tube was surrounded by a dry ice-acetone bath (-80°C.). The reaction flask was heated on a steam bath until the reaction began. The reaction proceeded so rapidly at times,

that it was necessary to remove the steam bath and cool the flask with cold water. As the rate of reaction began to decrease, the steam bath was replaced and heating was continued for 30 minutes. The average yield of formyl fluoride, which collected in the second U-tube, was 7-8 g or 29-34%.

#### Secondary-Butylmagnesium Bromide

The general procedure for the preparation of a Grignard reagent is given by Gilman, Zoellner and Dickey (12).

In a three-necked flask fitted with a reflux condenser, a mercury-seal stirrer, and a drop funnel were placed 3 g (0.125 mole) of dry magnesium turnings, 25 ml of absolute ether, and a small crystal of iodine. 17 g (0.125 mole) of secondary-butyl bromide was placed in the drop funnel and after 10 drops of this halide had been added to the reaction flask, 75 ml of absolute ether was added to the drop funnel. The reaction was started by means of gentle heating. Once the reaction had begun, the motor driven stirrer was started and the secondary-butyl bromide-ether solution was allowed to flow into the flask at a rate of 1-2 drops per second. The stirring was continued for an additional 30 minutes after the contents of the drop funnel had been added to the flask. The ether solution of the secondary-butylmagnesium bromide was used immediately to prepare the cadmium compound.

#### Secondary-Butylcadmium Bromide

The procedure suggested by Cason (7) was followed for the preparation of this compound.

An additional 50 ml of absolute ether was added to the Grignard re-

agent prepared by the above procedure. The drop funnel was replaced by a large test tube containing 22.9 g (0.125 mole) of anhydrous cadmium chloride. The connection between the flask and the test tube was a short piece of Tygon tubing. The cadmium chloride was added to the secondary-butylmagnesium bromide-ether solution during a period of 15-20 minutes. The solution was vigorously stirred throughout the addition and for a period of 30 minutes following the addition.

#### Synthesis of 2-Methyl-1-butanal

The formyl fluoride which was collected in the second U-tube, was distilled into a glass jacketed drop funnel containing 30 ml of absolute ether. The drop funnel jacket was filled with a dry ice-acetone mixture. The large test tube connected to the flask containing the organocadmium compound was replaced by this drop funnel. The organocadmium bromide-ether solution was cooled with a dry ice-acetone bath and the formyl fluoride-ether solution was added over a period of one minute. The mixture was stirred during the addition and for three hours thereafter. The mixture was allowed to come to room temperature by standing over night.

The mixture was hydrolyzed with 30 ml of dilute sulfuric acid and the ether layer was separated. The aqueous solution was extracted twice with 50 ml of ether. The ether solutions were combined, dried over calcium chloride, and fractionated. After the ether had been removed, 3 ml of a colorless liquid (b.p. 85-90°C., 640 mm) was obtained.

This liquid gave a positive Tollen's and Schiff's test. Its 2,4-dinitrophenylhydrazine derivative melted at 120 C. Huntress and















