



A study of the reactions of carbon monoxide with β -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 β -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 β -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
 β -DICARBONYL COMPOUNDS AND THEIR DERIVATIVES.

THE SYNTHESIS OF ALDEHYDES BY THE REACTION OF
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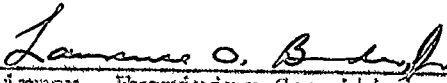
Master of Science in Chemistry

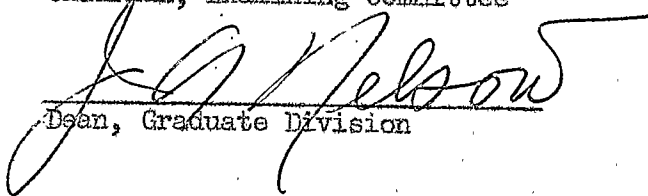
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Head of Major Department


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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 β -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 β -dicarbonyl compounds.

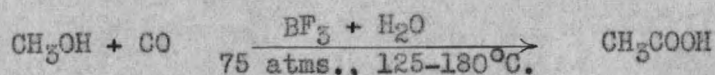
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Experimental details are given on the preparation of formyl fluoride and the synthesis of 2-methyl-1-butanal by the reaction of formyl fluoride with secondary-butylcadmium bromide. The synthesis of other aldehydes by using formyl fluoride and organocadmium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

