



# Organic Syntheses via Metal Carbonyls

Volume 2

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A Wiley-Interscience Publication  
JOHN WILEY & SONS

New York · London · Sydney · Toronto

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**Library of Congress Cataloging in Publication Data** (Revised)

Wender, Irving.

Organic syntheses via metal carbonyls.

Vol. 2 has imprint: New York, Wiley.

"A Wiley-Interscience publication."

Includes bibliographies and indexes.

1. Metal carbonyls. 2. Chemistry, Organic—Synthesis. I.  
Pino, Piero, joint author. II. Title.

QD411.W4

547'.2

67-13965

ISBN 0-471-93367-8 (v. 2)

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

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# Preface

Volume 1 of this series, published in 1968, covered the preparation, structure and properties of the metal carbonyls and their derivatives and discussed their use in three types of organic synthesis. This second volume is devoted entirely to a whole range of organic syntheses in which these transition metal compounds are used chiefly as catalysts and occasionally as stoichiometric reagents.

The metal carbonyls have for years been the most versatile and the most investigated homogeneous catalysts in nonaqueous phases. Studies of the properties of and organic syntheses via metal carbonyls since the late 1940s have led to concepts such as  $\pi$ -complex formation between unsaturated compounds and transition metal compounds, ligand and substrate insertions, associative and dissociative mechanisms, and oxidative addition and reductive eliminations. These reaction steps and mechanisms have usually been presented in reports of specific investigations of the hydroformylation (oxo) reaction but were then designated by different names.

Indeed, work with the metal carbonyls provided the impetus for the very rapid growth of the whole field of homogeneous catalysis that occurred during 1955–1970. In this period, it was shown that the above concepts had wide application in numerous homogeneous reactions related to those catalyzed by metal carbonyls; these included the vital fields of homogeneous hydrogenation, Ziegler–Natta type homogeneous polymerization, and olefin oxidation.

Interestingly, after opening the way to understanding homogeneous catalysis by transition metals, these same metal carbonyls and derivatives have, because of world events, become of paramount importance today. With a high price of oil and a shortage of natural gas, the countries with abundant indigenous or available coal reserves must fall back on this natural resource. This is resulting in the revival of carbon monoxide chemistry in general and carbonylation in particular, connected with attempts to synthesize fuels, petrochemicals (including olefins), and fine

chemicals starting with carbon monoxide or mixtures of carbon monoxide and hydrogen (synthesis gas).

The way to fuels and chemicals in the future will likely start with the conversion of coal to synthesis gas. Synthesis gas can be converted to liquid fuels via the Fischer–Tropsch reaction and other processes, and to methanol and hence to formaldehyde. It also will furnish the hydrogen for ammonia production. We can now go from methanol to acetic acid via an improved homogeneously catalyzed process. It is possible that the ethylene of the future will be produced via ethanol obtained by the homogeneous, metal carbonyl catalyzed reaction of methanol with synthesis gas (a reaction discovered in 1951, incidently). And it may well be that a significant part of our petrochemical and fuel economy in the last fifteen years of this century will rely on synthesis gas from coal. Therefore, the role of metal carbonyls and their derivatives, so well known as catalysts for reactions involving carbon monoxide, synthesis gas, and molecular hydrogen—already of great importance—will grow even larger in the years to come.

There is, of course, much research still to be done in catalysis by metal carbonyls, despite its relatively long history. Chemists must learn to use these and related metal complexes to synthesize organic compounds via homogeneous catalysis directly from carbon monoxide and hydrogen. Until recently, this direct synthesis could only be accomplished by using heterogeneous catalysts. There are many advantages in using homogeneous catalysts: milder conditions, greater selectivity, and less sensitivity to poisons. A breakthrough has been announced in the synthesis of ethylene glycol and similar alcohols from synthesis gas while using soluble, transition metal complexes. Further problems to be solved include the homogeneously catalyzed synthesis of methanol and methane from synthesis gas and the carbonylation of saturated carbon–hydrogen bonds.

We hope this second volume will furnish some of the necessary background to synthetic organic chemists and in general to researchers entering the field of carbon monoxide chemistry. It should also point the way to specific instances and general areas that need further research in the fields of carbon monoxide chemistry and homogeneous catalysis.

The editors contemplated compiling a list of known reactions of organic substrates catalyzed by metal carbonyls and their derivatives. This would obviously be of great value, especially if classified according to substrate, catalyst, other reactants, and references. But the number of these reactions is so large and the almost daily appearance of new homogeneously catalyzed reactions precluded this endeavor. We are thus most aware that these volumes merely scratch the surface by including only the more well-known reactions.

Due to the breadth of the field, the authors were asked for critical rather than for complete reviews of the literature. For this reason and despite occasional unavoidable delays in publication resulting in different periods of coverage of certain topics, the chapters should nevertheless give a view of how the chemistry of the different reactions was developed. No particular emphasis is given to industrial application of the reactions discussed, especially when reviews on these subjects have appeared. The one exception is the description of the synthesis of acrylic acid from acetylene, carbon monoxide, and water.

The various chapters in this volume are presented in what the authors consider a logical order: The first chapter relates the carbonylation of saturated organic compounds. The second and third chapters treat the homogeneously catalyzed reactions of olefins. The fourth and fifth chapters deal with allylic compounds and acetylenic substrates, respectively, which have more possibilities and pathways for reaction. The sixth chapter moves to the carbonylation of halogenated compounds. The seventh chapter summarizes a number of reactions involving iron carbonyls. The eighth chapter on decarbonylation involving transition metal complexes supplements and helps us understand all the chapters that precede it. The ninth and tenth chapters concern homogeneous reactions of unsaturated compounds that do not involve carbon monoxide but in which metal carbonyls are usually the catalyst precursors. The last chapter introduces us to symmetry-restricted reactions catalyzed by transition metal complexes, in which field further interesting developments are expected.

We thank the following persons who in various ways aided in the preparation of this book: R. F. Heck, J. F. Roth, N. v. Kutepow and W. Himmele of BASF, C. Zahn, and G. F. Pregaglia.

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*December 1975*

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**Organic Syntheses via  
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# Carbonylation of Saturated Oxygenated Compounds

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## I. INTRODUCTION

This chapter deals with the carbonylation of saturated aliphatic and aromatic compounds having oxygenated functional groups. No division will be made between aliphatic and aromatic substrates since aromatic unsaturation does not, as a rule, react under conditions chosen for carbonylation reactions.

The term "carbonylation" is used here as a generic term, including reactions such as formylation, hydroformylation, carboxylation, and homologation—all involving the introduction of a carbonyl group into an organic substrate.

## 2 Carbonylation of Saturated Oxygenated Compounds

TABLE 1  
Reactions of Saturated Oxygenated Substrates with CO

Reaction	Catalyst <sup>a</sup>
$\text{ROH} + \text{CO} \rightarrow \text{RCOOH}$	$\text{Co}_2(\text{CO})_8 + \text{I}_2$ ; Rh + HI
$\text{ROH} + \text{CO} \rightarrow \text{HCOOR}$	$\text{Co}_2(\text{CO})_8$
$\text{ROH} + \text{CO} + \text{H}_2 \rightarrow \text{RCH}_2\text{OH}$	$\text{Co}_2(\text{CO})_8$
$\text{ROR} + \text{CO} \rightarrow \text{RCOOR}$	$\text{Co}_2(\text{CO})_8 + \text{I}_2$
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{RCH} - \text{CHR} \end{array} + \text{CO} + \text{H}_2 \rightarrow \begin{array}{c} \text{CHO} \\   \\ \text{RCHCHOHR} \end{array}$	$\text{Co}_2(\text{CO})_8$
$\begin{array}{c} \text{OR} \\ \diagup \quad \diagdown \\ \text{H}_2\text{C} - \text{C} \\ \diagdown \quad \diagup \\ \text{OR} \end{array} + \text{CO} + \text{H}_2 \xrightarrow{-\text{ROH}} \begin{array}{c} \text{OR} \\ \diagup \quad \diagdown \\ \text{H}_2\text{C} - \text{C} \\ \diagdown \quad \diagup \\ \text{CHO} \end{array}$	$\text{Co}_2(\text{CO})_8$
$\text{R}'\text{C}(\text{OR})_3 + \text{CO} + \text{H}_2 \rightarrow \text{R}'\text{COOR} + \text{ROH} + \text{RCHO}$	$\text{Co}_2(\text{CO})_8$
$\text{RCOOR}' + \text{CO} \rightarrow \text{RCO}-\text{O}-\text{OCR}'$	$\text{CoBr}_2 + \text{Et}_4\text{NBr}$
$\begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ (\text{CH}_2)_n - \text{C} \\ \diagdown \quad \diagup \\ \text{O} \end{array} + \text{CO} + \text{H}_2 \xrightarrow{\text{H}_2\text{O}} \begin{array}{c} \text{COOH} \\   \\ (\text{CH}_2)_n \\   \\ \text{COOH} \end{array}$	$\text{Ni}(\text{CO})_4 + \text{I}_2$
$\begin{array}{c} \text{RCHNHCOCH}_3 \\   \\ \text{OH} \end{array} + \text{CO} \rightarrow \begin{array}{c} \text{RCHNHCOCH}_3 \\   \\ \text{COOH} \end{array}$	$\text{Co}_2(\text{CO})_8$

<sup>a</sup> Catalyst generally used.

The reactions that will be considered here are listed in Table 1.

These reactions are catalyzed by group VIII metals, especially Fe, Co, Ni, in the form of metal carbonyls or other derivatives which under reaction conditions are transformed into carbonyls. More recently, Ir, Rh, Ru, Os, Pt, and Pd derivatives have been used as catalysts for some of these reactions.

In some cases (especially in carbonylation of alcohols, esters, and ethers) halogens and organic or inorganic halides are used as promoters.

The presence of  $\text{H}_2$  or of compounds containing active hydrogen generally increases the rate of these reactions so that they may be carried out at lower temperatures.

All the listed reactions, apart from the synthesis of acetic acid, have received little attention as compared with the hydroformylation of olefins.

This is probably due to the lack of practical importance of these reactions which, in some cases, is related to their low selectivity.

## II. CARBONYLATION OF ALCOHOLS

### A. Introduction

Different products, depending on the catalyst, reagents, and reaction conditions used, may be obtained by carbonylation of alcohols in the presence of metal carbonyls.

The simple addition of CO to an alcohol may yield either its formic ester or a carboxylic acid having one more carbon atom (reaction 1). Both reactions are thermodynamically possible in the same range of pressures



and temperatures (Table 2), the synthesis of acids being favored below 200°C. By using the appropriate catalyst and reaction conditions, the formation of either may be favored.

When H<sub>2</sub> is also present, the alcohol having one more carbon atom in the chain is formed instead of the carboxylic acid (see homologation of alcohols, II-D).

### B. Synthesis of Carboxylic Acids

The synthesis of carboxylic acids from alcohols and CO (Eq. 2) in the presence of acid catalysts has been known for a long time (1); although it

TABLE 2  
Thermodynamic Data of Some Carbonylation Reactions of Alcohols<sup>a</sup>

Reaction	$\Delta H_{298}^{\circ}$ (kcal/mole)	$\Delta G_{298}^{\circ}$ (kcal/mole)
$\text{CH}_3\text{OH}_{(g)} + \text{CO}_{(g)} = \text{HCOOCH}_3_{(g)}$	-10.20	+0.06
$\text{CH}_3\text{OH}_{(g)} + \text{CO}_{(g)} = \text{CH}_3\text{COOH}_{(g)}$	-30.23	-19.81
$\text{CH}_3\text{OH}_{(g)} + \text{CO}_{(g)} + 2\text{H}_{2(g)} = \text{CH}_3\text{CH}_2\text{OH}_{(g)} + \text{H}_2\text{O}_{(g)}$	-35.53	-23.44

<sup>a</sup> Calculated according to O. A. Hougen, K. M. Watson, and R. A. Ragatz, *Chemical Process Principles*, John Wiley, New York, 2nd ed., 1954, using the values of the heats and of the free energies of formation of the reactants and products listed in *Chemical Engineers Handbook*, R. H. Perry, C. H. Chilton, and S. D. Kirkpatrick, Eds., McGraw-Hill, New York, 4th ed., 1963, pp. 3-134.



#### 4 Carbonylation of Saturated Oxygenated Compounds

has been studied by numerous workers, it has never achieved practical importance, apart from the Koch synthesis (2), owing to its low yield.



The use of metal carbonyls or of other transition metal complexes as catalysts for this synthesis first received attention only after Reppe's work (3,4).

Because of its practical importance (4-20), most of the activity in the field has been concentrated on the synthesis of acetic acid from methanol and CO. These investigations (4,7,21-25), however, have been extended to the higher homologs of methanol and to secondary (7,21,26), tertiary (21,26), unsaturated (27,28), and aryl-substituted alcohols (21), as well as to diols (4,21,25,26,29).

Table 3 lists a selection of results obtained from the carbonylation of alcohols to acids. The metals generally used as catalysts are Ni and Co; Fe shows only low activity (10). Halogens are generally used as promoters. The temperature and pressure necessary for this reaction (200-300°C; 200-700 atm) are higher than those generally used for the carbonylation of other saturated substrates.

Discrepancies are found in the literature on the composition of the carbonylation products of many alcohols (4,21,26). They are probably attributable to difficulties existing up to a few years ago in the separation, identification, and quantitative determination of these compounds in complex mixtures.

The results obtained by Reppe and co-workers on the carbonylation of propyl and *sec*-butyl alcohols (4) and by Simons on the carbonylation of butyl and *sec*-butyl alcohols (26) all clearly show that this reaction does not lead, as first supposed (21), to the formation of only one product, but to a mixture of isomeric compounds. The carboxyl group generally adds to the carbon atom carrying the hydroxyl group in the starting alcohol; complications arise mainly from the formation of olefins due to dehydration of the alcohol.

Secondary alcohols react faster than the corresponding primary compounds (21). Tertiary alcohols are mainly dehydrated to the corresponding olefins (21,26).

Dicarboxylic acids may be obtained from diols; for example, pimelic acid is obtained in 94% yield from 1,5-pentanediol (4). Other diols tested have given much lower yields of dicarboxylic acids, with monocarboxylic acids, esters, and ethers formed as by-products.

The carbonylation of alcohols yields, besides carboxylic acids, a number of other products, whose importance and relevance depend on reaction conditions and on the catalysts used. The problem is general, but it has