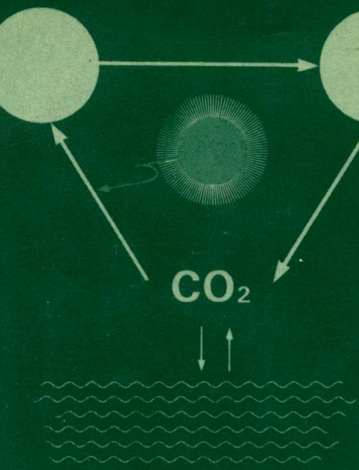

Organic and Bio-organic Chemistry of Carbon Dioxide

Edited by

S. Inoue and N. Yamazaki

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Preface

While it may seem strange to discuss carbon dioxide, an inorganic compound, in the context of "organic and bio-organic chemistry," carbon dioxide is one of the essential building blocks of the organic substances produced by photosynthetic processes in green plants and some microorganisms. The consumption of these organic materials with eventual conversion to carbon dioxide is the basis of human life on this planet.

The accelerating consumption of fossil fuels, products of carbon dioxide fixation in prehistoric times, has reportedly increased the atmospheric carbon dioxide concentration in recent years, probably affecting the world's weather. Diminishing fossil fuel supplies and possible environmental hazards point to the need for greater chemical utilization of carbon dioxide. While industrial applications have been limited so far, simulation of certain efficient biochemical carbon dioxide fixation reactions may lead to new syntheses with potential practical use.

Emphasizing recent developments in the field, this book provides a full overview of the organic and bio-organic chemistry of carbon dioxide. Organometallic and macromolecular synthetic reactions are given special treatment in light of significant new findings in these areas. Other chapters focus on biochemical and model reactions involving carbon dioxide. All are subjects of increasing interest at a time when improved utilization of our planet's carbon resources has become critically important.

The editors wish to express their profound appreciation to the authors for their fine articles, which will certainly contribute much to the enhanced understanding and use of this fundamental small molecule. We are also indebted to Mrs. G. D. Allinson and other members of the staff at Kodansha for their linguistic and editorial assistance in the preparation of this book.

Shohei INOUE
Noboru YAMAZAKI

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4.2 Ring-Opening and Addition Polymerizations involving Carbon Dioxide

1

Introduction

Shohei Inoue
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Human beings and all other living things on Earth depend for their existence on the process of photosynthesis, the fixation of carbon dioxide by green plants and some micro-organisms, using solar energy. This reaction reduces carbon dioxide, the most oxidized form of carbon, to carbohydrate under moderate conditions. Chemists have long dreamed of imitating this reaction in a test tube

The chemical utilization of carbon dioxide as a resource for the production of useful substances has been rather limited, however.

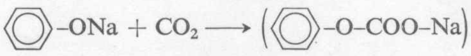
At present, the largest industrial organic use of carbon dioxide as a material is in the synthesis of urea from carbon dioxide and ammonia, a process which was first used on a small scale in Germany in 1920. The synthesis involves two reaction steps: very rapid formation of ammonium carbamate (Eq. 1.1), and dehydration to urea (Eq. 1.2) under rigorous conditions such as high temperature and high pressure.

$$CO_2 + 2\ NH_3 \rightleftarrows [H_2NCOO^-]\,[NH_4^+] \tag{1.1}$$

$$[H_2NCOO^-]\,[NH_4^+] \longrightarrow H_2NCONH_2 + H_2O \tag{1.2}$$

These two reaction setps illustrate well the characteristics of the reactivity of carbon dioxide: high reactivity toward the base (nucleophile), and low reactivity of the product thus formed, a carboxylate.

Another industrial process is the synthesis of hydroxybenzoic acid from carbon dioxide and an alkali metal salt of phenol, the Kolbe-Schmitt reaction, discovered in 1860. This synthesis also has two steps: formation of a complex between carbon dioxide and phenolate (Eq. 1.3), and the transfer of a carboxyl group to the aromatic ring (Eq. 1.4).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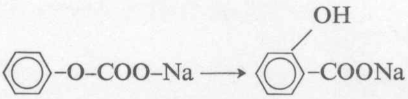

(1.4)

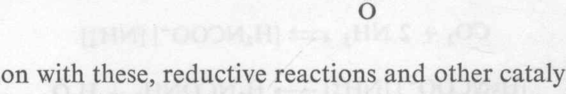
The carbon dioxide-phenolate complex can transfer a carboxyl group to another organic molecule and is regarded as a carrier of activated carbon dioxide.

One of the typical reactions of carbon dioxide is that with organometallic compounds. Even the very early literature concerning the formation of Grignard reagents described the reaction of such compounds with carbon dioxide to form carboxylic acid (Eq. 1.5).

$$R\text{–}MgX + CO_2 \longrightarrow R\text{–}COO\text{–}MgX \tag{1.5}$$

This reaction is of practical importance in the synthesis of carboxylic acid on a laboratory scale. Related is the carboxylation of an active hydrogen compound with a base.

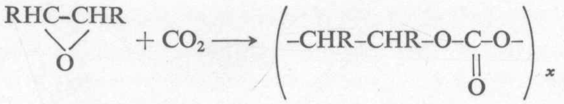
In the development of organotransition metal chemistry during the 1970s, there were numerous reports of reactions between a transition metal alkyl or hydride and carbon dioxide that gave the corresponding carboxylic and formic acids, as in the Grignard reaction. In addition to these "normal" insertion reactions of carbon dioxide, there has been reported a reaction involving an "abnormal" insertion that formed a metal-carbon bond but not a metal-oxygen bond (Eq. 1.6).



$$Et\text{–}Co\,(PPh_3)_2 + CO_2 \longrightarrow Et\text{–}O\text{–}\underset{\underset{\displaystyle O}{\|}}{C}\text{–}Co\,(CO_3)_x(PPh_3) \tag{1.6}$$

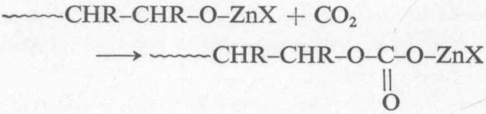
In connection with these, reductive reactions and other catalytic fixations of carbon dioxide with transition metal systems are currently being developed in expectation of novel processes that may lead to significant new syntheses.

Progress was made in the same decade in the syntheses of macromolecules using carbon dioxide as a starting material. The first example was the copolymerization of carbon dioxide and epoxide (Eq. 1.7).

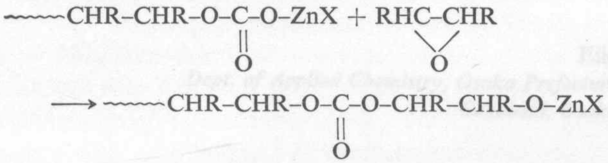


(1.7)

This is a catalytic fixation of carbon dioxide with an organozinc system and is thought to involve the insertion of carbon dioxide into a zinc alkoxide as one of the two elementary steps (Eqs. 1.8 and 1.9).



$$\sim\!\sim\!\sim \text{CHR–CHR–O–ZnX} + \text{CO}_2 \longrightarrow \sim\!\sim\!\sim \text{CHR–CHR–O–}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{–O–ZnX} \qquad (1.8)$$



(1.9)

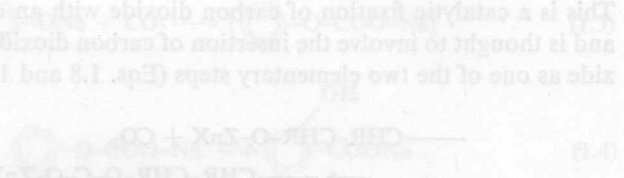
Since the discovery of this technique, a number of reactions that produce high molecular weight polymers or oligomers with carbon dioxide as a starting material have been reported, including addition polymerization and condensation polymerization reactions.

Another topic of current interest in the chemistry of carbon dioxide is the development of models for biological carbon dioxide fixation. Such studies will not only increase our understanding of biochemical reactions but will also lead to novel synthetic processes of industrial importance by mimicking the characteristics of certain effective biochemical processes.

The growing interest in "biomimetic" chemistry of carbon dioxide is, of course, the result of studies of biological carboxylations in recent years. Recent research concerned with photosynthesis, a representative of biological carbon dioxide fixation reactions, has uncovered various reactions that must be added to the classical Calvin cycle. Reactions encountered in some micro-organisms are of particular interest for their apparent simplicity and for their significance in biological and chemical evolution. There has also been progress recently in studies of other important biological reactions of carbon dioxide, such as the reversible hydration of carbon dioxide with carbonic anhydrase and the carbon dioxide fixation accompanying carboxyl transfer with biotin enzymes.

Advances in the chemistry and biological chemistry of carbon dioxide will continue to provide much information for the understanding and possible utilization of this fundamental substance.

synthesis, discovered in 1860. This synthesis also has the [illegible] formation of a complex between carbon dioxide and phenolate (Eq. 1.3), and the transfer of a carboxyl group to the aromatic ring (Eq. 1.4).



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The carbon dioxide–phenolate complex can transfer a carboxyl group to another organic molecule and is regarded as a carrier of activated carbon dioxide.

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[illegible] of practical importance in the synthesis of carboxylic [illegible] Related is the carboxylation of an active [illegible]

[illegible]

syntheses.

[illegible]

was the copolymerization [illegible]

2

Organic Syntheses with Carbon Dioxide

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When the oil crisis struck in 1973, it came as a great surprise to many people that a large amount of petroleum in the world changes into carbon dioxide every day. It is clear that if this carbon dioxide could be used as a carbon source for various organic syntheses, mankind would benefit tremendously.

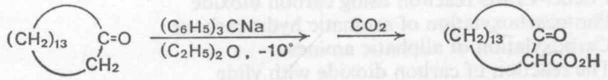
Although a number of organic syntheses using carbon dioxide as a starting material have been found, carbon dioxide has been employed for industrial use for urea synthesis, and, on a small scale, for the Kolbe-Schmitt reaction. If we consider recycling of resources, we see that organic synthetic reactions using carbon dioxide are many fewer in number than those using carbon monoxide. With the recent progress in research, however, organic synthetic reactions using carbon dioxide should soon assume a position of equal importance.

In this chapter, we will discuss the following questions: What approaches have recent studies on organic synthesis using carbon dioxide taken? What directions should future research pursue?

As there are a number of reviews[1–6] on carbon dioxide, we will focus the discussion on research since 1970 that has dealt with organic synthetic reactions using carbon dioxide; we have excluded organometallic reactions because they are described in detail in Chapter 3.

2.1. CARBOXYLATION OF ACTIVE HYDROGEN COMPOUNDS

It is well known that carbon dioxide is readily inserted into various organometallic compounds to produce metal carboxylates, which then produce the corresponding carboxylic acids upon acidification with a strong acid such as hydrochloric or sulfuric acid. The insertion reaction of carbon dioxide in the synthesis of carboxylic acids has been employed in the laboratory to characterize the formation of carbanions. This reaction was first achieved with camphor in 1868 (Eq. 2.1).[7] Another example of this reaction is the carboxylation of cyclopentadecanone, whose carbanion is formed by treatment with triphenylmethylsodium (Eq. 2.2).[8]



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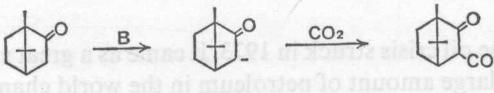
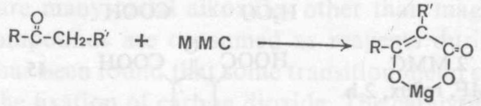


(2.2)

2.1.1. Stiles' Reagent (MMC)

A useful synthetic reaction for carboxylic acids was discovered by Stiles and Finkbeiner.[9] With this, the formation of enolate carbanion and its carboxylation can take place simultaneously by reaction with methyl methoxymagnesium carbonate (MMC) (Eqs. 2.3 and 2.4), which is obtained by treating magnesium methoxide with carbon dioxide in dimethylformamide (DMF). The reverse reaction is prevented by the formation of a magnesium chelate between the carboxyl group and the enolate. This reaction may be applied to many other substrates with activated carbon atoms, as shown in Table 2.1.



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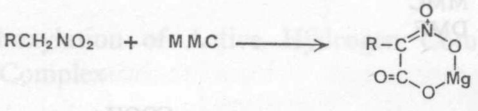
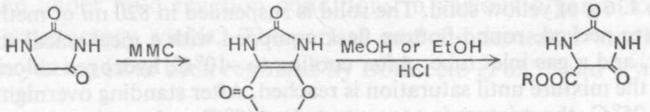


(2.4)

In this reaction, carboxylic acids are obtained by careful acidification of the reaction mixture containing magnesium chelate (1, Eq. 2.3) with a mineral acid such as hydrochloric acid or sulfuric acid, but the resulting carboxylic acids (β-oxocarboxylic acids, α-nitrocarboxylic acids, etc.) are too unstable to be stored even for several days. There are therefore some disadvantages in using these carboxylic acids as starting materials in synthetic reactions except when employing them as reaction intermediates. Direct esterification of the magnesium chelates (1) to eliminate the problem has been reported (Eqs. 2.5 and 2.6).[17,18]



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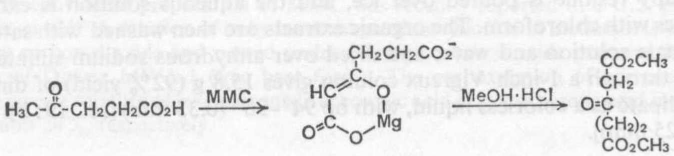
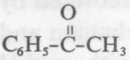
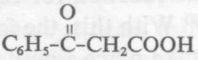
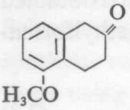
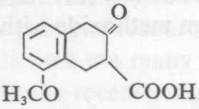
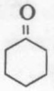
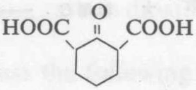
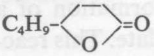
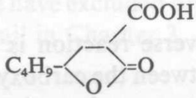
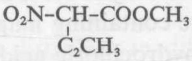


92%

(2.6)

Table 2.1 Carboxylation of active hydrogen compounds with MMC.

Substrate	Reaction conditions	Reaction product	Yield (%)	Reference
 $C_6H_5-C(=O)-CH_3$	MMC DMF	 $C_6H_5-C(=O)-CH_2COOH$	68	10
	MMC DMF, 130°C, 4 h		44	11
	2 MMC DMF, reflux, 2 h		45	12
	MMC DMF			13
	MMC DMF		98	14
O_2NCH_3	MMC DMF	O_2N-CH_2COOH	63	15
$O_2N-CH_2CH_2CH_3$	MMC CH_2N_2 DMF	 $O_2N-CH(C_2H_5)-COOCH_3$	44	16

Direct esterification plays an important role in the general procedure for carboxylation using MMC.

General procedure *Dimethyl β-ketoadipate*. A solution of 10.6 g (91.4 mmol) of levulinic acid in 360 m*l* (920 mmol) of 2.56 M MMC in DMF is heated at 135° C for 24 h. The DMF is removed by distillation under vacuum at 60° C. Trituration of the residue with ether after filtration and air drying gives 136 g of yellow solid. The solid is suspended in 820 m*l* of methanol in a 3-*l*, three-necked, round-bottom flask equipped with a mechanical stirrer, a condenser, and a gas inlet tube. After cooling to −10° C, hydrogen chloride is passed over the mixture until saturation is reached. After standing overnight and warming to 25° C, the mixture is concentrated at 40° C under reduced pressure. The syrupy residue is poured over ice, and the aqueous solution is extracted four times with chloroform. The organic extracts are then washed with saturated bicarbonate solution and water and dried over anhydrous sodium sulfate. Distillation through a 1-inch Vigreux column gives 15.8 g (92% yield) of dimethyl β-ketoadipate as a colorless liquid, with bp 94°–96° (0.35 mm) [ref. 19: bp 110°–111° (0.25 mm)].