A mechanistic study of thermal Fe(CO)₅ mediated CO insertion into vinylcyclopropanes

Matthias M. Schulze *, Ulrich Gockel

Institut für Organische Chemie und Biochemie, Gerhard-Domagk-Str. 1, 53121 Bonn, Germany

Received 14 March 1996; revised 30 April 1996

Abstract

The mechanism of thermally mediated CO insertion into vinylcyclopropanes by Fe(CO)₅ has been studied using deuterium labelled starting materials. The broad distribution of deuterium in the enone products suggests formation of an intermediate iron π-allyl hydride complex that is capable of internal deuterium delivery to several positions. The mechanistic differences between thermal and photoinduced CO insertion into vinylcyclopropanes are discussed.

Keywords: Iron; Iron carbonyl; Carbonylation; Insertion reaction; Vinylcyclopropane

1. Introduction

The carbonylation of organic substrates by various metal carbonyls is one of the most prominent reactions of this important class of complexes [1]. It has been demonstrated that the use of metal carbonyls in the conversion of olefins, and related unsaturated compounds, to ketones is a powerful tool in organic synthesis [2]. Owing to its low cost and availability, many studies have been carried out using pentacarbonyl iron [3]. The reactivity of three-membered ring compounds, resulting from ring strain, makes them interesting substrates for carbonylation. The utilization of vinylcyclopropanes as coordinating components has attracted much attention in the past, and has resulted in the discovery of several reaction pathways [4], among them the conversion to dienes and ketones. We have recently reported the selective production of these compounds from vinylcyclopropanes using Fe(CO)₅ and have demonstrated that the outcome is dependent on the electronic properties of the double bond [5]. Since established mechanistic considerations (vide infra) could not provide a reasonable explanation for the observed experimen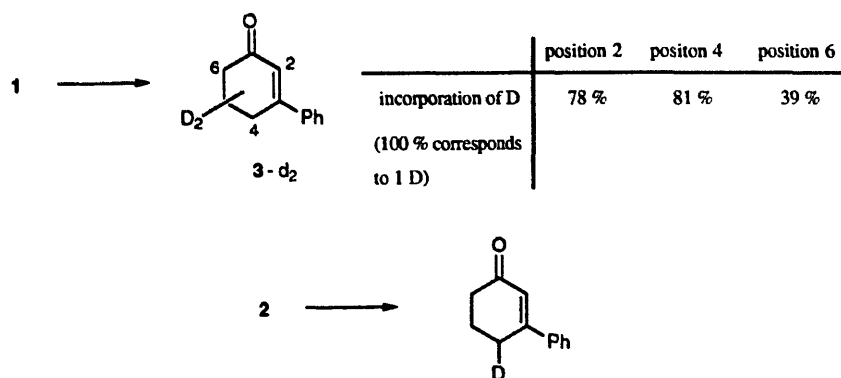tal results, we initiated an investigation to examine the CO insertion into vinylcyclopropanes by the thermally mediated action of Fe(CO)₅. While performing the reaction under irradiation with UV-light at low temperatures has allowed the isolation of metal-containing intermediates [6], conducting the sequence at elevated temperatures excludes the characterization of reactive intermediates due to their sensitivity. Therefore, we made use of the readily accessible deuterium labelled olefins 1 and 2, in order to study the mechanism of the reaction. Such a methodology has been successfully applied in the elucidation of palladium [7] and rhodium [8] -assisted reactions of similar vinylcyclopropanes.

1   2   3   4
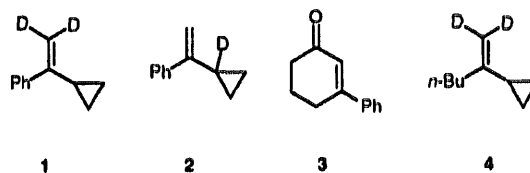
2. Results and discussion

The formation of ketone 3 appeared to be well suited for mechanistic study, because it could be obtained

* Corresponding author. Tel.: (+49) (228) 73 55 88; Fax: (+49) (228) 73 53 88.

	position 2	positon 4	position 6
incorporation of D	78 %	81 %	39 %
(100 % corresponds to 1 D)			

Scheme 1.

from 1-d_0 as the sole product and in high yield (greater than 70%). Furthermore, its ^{1}H NMR spectrum exhibits a set of well separated signals and, additionally, each peak can be readily assigned.

^{1}H NMR (400 MHz, CDCl$_3$) δ = 2.15 (quin, J = 6 Hz; 5-H$_2$), 2.49 (t, J = 6 Hz; 6-H$_2$), 2.78 (td, J = 6 and 1.5 Hz; 4-H$_2$), 6.42 (t, J = 1.5 Hz; 2-H), 7.41, 7.54 (2 mc, Ph).

Initial experiments focused on determining whether the carbonylation process is intra- or intermolecular. Exposure of a mixture of 1 and 1-d_0 to Fe(CO)$_5$ at 150°C for 90 min (15% conversion) and 15 h (100% conversion) followed by oxidative work-up with ceric ammonium nitrate (CAN) gave 3-d_2 and 3 respectively. Mass spectral analysis of the isomeric products indicated that scrambling of deuterium occurred only to a minor extent in both cases. The absence of crossover products in these experiments demonstrates the intramolecularity of the deuterium shifts involved in the carbonylation process (for instance, see Ref. [9]). It should be mentioned at this stage that loss of deuterium was not observed in the work-up step (acidic conditions), and, furthermore, incorporation of deuterium into crude 3 did not take place with CAN in D$_2$O. Therefore,

the position of the deuterium atoms in 3-d_2 is a result of carbonylation of 1 and not of any subsequent transformations.

The location of the deuterium label in 3-d_2 was determined by ^{1}H NMR spectroscopy. Integration of the spectrum showed that the deuterium was distributed among the olefinic and two methylene group positions when employing 1. Its ratio was not substantially affected by the reaction time or the work-up procedure (CAN or trimethyl-N-oxide). A single product was obtained from the reaction with 2. Scheme 1 summarizes these data.

In order to check the influence of the phenyl moiety in 1 and 2 during the reaction, we subjected the butyl analogue 4 to the above mentioned procedure. The enone 5 showed a labelling pattern similar to 3-d_2, as determined by NMR spectroscopy (Scheme 2). Thus, any participation of the phenyl substituent in the course of the reaction can be excluded.

A mechanistic rational developed by Aumann [6] for the photoinduced CO insertion cannot account for the labelling pattern observed here. The characteristic steps in the Aumann mechanism are outlined in Scheme 3.

Since the D atoms in 3-d_2 have migrated across the

|	position 2	positon 4	position 6
incorporation of D	86 %	68 %	46 %
(100 % corresponds to 1 D)			
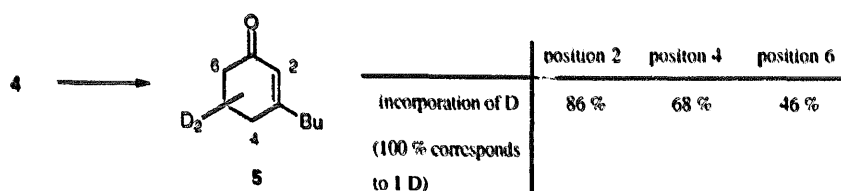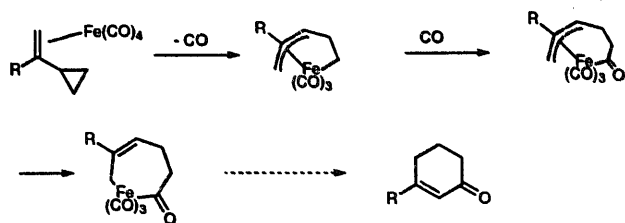
Scheme 2.

Scheme 3.

molecule, a species capable of internal H/D shifting has to be assumed. We consider the involvement of an iron hydride complex an appropriate reaction pathway for our conversions. Application to the carbonylation process leads to the following rational (Scheme 4).

The tetracarbonyl iron species **6** gives the coordinatively unsaturated complex **7** at elevated temperatures. Opening of the cyclopropane ring leads to the formation of the σ,π-allyl complex **8**, in agreement with the mechanism shown in Scheme 3. This species could isomerize to the iron π-allyl hydride **9** under the applied conditions (150 °C). Earlier studies, concerning iron π-allyl hydride complexes, indicated that H/D exchange

takes place between a deuterated ligand and the metal moiety [10]. Complex **9** is therefore transformed to **10** where deuterium is enriched at the iron. The H/DFe(CO)$_3$ group could then undergo a 1,3 shift yielding **11**. A second H/D exchange is responsible for the incorporation of D in the terminal position of **11**, resulting in **12**. The CO insertion seems to proceed exclusively from **9/10** since cyclization from **11/12** would give an isomeric cyclohexenone. Sterical hindrance in the transition state of the cyclocarbonylation might be decisive for the selective generation of **13**. This primary insertion product is rapidly converted to **3**-d_2 under the applied conditions. The suggestion of the cyclocarbonylation step draws analogy from the reported preparation of enones from tricarbonyl iron 1,3-diene complexes upon exposure to Lewis acids [11]. Inclusion of **8** complies with the mechanistic route proposed by Aumann. Another feature of this explanation is its compatibility with competing diene formation. Electronic activation of the allyl moiety in **9** could be responsible for the observed selective diene production in electron deficient vinylcyclopropanes. Further investigations regarding this topic are currently being elaborated in this laboratory and will be reported in due course.
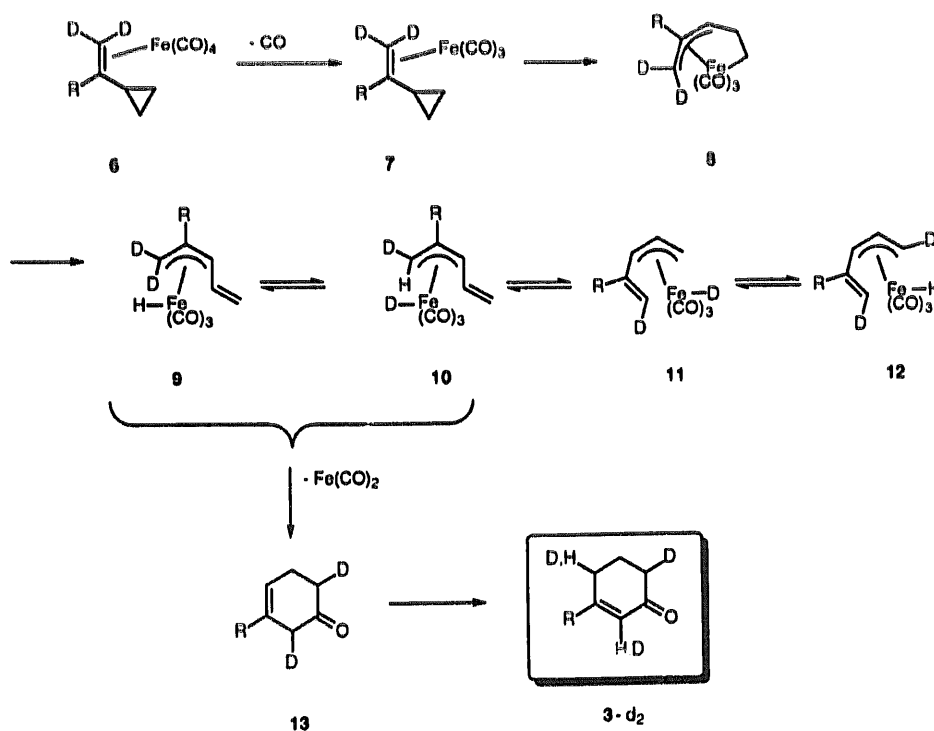
Scheme 4.

Acknowledgements

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