Selective hydrogenation of the carbonyl group of α,β-unsaturated aldehydes to alcohols with iridium(I) complexes

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(Received August 29th, 1989; in revised form February 17th, 1990)

Abstract

The hydrogenation of $C_6H_5CH=CHCHO$ (1), $C_6H_5CH=C(CH_3)CHO$ (6) and $C_6H_5CH=C(Cl)CHO$ (7) by $Ir(ClO_4)(CO)(PPh_3)_2$ (2), $IrCl(PPh_3)_3$ (8), $IrCl(CO)(PPh_3)_2$ (9) and $[Ir(CO)(PPh_3)_3]ClO_4$ (10) occurs primarily at the carbonyl group to give unsaturated alcohols, $C_6H_5CH=CHCH_2OH$ (5), $C_6H_5CH=C(CH_3)CH_2OH$ (11) and $C_6H_5CH=C(Cl)CH_2OH$ (12) at 50°C under 9 atm of hydrogen. Compound 5 is isomerized to $C_6H_5CH_2CH_2CHO$ (3) by 2, 8 and 9 but not by 10. The carbonyl group of 3 is further hydrogenated to produce the saturated alcohol, $C_6H_5CH_2CH_2CH_2OH$ (4) in the presence of 2, 8 and 9. The isomerizations: 5 → 3 by 10, and 11 → $C_6H_5CH_2CH(CH_3)CHO$ and 12 → $C_6H_5CH_2CH(Cl)CHO$ by 8 and 9 probably do not occur for steric reasons; the interaction between the internal olefinic group and the iridium with bulky ligands is hindered.

Introduction

The selective hydrogenation of a particular functional group in a compound containing two different functional groups is a very useful method in synthetic chemistry. The hydrogenation of a carbonyl group of an organic compound by transition metal complex catalysts is difficult whereas hydrogenation of an olefinic group is one of the most frequently studied catalytic reactions by transition metal complexes [1]. It has been reported that the hydrogenation of unsaturated aldehyde, $C_6H_5CH=CHCHO$ (1) with $Ir(ClO_4)(CO)(PPh_3)_2$ (2) produces the saturated aldehyde, $C_6H_5CH_2CH_2CHO$ (3) and the saturated alcohol, $C_6H_5CH_2CH_2CH_2OH$ (4) but not the unsaturated alcohol, $C_6H_5CH=CHCH_2OH$ (5), and it was suggested that the hydrogenation of 1 by 2 occurs independently at the carbonyl and the olefinic groups [2]. In our preliminary experiments, however, 5 was observed in the catalytic reactions of 1 with 2 under the experimental conditions that were different

from those previously reported, i.e., different temperature, pressure of hydrogen and concentrations of 1 and 2 [cf. text and reference 2]. This observation led us to investigate details of hydrogenation of 1 and its derivatives, $C_6H_5CH=C(CH_3)CHO$ (6) and $C_6H_5CH = C(Cl)CHO$ (7) by 2 and related iridium(I) complexes, namely, $IrCl(PPh_3)_3$ (8), $IrCl(CO)(PPh_3)_2$ (9) and $[Ir(CO)(PPh_3)_3]ClO_4$ (10).

We report the selective hydrogenation of the carbonyl group of cinnamaldehydes by the four-coordinated iridium(I) compounds, 2, 8–10.

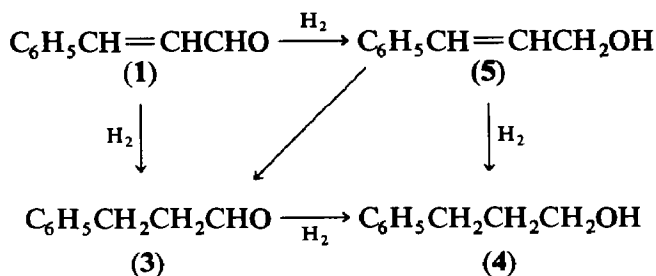## Results and discussion

Hydrogenation of $C_6H_5CH=CHCHO$ (1). Hydrogenation of 1 by 2, 8 and 9 produces $C_6H_5CH=CHCH_2CH_2OH$ (5), $C_6H_5CH_2CH_2CHO$ (3) and $C_6H_5CH_2$ CH_2OH (4) (Table 1). Compound 5 is evidently the product of hydrogenation that occurs at the carbonyl group of 1 whereas compound 3 may be obtained in two different ways, (i) direct hydrogenation of the olefinic group of 1 and (ii) double bond migration of the hydrogenation product, 5 followed by rapid ketonization as observed and discussed previously in the reactions of β,γ-unsaturated alcohols with 2 and related rhodium complexes [3,4] (see Scheme I). In order to determine the major route for the production of 3, the hyrogenation of a different compound containing both carbonyl and olefinic groups was investigated. Reaction of 1,2,3,6-tetrahydrobenzaldehyde (3 mmole) with 2 (0.1 mmole) in $CDCl_3$ (2.0 ml) at 50°C under hydrogen ($P(H_2)$ 9 atm) for 50 minutes produced the hydrogenated product carbonyl group in 95% yield with practically no hydrogenated olefinic group products (eq. 1). It was also found from a previous study that 2

$$\text{CHO} \longrightarrow \text{CH}_2\text{OH} \tag{1}$$

rapidly catalyzes the isomerization of 5 under hydrogen to give 3 [5]. Accordingly, we suggest that 3 is produced mainly by the isomerization of 5, i.e., $1 \rightarrow 5 \rightarrow 3$ (but this does not completely exclude the direct hydrogenation, $1 \rightarrow 3$).

Compound 4 can also be produced by two reactions, viz., the hydrogenations of the olefinic group of 5, and the carbonyl group of 3 (see Scheme 1). However, the production of 4 seems to occur mainly by the hydrogenation of the carbonyl group ($3 \rightarrow 4$) since it was found that the reaction of 5 with 2 under hydrogen rapidly gives the only isomerization product, 3 (100%) which in turn slowly hydrogenated to give 4 [5]. In short, compound 2 selectively catalyzes the hydrogenation of the carbonyl group of 1 to give 5, and of 3 to give 4, rather than that of the olefinic groups of 1 and 5. The hydrogenation products (3 and 4) observed in the previous report under different experimental conditions [2] may also be the products of carbonyl group hydrogenation with 2. Then a question arises of why the isomerization of 5 to 3 is faster than the hydrogenation of 1 to 3 and of 5 to 4 while both reactions should involve the interactions between iridium and the olefinic group of 1 and 5. This is probably because of the relative ease with which the β-hydrogen is eliminated from $C_6H_5CH_2CH(Ir-H)CHO$ to give 3, and from $C_6H_5CH_2CH(Ir-H)CH_2OH$ to give 3 or 4 as discussed previously [5]. It is reasonable to assume that compound 2 and the related compounds 8 and 9 behave similarly in the catalytic reactions of 1.

$$C_6H_5CH=CHCHO \xrightarrow{\ H_2\ } C_6H_5CH=CHCH_2OH$$
$$\textbf{(1)} \qquad\qquad\qquad \textbf{(5)}$$

$$C_6H_5CH_2CH_2CHO \xrightarrow[H_2]{} C_6H_5CH_2CH_2CH_2OH$$
$$\textbf{(3)} \qquad\qquad\qquad \textbf{(4)}$$

Scheme 1. Possible pathways for catalytic hydrogenation of $C_6H_5CH=CHCHO$ (1) with $Ir(ClO_4)(CO)(PPh_3)_2$ (2), $IrCl(PPH_3)_3$ (8) and $IrCl(CO)(PPh_3)_2$ (9) under hydrogen. $1 \rightarrow 5 \rightarrow 3 \rightarrow 4$ is the major reaction pathway for production of 4.

Surprisingly, the carbonyl group-hydrogenated compound 5 is the only product in the reaction of 1 with 10 that has three bulky PPh_3 ligands coordinated to iridium whereas 5 and the isomerization product 3 are produced in reactions of 1 with another tris(triphenylphosphine)iridium(I) complex, 9. In order to obtain information on the relative catalytic activities of 9 and 10, attempts were made to observe dissociation of PPh_3 from 9 and 10 at $50\,^\circ C$, but without success (see Experimental).

Hydrogenation of $C_6H_5CH=C(CH_3)CHO$ (6) and $C_6H_5CH=C(Cl)CHO$ (7). Steric effects of the substituents (CH_3, Cl) are prominent in the hydrogenation of 6 and 7. The hydrogenation of 6 and 7 and the isomerization of $C_6H_5CH=C(CH_3)CH_2OH$ (11) and $C_6H_5CH=C(Cl)CH_2OH$ (12) to the corresponding saturated

Table 1

Hydrogenation of $C_6H_5CH=CRCHO$ (R=H, CH_3, Cl; 15 mmole) with $Ir(ClO_4)(CO)(PPh_3)_2$ (2), $IrCl(PPh_3)_3$ (8), $IrCl(CO)(PPh_3)_2$ (9), $[Ir(CO)(PPh_3)_3]ClO_4$ (10) (0.1 mmole) in $CDCl_3$ (2.0 ml) at $50\,^\circ C$ under 9 atm of hydrogen. $A = C_6H_5CH=CRCH_2OH$; $B = C_6H_5CH_2CHRCHO$; $C = C_6H_5CH_2CHRCH_2OH$; $D =$ hydrogenolysis products (saturated and/or unsaturated hydrocarbons) and small amounts of unknown products; $S =$ reactant.

Catalyst	Reactant	Product (%) [a]					Time (h)
		A	B	C	D	S	
2	$C_6H_5CH=CHCHO$	45	5	25		25	1
		38		62			3
	$C_6H_5CH=C(CH_3)CHO$	85			15		3
	$C_6H_5CH=C(Cl)CHO$	24				76	3
8	$C_6H_5CH=CHCHO$	6	30	9	7	48	3
			10	80	10		5
	$C_6H_5CH=C(CH_3)CHO$	5				95	3
	$C_6H_5CH=C(Cl)CHO$	11				89	3
9	$C_6H_5CH=CHCHO$	10	45	10	15	15	20
	$C_6H_5CH=C(CH_3)CHO$	18				82	20
	$C_6H_5CH=C(Cl)CHO$	14			24	62	20
10	$C_6H_5CH=CHCHO$	6				94	20
		24 [b]				76 [b]	20
	$C_6H_5CH=C(CH_3)CHO$	3				97	20
	$C_6H_5CH=C(Cl)CHO$	4				96	20

[a] Average values obtained in at least three experiments. Experimental errors are ca. $\pm 15\%$. [b] Complex 10 (0.5 mmole) and $C_6H_5CH=CHCHO$ (15 mmole) were used to observe a significant amount of $C_6H_5CH=CHCH_2OH$.

aldehydes do not occur probably because of the difficulties in the interactions between the metal and the olefinic group of **6, 7, 11** and **12**, and the nature of the substituents.

It is well known that **2, 10** and the related rhodium(I) complexes [5,6] in addition to some other transition metal complexes [7] catalyze the hydrogenolysis of alcohols to produce hydrocarbons. Thus, most of the hydrocarbons listed in Table 1 are probably products of metal complex-catalyzed hydrogenolysis of **4, 5, 11** and **12**.

Catalytic activities of Ir(ClO₄)(CO)(PPh₃)₂ (2), IrCl(PPh₃)₃ (8), IrCl(CO)(PPh₃)₂ (9) and [Ir(CO)(PPh₃)₃]ClO₄ (10). These iridium(I) complexes show somewhat different activities for the reactions of cinnamaldehydes (see Table 1) and so deserve some comment. The reactions in general are faster with **2** and **8** than with **9** and **10**. The perchlorato group of **2** is known to be so labile [7] that it is readily replaced by aldehydes and alcohols [8,9] while no report has appeared on the lability and the dissociation of a ligand of **8, 9** and **10**. The faster catalytic reactions with **2** are probably because of the lability of the perchlorato group. Why the catalytic activity of **8** is higher than those of **9** and **10** is not clear, although lower activity of **10** is probably due to the steric effects of the three bulky PPh₃ ligands.

In summary, the hydrogenation of the α,β-unsaturated aldehydes, **1, 6** and **7** by the iridium(I) complexes, **2, 8, 9** and **10** occurs mainly at the carbonyl group to give the unsaturated alcohols, **5, 11** and **12**. In the presence of **2, 8** and **9, 5** undergoes isomerization to saturated aldehyde **3** whereas **11** and **12** do not. The isomerization of **5** to **3**, however, does not occur in the presence of **10**. The carbonyl group of **3** is further hydrogenated to give the saturated alcohol **4** in the presence of **2, 8** and **9**. The other hydrogenolysis products, the hydrocarbons, are also observed in the reactions of **2, 8** and **9**.

Experimental

Caution. Although we have not experienced an accident thus far, precautions must be taken when handling compounds containing the ClO_4^- group since they are potentially explosive [10].

Methods. A standard vacuum line and Schlenk glassware were used in handling metal complexes. A Varian 60 MHz (EM-360) or a Bruker WP 80 MHz spectrometer, a Shimadzu UV-240 spectrophotometer and a Varian 3700 Gas Chromatograph were used in the study.

Materials. $C_6H_5CH=CHCHO$, $C_6H_5CH=C(CH_3)CHO$, $C_6H_5CH=C(Cl)CHO$, $C_6H_5CH=CHCH_2OH$ and a 1,2,3,6-tetrahydrobenzaldehyde were purchased from Fluka and Aldrich and used without further purification. $Ir(ClO_4)(CO)(PPh_3)_2$ [8], $IrCl(PPh_3)_3$ [11], $IrCl(CO)(PPh_3)_2$ [12] and $[Ir(CO)(PPh_3)_3]ClO_4$ [8] were prepared by published procedures.

Catalytic hydrogenations. All the catalytic reactions of the unsaturated aldehydes with the metal complexes were carried out exemplified below for the reaction of $C_6H_5CH=CHCHO$ (1) with $Ir(ClO_4)(CO)(PPh_3)_2$ (2). A 0.1 mmole (80 mg) of **2** and 15 mmoles (810 mg) or **1** were added in 2.0 ml of CDCl₃ (Fluka 31330) under hydrogen in a bomb type reactor (Parr 1341; volume 360 ml) into which hydrogen was introduced until the pressure reached 9 atm at 25°C. The reactor was then placed in an oven maintained at 50°C for a certain period of time

and cooled in an ice bath before it was opened for the identification and analysis of the reactants and the products by proton NMR spectroscopy and GC.

Reactant and product analysis. The identification of reactants and products and their analysis were mainly carried out by proton NMR spectroscopy of the reaction mixture but in some cases by GC with coinjection of an authentic sample. Proton NMR signals (in $CDCl_3$) employed for analysis are as follows: $C_6H_5CH=CHCHO$, δ 9.70 (doublet); $C_6H_5CH=CHCH_2OH$, δ 4.25 (doublet, broad); $C_6H_5CH_2CH_2$ CHO, δ 2.5–3.0 (multiplet); $C_6H_5CH_2CH_2CH_2OH$, δ 3.6 (triplet), 2.6 and 1.8 (multiplet); $C_6H_5CH=C(CH_3)CHO$, δ 9.55 (singlet); $C_6H_5CH=C(CH_3)CH_2OH$, δ 4.21 (singlet); $C_6H_5CH=C(Cl)CHO$, δ 9.35 (singlet); $C_6H_5CH = C(Cl)CH_2OH$, δ 4.30 (singlet).

Attempts to observe dissociation of PPh_3 from $IrCl(PPh_3)_3$ (8) and [Ir(CO) $(PPh_3)_3]ClO_4$ (10). The addition of an excess of PPh_3 ($PPh_3/Ir = 10$) to a solution of **8** or **10** ([Ir] 4.0×10^{-5} M) at 50°C under nitrogen caused no significant changes in the absorbances of the three prominent bands of **8** and **10** in the visible region.

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