

Homogeneous Catalytic Hydrogenation of Ketones with Carbonylperchloratobis (triphenylphosphine) iridium(I)

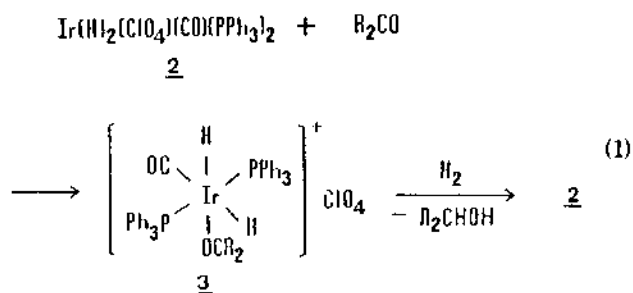
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There has been only a few reports on the catalytic hydrogenation of carbonyl group with iridium complexes.¹⁻⁸ Iridium complexes which show catalytic activities for the hydrogenation of ketones to aldehydes are mostly either cationic species¹⁻⁴ or precursors that seem to become cationic species under the catalytic conditions.^{4,6} It has been recently found that $\text{Ir}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (**1**) reacts with unsaturated aldehydes to produce cationic four coordinated iridium(I) complexes, $[\text{IrL}(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ ($\text{L} = \text{trans-CH}_3\text{CH}=\text{CHCHO}$, $\text{trans-C}_6\text{H}_5\text{CH}=\text{CHCHO}$) where L are coordinated through the oxygen atom of the carbonyl group⁹ and complex **1** is catalytically active for the hydrogenation of aldehydes to alcohols at 25°C under atmospheric pressure of hydrogen.¹⁰ We now wish to report the hydrogenation of ketones to alcohols with **1** which is known to react with acetone to produce cationic four coordinated iridium(I) complex, $[\text{Ir}(\text{acetone})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$.¹¹


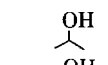

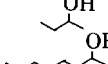
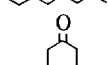
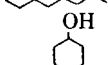











Hydrogenation of ketones to alcohols with **1** is summarized in Table 1. The hydrogenation is extremely slow at 25°C under atmospheric pressure of hydrogen, e.g., less than 1% of $(\text{CH}_3)_2\text{CO}$ (3.0 mmole) was hydrogenated to $(\text{CH}_3)_2\text{CHOH}$ in the presence of **1** (0.1 mmole) in CDCl_3 (2.0 ml) at 25°C under hydrogen (P_{H_2} + vapor pressure of solution = 1 atm) for 5 hours. It is apparent in Table 1 that the relative rates of the hydrogenation are readily understood by the relative ease for the interaction between the carbonyl group and iridium.

It has been found in this study that the isolated iridium complex from the solution of **1** and ketones in CHCl_3 after being treated under catalytic conditions (70°C under $P_{\text{H}_2} = 3$ atm) was identified as $\text{Ir}(\text{H})_2(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (**2**).¹² It has been also found in this study that the reactions of **2** with ketones under nitrogen at 70°C produce alcohol (see Experimental). Accordingly, a cationic dihydrido(ketone)iridium (III) complex (**3**) is suggested as the intermediate for the hydrogenation although it has not been isolated thus far (equation 1). A dihydridometal complex, $L_n\text{M}(\text{H})_2(\text{OCR}_2)$, analogous to **3**, was previously suggested as the intermediate in the hydrogenation of carbonyl compounds to alcohols.¹³



Production of $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3$ and $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_3$ in the reactions of $\text{C}_6\text{H}_5\text{COC}_2\text{H}_5$, and $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$ and C_6H_5

Table 1. Hydrogenation of Ketones (3.0 mmol) with $\text{Ir}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (0.1 mmol) in CDCl_3 (2.0 ml) at 70°C under Hydrogen ($P_{\text{H}_2} = 3$ atm) for Hours

substrate	product	yield (%)
		75
		67
		67
		100
		100
		49
 a		6
 b		6
	no reaction	

^a $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$ (27%) and $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{-O-CH}(\text{CH}_3)\text{C}_6\text{H}_5$ (9%) were also produced. ^b $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3$ (4%) and $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_3$ (5%) were also produced.

$\text{CH}(\text{CH}_3)\text{-O-CH}(\text{CH}_3)\text{C}_6\text{H}_5$ in the reactions of $\text{C}_6\text{H}_5\text{COCH}_3$ in Table 1 will be discussed elsewhere.

Experimental

$\text{Ir}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ and $\text{Ir}(\text{H})_2(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ were prepared by the literature methods.^{11,12} Ketones were purchased from either Aldrich or Fluka and used without further purification. Products were analyzed by ¹H NMR (Varian 60 MHz (EM-360)) and GC (Varian 3700).

Hydrogenation of Ketones with $\text{Ir}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$. A 0.1 mmole (0.08 g) of $\text{Ir}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ and 3.0 mmoles of a ketone were dissolved in CDCl_3 (2.0 ml) in a bomb reactor (Parr 1341; volume 360 ml) under hydrogen and the cap was applied before hydrogen was introduced into the reactor through the valve up to 3 atm. Then the reactor was placed in an oven maintained at 70°C for 5 hours. The reaction mixture was cooled down at room temperature and analyzed by ¹H NMR and GC.

Reaction of $\text{Ir}(\text{H})_2(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ with Ketones under Nitrogen. A 0.5 mmole (0.4g) of $\text{Ir}(\text{H})_2(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ and 2.5 mmole of a ketone were added into 5.0 ml of CDCl_3 under nitrogen in a bomb reactor (Parr 1341; volume 360 ml) which was then placed in an oven maintained at 70°C for 5 hours. Product analyses by ¹H NMR and GC showed

production of 0.1-0.2 mmole of corresponding alcohol depending on the reactants, ketones. (It should be noted that the reductive elimination, $\text{Ir}(\text{H})_2(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2 \rightarrow \text{Ir}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2 + \text{H}_2$, is significant at 70°C for 5 hours.)

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Reaction of 1-Ethoxy-1-(Trimethylsiloxy)-2-(Trimethylsilyl) Propene with Aldehydes-Synthesis of α, β -Unsaturated Carboxylic Esters

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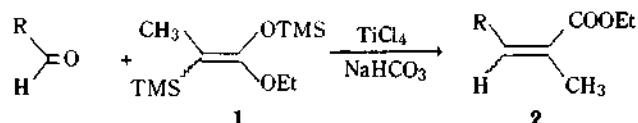
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Peterson olefination is referred to as an elimination reaction of β -hydroxyalkylsilanes¹. Recently, it was reported that 4,5-dihydro-5-methyl-2-(trimethylsiloxy)-3-(trimethylsilyl) furan reacts with aldehydes to produce α -ethylidene- γ -butyrolactones². We have also reported³ that the reaction of bis(trimethylsiloxy)ketene acetal of trimethylsilylacetic acid with carbonyl compounds directly afforded α, β -unsaturated carboxylic acids in moderate to good yields.

Because of our interest in the use of the ketene acetals of α -(trimethylsilyl)carboxylates for the olefination^{4,5} of carbonyl compounds, we have examined the reaction of the ketene acetal of ethyl 2-(trimethylsilyl)propanoate, 1-ethoxy-1-(trimethylsiloxy)-2-(trimethylsilyl)propene (**1**), with aldehydes in the presence of titanium tetrachloride.



The ketene acetal **1** (bp: 70-72°C/12 mmHg)⁶ was prepared in 65% yields by silylating⁷ ethyl 2-(trimethylsilyl)propanoate, which was obtained by the reaction⁸ of ethyl propanoate with trimethylsilyl triflate in the presence of triethylamine. Reaction of this ketene acetal **1** with aldehydes produced the mixture of *cis*- and *trans*- α, β -unsaturated carboxylic esters **2** in moderate yields (see Table). The ratio of *cis*- and *trans*-isomers was esti-

Table 1. Synthesis of α -methyl- α, β -unsaturated Carboxylic Acid Ethyl Esters

R	Yield (%) ^a	E/Z ratio ^b
Phenyl	67	1.4
m-NO ₂ -Ph	70	1
p-NO ₂ -Ph	62	1
p-MeO-Ph	72	1.6
PhCH=CH-	65	1
CH ₃ CH=CH-	68	1
PhCH ₂ CH ₂ -	62	1.2
CH ₃ CH ₂ CH ₂ -	43	1

^aIsolated by silica gel column chromatography. ^bBased on the ¹H-nmr integration data of the olefinic methyl protons of the products.

mated from the proton nmr spectral data and found to be nearly unity (see Table).

A typical procedure for the olefination of aldehydes with the above ketene acetal **1** is exemplified as follows. To a stirred solution (-78°C) of 0.3 ml (3.0 mmol) of benzaldehyde in 15 ml of dry dichloromethane, was added dropwise 10 ml of 1.0 M solution of titanium tetrachloride in dichloromethane followed by a solution of 3.5 mmol of the ketene acetal **1** in 5 ml of dichloromethane. After stirred for 5 hr at -78°C, the mixture was treated with 0.1 ml of 5% aqueous sodium bicarbonate solution and allowed to warm to room temperature.