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Hydrogenation of α,β-Unsaturated Carbonyl Compounds by Carbon monoxide and Water with $Rh_6(CO)_{16}$ Catalyst under Mild Conditions

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Synopsis. By controlling such factors as the concentration of water and amine, the carbon–carbon double bond of α,β-unsaturated carbonyl compounds could be selectively hydrogenated under mild water–gas shift reaction (WGSR) conditions using a $Rh_6(CO)_{16}$–Et_3N catalyst system. The reaction proceeded at room temperature under atmospheric pressure of CO.

The water–gas shift reaction (WGSR) has recently been applied to unique organic synthesis such as selective hydrogenation and specific carbonylation.[1—3] We also have studied the application of the WGSR using rhodium carbonyl cluster catalysts.[4—6] During the course of our study on the rhodium-catalyzed reactions with CO and H_2O in mild conditions, we have found that a reaction system which contains a large amount of water is effective for the hydrogenation of α,β-unsaturated carbonyl compounds at room temperature and under atmospheric pressure of CO. The present paper deals with the results of these studies.

Experimental

General Procedure. Solvents were purified by standard methods. $Rh_6(CO)_{16}$ was prepared according to the reported method.[7] All other chemicals used were commercial samples.

The hydrogenation reactions were performed as the following procedure: $Rh_6(CO)_{16}$ (9.4×10^{-3} mmol) was placed in a vessel, the reaction system was evacuated and flushed three time with CO and then a solution containing olefin (0.5 mmol), 2-ethoxyethanol (2 ml), H_2O (2 ml), and triethylamine (1 ml) was added to the vessel. The solution was heated to 40°C with stirring under atomospheric pressure of CO which was supplied from a baloon attached to the reaction vessel. After an appropriate time, products were analyzed by gas chromatography. The experimental data shown in Table 1 and Figs. 1, 2, and 3 are those obtained when the reactions were stopped before the complete conversion of a substrate.

Hydrogenation Reactions of α,β- Unsaturated Carbonyl Compounds. By the general procedure, the reactions were carried out at 30°C for 20 h and products except 2,3,4,5-tetraphenyl-2-cyclopenten-1-one were analyzed by gas chromatography and identified by usual spectroscopic methods. 2,3,4,5-Tetraphenyl-2-cyclopenten-1-one was isolated after the purification by chromatography on silica gel.

Results and Discussion

Table 1. Effect of the Solvent[a)]

Solvent	Yield of 4-phenyl-2-butanone (%)
2-Ethoxyethanol	45
EtOH	22
MeOH	20
Dioxane	24
THF	17
Acetone	6
Acetonitrile	4
DMF	5
Benzene	0

a) Reaction conditions: $Rh_6(CO)_{16}$, 9.4×10^{-3} mmol; olefin, 0.5 mmol; solvent, 2 ml; H_2O, 2 ml; Et_3N, 1 ml; 40°C; 5 h; CO, atmospheric pressure.

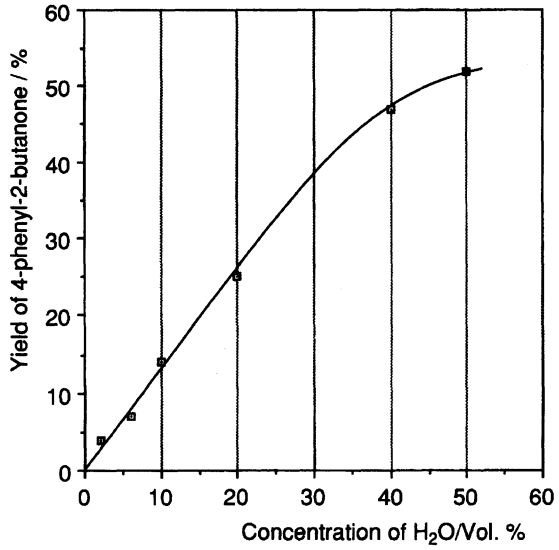


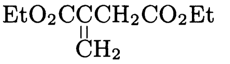
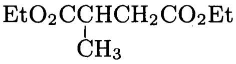
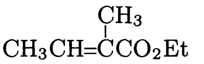
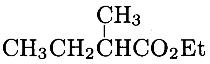
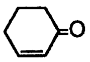
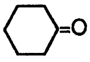
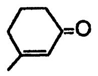
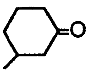
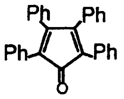
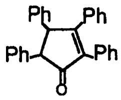
Fig. 1. Effect of the concentration of water. Reaction conditions: $Rh_6(CO)_{16}$, 9.4×10^{-3} mmol; benzylideneacetone, 0.5 mmol; 2-ethoxyethanol+H_2O, 4 ml; Et_3N, 1 ml; CO, atmospheric pressure; 40°C; 5 h.

Catalysis of WGSR usually requires high reaction temperaure and pressure. During the course of the investigation of the rhodium-catalyzed reactions with CO and H_2O in the presence of Et_3N under mild conditions, we found that the carbon–carbon bond of α,β-unsaturated carbonyl compounds were selectively hydrogenated at ambient temperature and pressure.

$$\mathrm{RCH{=}CHCOR' + CO + H_2O} \xrightarrow[\mathrm{Rh_6(CO)_{16},Et_3N}]{} \mathrm{RCH_2CH_2COR' + CO_2}$$

We have investigated at first the reaction using benzylideneacetone as a typical substrate to survey the catalytic activity under various reaction conditions and

Table 2. Hydrogenation of Various Olefins[a)]

Entry	Substrate	Product	Conversion/%	Selectivity/%
1	$PhCH{=}CHCO_2Ph$	$PhCH_2CH_2CO_2Ph$	83	80
2	$PhCH{=}CHCOCH_3$	$PhCH_2CH_2COCH_3$	90	100
3	$PhCH{=}CHCO_2Me$	$PhCH_2CH_2CO_2Me$	31	35
4	$Ph_2C{=}CHCO_2Et$	$Ph_2CHCH_2CO_2Et$	0	0
5	$CH_2{=}CHCO_2Et$	$CH_3CH_2CO_2Et$	100	60
6	$CH_3CH{=}CHCO_2Et$	$CH_3CH_2CH_2CO_2Et$	79	89
7	 $EtO_2C\underset{\underset{CH_2}{\|}}{C}CH_2CO_2Et$	 $EtO_2C\underset{\underset{CH_3}{\mid}}{C}HCH_2CO_2Et$	98	91
8	 $CH_3CH{=}\overset{\overset{CH_3}{\mid}}{C}CO_2Et$	 $CH_3CH_2\overset{\overset{CH_3}{\mid}}{C}HCO_2Et$	0	0
9	$(CH_3)_2C{=}CHCO_2Et$	$(CH_3)_2CHCH_2CO_2Et$	0	0
10	$EtO_2CCH{=}CHCO_2Et$	$EtO_2CCH_2CH_2CO_2Et$	99	58
11			100	100
12			46	100
13			35	100

a) Reaction conditions: $Rh_6(CO)_{16}$, 9.4×10^{-3} mmol; 2-ethoxyethanol, 2 ml; H_2O, 2 ml; Et_3N, 1 ml; 30°C; 20 h; CO, atmospheric pressure.

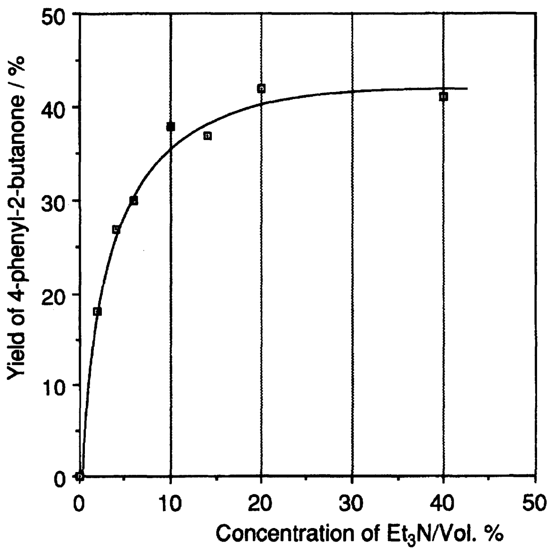


Fig. 2. Effect of the concentration of amine. Reaction conditions: $Rh_6(CO)_{16}$, 9.4×10^{-3} mmol; benzylideneacetone, 0.5 mmol; 2-ethoxyethanol+Et_3N, 3 ml; H_2O, 2 ml; CO, atmospheric pressure; 40°C; 5 h.

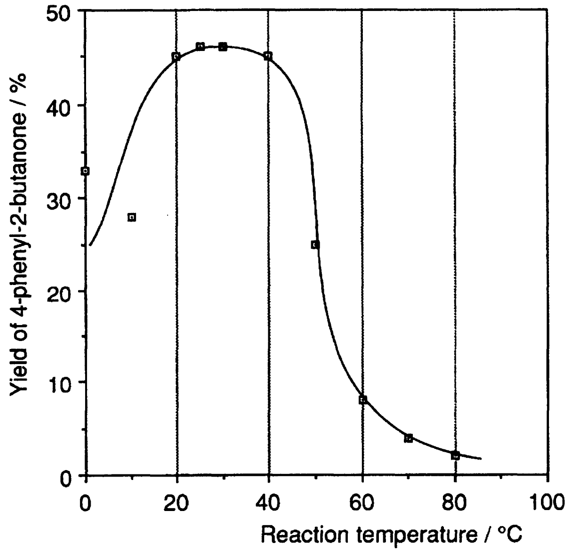


Fig. 3. Effect of the reaction temperature. Reaction conditions: $Rh_6(CO)_{16}$, 9.4×10^{-3} mmol; benzylideneacetone, 0.5 mmol; 2-ethoxyethanol, 2 ml; H_2O, 2 ml; Et_3N, 1 ml; CO, atmospheric pressure; 5 h.

found that the present catalytic system is quite sensitive to a number of factors, that is, the concentration of water and amine as well as the kind of solvents strongly effected the activity of the system for the hydrogenation of benzylideneacetone. Among them the concentration of water played an important role in the hydrogenation. As the concentration of water increased, the reaction activity was drastically increased. The effect of the concentration of water on the activity of the system is shown in Fig. 1. The hydrogenation rate of benzylideneacetone to 4-phenyl-2-butanone increased linearly with an increase of the concentration of water up to 40% of total volume. When the concentration of water was exceeded 40% of total volume, the reaction system became heterogeneous and the degree of the increase in the rate was lowered. The concentration of triethylamine also has a noticeable influence on the activity as shown in Fig. 2. The reaction did not proceed without triethylamine. Increasing the concentration of triethylamine up to 20% of total volume, the reaction activity increased. In the presence of triethylamine more than 20% of total volume, the activity was almost constant. The solvent has a considerable influence on the activity as shown in Table 1. The suitability of the solvent follows the order: 2-ethoxyethanol > ethanol≈methanol≈dioxane≈tetrahydrofuran > acetone≈acetonitrile≈N,N-dimethylformamide; there is no reaction in benzene.

In order to obtain the information of the temperature dependence on the reaction, a series of reactions were carried out at temperatures in the range of 0—80°C. The results are shown in Fig. 3. Increase in the reaction temperature up to 20°C resulted in higher activity and a maximum in the yield of 4-phenyl-2-butanone was obtained at the temperature range of 20—40°C. Above 40°C, the activity decreased rapidly and the reaction was extremely depressed at 60°C. Scrutiny of operation conditions has revealed to be the optimum conditions that the reaction is carried out at 20—40°C in the reaction system composed of 40% of 2-ethoxyethanol, 40% of water and 20% of triethylamine.

The hydrogenation of various α,β-unsaturated carbonyl compounds was tried at 30°C for 20 h. The results are summarized in Table 2. Mono and disubstituted olefins could be reduced under these reaction conditions. But trisubstituted olefins except 3-methyl-2-cyclohexene did not react. The reaction seems to be governed by the steric factors around carbon–carbon double bond. 2,3,4,5-Tetraphenyl-2,4-cyclopentadien-1-one was reduced to 2,3,4,5-tetraphenyl-2-cyclopenten-1-one.

In summary, this work demonstrates that the carbon–carbon double bond of α,β-unsaturated carbonyl compounds can be selectively hydrogenated at ordinary temperature and pressure in the present reaction system.

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