

THE RUTHENIUM COMPLEX-CATALYZED REDUCTION OF KETONES BY FORMIC ACID

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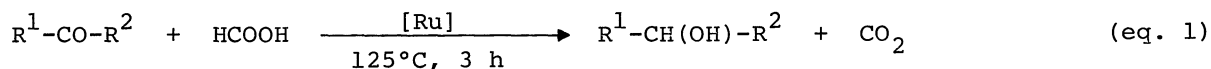
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An equimolar mixture of a ketone and formic acid was heated without solvent at 125°C for 3 h in the presence of a catalytic amount of dichlorotris(triphenylphosphine)ruthenium(II) to give the corresponding secondary alcohols in excellent yields.

Catalytic transfer hydrogenation is of current interest.¹⁾ Ruthenium and palladium compounds are efficient catalysts for transfer hydrogenation of olefinic bonds using alcohols and formic acid as hydrogen donors.²⁾ Formic acid is also used for conversion of benzaldehydes, acetophenones, and acetylpyridines to toluenes, ethylbenzenes, and ethylpyridines, respectively, in the presence of metal compounds, zinc or solid catalysts.³⁾ Little attention, however, has been paid to selective transformation of carbonyl compounds to alcohols with formic acid.

This study deals with an equimolar reaction between ketones and formic acid under mild conditions (without solvent, at 125°C) in the presence of a catalytic amount of dichlorotris(triphenylphosphine)ruthenium(II), affording a facile method for selective conversion of a variety of ketones to the corresponding secondary alcohols in excellent yields. The present method has several advantages: (1) No use of molecular hydrogen, and (2) simple procedure and easy separation of products.

The typical procedure for the reaction is as follows. A mixture of a ketone (160 mmol), formic acid (160 mmol), and $\text{RuCl}_2(\text{PPh}_3)_3$ (0.20 mmol) was stirred under an argon atmosphere at 125°C for 3 h using a 100 ml stainless autoclave. The products were analyzed by GLC or were separated by distillation and determined by means of IR, and ^1H and ^{13}C NMR spectra.



Some representative results are listed in Table. A variety of ketones were reduced to the corresponding alcohols in high yields by this method. Acetophenone selectively gave 1-phenylethanol in 85% yield (Run 1). As Run 2 shows, the combination of $\text{RuCl}_2(\text{PPh}_3)_3$ with molecular hydrogen instead of formic acid, however, gave much poorer yields of 1-phenylethanol. The active species for the reduction may be a ruthenium hydride complex which is formed by the direct reaction of ruthenium complex with formic acid, although formic acid decomposes to hydrogen and carbon dioxide in the presence of transition metal complexes.⁴⁾ Among ruthenium complexes used as catalyst precursors for this reaction, $\text{RuCl}_2(\text{PPh}_3)_3$ has the highest activity, followed by $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$, $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$, $\text{Ru}_3(\text{CO})_{12} + 9\text{PPh}_3$, and $\text{Ru}_3(\text{CO})_{12}$.

Table. The ruthenium complex-catalyzed reduction of ketones with formic acid^{a)}

Run	Ketone	Product (%) ^{b)} (based on the amount of ketone used)	Ketone recovered (%)	
1	Acetophenone	1-Phenylethanol	85	15
2 ^{c)}	Acetophenone	1-Phenylethanol	16	84
3	Cyclohexanone	Cyclohexanol	78	22
4	2-Butanone	2-Butanol	85	10
5	3-Pentanone	3-Pentanol	38	54
6	2-Hexanone	2-Hexanol	72	13
7	3-Hexanone	3-Hexanol	50	50
8	2,4-Dimethyl-3-pentanone	2,4-Dimethyl-3-pentanol	trace	~100
9	Ethyl acetoacetate	Ethyl 3-hydroxybutyrate	(39)	~0
		1-Methyl-2-ethoxycarbonylethyl 3-hydroxybutyrate	(23)	
10	Ethyl pyruvate	Ethyl lactate	(78)	~0
11	2-Ethylhexanal	2-Ethylhexanol	63	15
		2-Ethylhexyl formate	20	

a) A mixture of a ketone (80-160 mmol), formic acid (80-160 mmol), and $\text{RuCl}_2(\text{PPh}_3)_3$ (0.10-0.20 mmol) was stirred at 125°C for 3 h.

b) Determined by GLC. The figures in parentheses show isolated yields.

c) Under pressures of hydrogen (initial pressure 74 atm/20°C) without formic acid.

Cyclohexanone, 2-butanone, and 2-hexanone were smoothly reduced to cyclohexanol, 2-butanol, and 2-hexanol, respectively, in 72-85% yields. On the other hand, 3-pentanone and 3-hexanone gave the corresponding alcohols in poorer yields (38-50%), and such ketone as 2,4-dimethyl-3-pentanone with a bulky group had low reactivity for this reaction. Thus, this procedure appears to be most applicable for methyl alkyl or aryl ketones. Ethyl pyruvate gave quantitatively ethyl lactate. Ethyl acetoacetate was also readily reduced to give two products, ethyl 3-hydroxybutyrate and 1-methyl-2-ethoxycarbonylethyl 3-hydroxybutyrate.

A formyl group is also reduced by this method. 2-Ethylhexanal gave two products, 2-ethylhexanol (63%) and 2-ethylhexyl formate. The reduction of the ketones gives almost no formates as by-products.

The results obtained here demonstrate that this procedure can be widely applicable for conversion of ketones to secondary alcohols but for that of aldehydes to primary alcohols with some difficulty because of a formate formation.

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