Pergamon

Tetrahedron Letters, Vol. 36, No. 7, pp. 1059-1062, 1995
Elsevier Science Ltd
Printed in Great Britain
0040-4039/95 $9.50+0.00

0040-4039(94)02453-7

Hydrogenation of Carboxylic Acids Using Bimetallic Catalysts Consisting of Group 8 to 10, and Group 6 or 7 Metals

De-Hua He, Noriko Wakasa, and Takamasa Fuchikami*

Sagami Chemical Research Center

Nishi-Ohnuma 4-4-1, Sagamihara, Kanagawa 229, Japan

Abstracts: Hydrogenation of carboxylic acids to alcohols was effectively catalyzed by bimetallic systems consisting of Group 8 to 10 late transition-metals, and Group 6 or 7 early transition-metal carbonyls. These catalysts easily converted α,ω-dicarboxylic acid monoesters into ω-hydroxyalkanoic esters in good yields.

Transition-metal catalyzed hydrogenation has provided one of the most useful tools for the transformation of functional groups to synthetic organic chemists.1) However, catalytic reduction of carboxylic acid derivatives has remained to be solved, where McAlees and McCrindle established the following increasing order of difficulty for various carbonyls: acid chlorides > aldehydes, ketones > anhydrides > esters > carboxylic acids > amides.2) Among them, the reduction of carboxylic acids to alcohols is quite important from industrial and practical points of view. Although there have been reported some transition-metal catalysts for the reduction of carboxylic acids, they required vigorous conditions (high pressures and elevated temperature) for successful reductions, and gave a mixture of alcohols, esters, ethers, and hydrocarbons.1) Here, we wish to report new bimetallic catalytic systems consisting of Group 8 to 10 late transition-metal compounds, and Group 6 or 7 early transition-metal carbonyls for a facile and selective transformation of carboxylic acids to alcohols, and α,ω-dicarboxylic acid monoesters to ω-hydroxyalkanoic acid monoesters.

Initially, the effectiveness of Group 6 to 10 transition-metals themselves was reexamined using pentadecanoic acid (**1a**) as a substrate. Although Rh/Al_2O_3 afforded 15 % yield of pentadecanol (**2a**) at 170 °C, none of them showed a significant catalytic activity under the conditions of below 180 °C and 100 atm of hydrogen pressure. Surprisingly, bimetallic catalysts consisting of Group 8 to 10 late transition-metal complexes such as $Rh(acac)_3$, $Ru(acac)_3$, or $Ru_3(CO)_{12}$ and Group 6 or 7 early transition-metal carbonyls such as $Mo(CO)_6$, $W(CO)_6$, or $Re_2(CO)_{10}$ exhibited extremely powerful reducing ability in the hydrogenation of pentadecanoic acid (**1a**) to give pentadecanol (**2a**) in excellent yields.3)

Typical procedure is as follows: In a 10 ml stainless autoclave was placed 4.0 mg (1 mol%) of tris(acetylacetonato)rhodium, 3.3 mg (0.5 mol%) of rhenium carbonyl, 242.4 mg (1.0 mmol) of pentadecanoic acid (**1a**), and 1.0 ml of dimethoxyethane as a solvent. The autoclave was pressurized by hydrogen to 100 atm and the mixture was stirred for 16 h at 160 °C. GLC analysis of the reaction mixture showed the formation of pentadecanol (**2a**) (97 %) in addition to pentadecane (3 %).

$$\underset{1}{\text{R-COOH}} \quad + \quad \underset{100\ \text{atm}}{H_2} \xrightarrow[\text{DME}]{\text{cat.}} \underset{2}{\text{R'-}CH_2OH}$$

a: $R=R'=n\text{-}C_{14}H_{29}$
b: $R=R'=n\text{-}C_{15}H_{31}$
c: $R=R'=n\text{-}C_{12}H_{25}$
d: $R=R'=n\text{-}C_9H_{19}$
e: $R=R'=n\text{-}C_5H_{11}$
f: $R=R'=(n\text{-}C_3H_7)_2CH$
g: $R=R'=c\text{-}C_6H_{11}$
h: $R=n\text{-}C_{10}H_{21}CH=CH$, $R'=n\text{-}C_{12}H_{25}$
i: $R=Ph$, $R'=c\text{-}C_6H_{11}$

Table 1. Hydrogenation of Carboxylic Acids.[a]

Substrate	cat.		Temp. (°C)	Yield (%)
1a	$Rh(acac)_3$		170	2[b]
	5% Rh/Al_2O_3		170	15[b]
	$Ru(acac)_3$		160	2[b]
	$Ru_3(CO)_{12}$		160	0[b]
	5% Pd/C		160	1[b]
	5% Pt/Al_2O_3		170	0[b]
	$Re_2(CO)_{10}$		170	1[b]
	$Mo(CO)_6$		170	0[b]
	$W(CO)_6$		180	0[b]
	$Rh(acac)_3$	$Re_2(CO)_{10}$	160	97
	$Rh(acac)_3$	$Mo(CO)_6$	160	93
	5% Rh/Al_2O_3	$Re_2(CO)_{10}$	140	93
	5% Rh/Al_2O_3	$Mo(CO)_6$	150	98
	5% Rh/Al_2O_3	$W(CO)_6$	180	84
	$Ru(acac)_3$	$Re_2(CO)_{10}$	160	93
	5% Ru/Al_2O_3	$Mo(CO)_6$	160	95
	$Ru_3(CO)_{12}$	$Re_2(CO)_{10}$	160	95
	5% Pd/C	$Re_2(CO)_{10}$	160	93
	5% Pt/Al_2O_3	$Re_2(CO)_{10}$	170	86
1b	5% Rh/Al_2O_3	$Mo(CO)_6$	145	93
1c	5% Rh/Al_2O_3	$Mo(CO)_6$	150	97
1d	5% Rh/Al_2O_3	$Mo(CO)_6$	150	98
1e	5% Rh/Al_2O_3	$Mo(CO)_6$	150	95
1f	5% Rh/Al_2O_3	$Mo(CO)_6$	155	89
1g	5% Rh/Al_2O_3	$Mo(CO)_6$	150	93
1h	5% Rh/Al_2O_3	$Mo(CO)_6$	150	89
1i	5% Rh/Al_2O_3	$Mo(CO)_6$	150	99

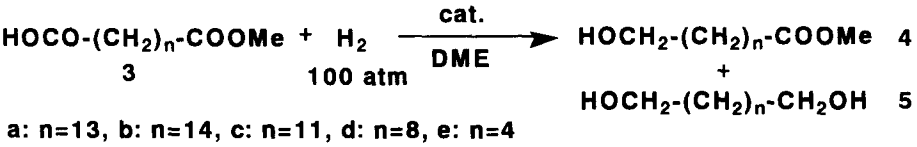
[a] All reactions were carried out with substrate (1.0 mmol) and catalyst (0.01 eq.) in DME (1 ml) at given temperature for 16 h.

[b] Most of the starting material was recovered unchanged.

The representative results were shown in Table 1. Synergistic effects of $Re_2(CO)_{10}$, $Mo(CO)_6$, or $W(CO)_6$ were observed with not only homogenous ($Rh(acac)_3$, $Ru(acac)_3$, or $Ru_3(CO)_{12}$) but also heterogeneous (Rh/C, Rh/Al_2O_3, Ru/Al_2O_3, Pd/C, or Pt/Al_2O_3) catalysts. It is noteworthy that in the present conditions by-product was only hydrocarbon (pentadecane) and no ester (pentadecyl pentadecanoate) was detected by GLC analyses.[3] Reaction temperature is very critical in the present catalytic systems. Higher temperature resulted in the increase in the formation of pentadecane, while lower temperature significantly reduced the conversion of the starting acid. The best temperatures for each catalysts are listed in Tables. On using Rh/Al_2O_3 and $Re_2(CO)_{10}$ as catalysts, the reaction took place even at 140 °C and gave alcohol **2a** in 93 % yield. Synergistic effect of $W(CO)_6$ was rather lower, so elevated temperature (180 °C) was required in the same reaction. The present catalytic system was also effective for the reduction of a variety of fatty acids and aromatic carboxylic acids, where hydrogenation of aromatic ring as well as carbon-carbon double bond took place easily as shown in Table 1 (**1h** and **1i**). No formation of esters was detected in any reactions.

Next, we applied the present catalytic system to the preparation of ω-hydroxyalkanoic acid derivatives, which are key intermediates for pharmaceutical, scented, and polymeric materials. The present catalysts exhibited the potent catalytic activities toward the hydrogenation of α,ω-dicarboxylic acids themselves, however, the selectivity was rather low and a mixture of ω-hydroxyalkanoic acids and α,ω-diols was obtained in good yields. A successful transformation was performed using α,ω-dicarboxylic acid monoesters (**3**) as substrates, which can be easily prepared by barium-mediated half-hydrolysis of α,ω-dicarboxylic acid diesters.[4]

Bimetallic catalysts consisting of Rh-Re, Rh-Mo, and Ru-Re were particularly effective for the reduction of pentadecanedioic acid monomethyl ester (**3a**) at 140-170 °C to give methyl ω-hydroxypentadecanoate (**4a**) in 80-89 % yields with α,ω-pentadecanediol (**5a**) in 7-17 % yields as shown in Table 2. It is very surprising that a carboxyl group undergoes the reduction faster than an ester group by the present catalysts, whereas the existing catalyst such as copper chromite is effective upon the hydrogenation of an ester part under more vigorous conditions.[5]



$$\underset{\mathbf{3}}{HOCO\text{-}(CH_2)_n\text{-}COOMe} + \underset{100\ atm}{H_2} \xrightarrow[DME]{cat.} \begin{array}{l} HOCH_2\text{-}(CH_2)_n\text{-}COOMe \quad \mathbf{4} \\ \quad + \\ HOCH_2\text{-}(CH_2)_n\text{-}CH_2OH \quad \mathbf{5} \end{array}$$

a: n=13, b: n=14, c: n=11, d: n=8, e: n=4

As Table 2 shows, the reduction of α,ω-dicarboxylic acid monoesters **3b-e** gave ω-hydroxyalkanoates **4b-e** in good yields under the same reaction conditions, regardless of the number of methylene unit in the molecules. It is noteworthy that neither polymeric product nor lactone arising from intermolecular or intramolecular condensation of formed **4** was observed, and also no hydrolysis of **3** or **4** by formed water took place under these conditions. Trace amounts of hydrocarbons and monoalcohols were detected as by-products in some reactions.

In conclusion, bimetallic catalysts consisting of Group 8 to 10 late transition-metal compounds and Group 6 or 7 early transition-metal carbonyls was proved to exhibit extremely powerful reducing ability in the hydrogenation of carboxylic acids, and unique selectivity to reduce carboxylic acid part rather than ester part in the hydrogenation of α, ω-dicarboxylic acid monoesters.

Table 2. Hydrogenation of Dicarboxylic Acid Monomethyl Ester.[a]

Substrate	cat.		Temp. (°C)	Yield (%) 4	Yield (%) 5
3a	$Rh_6(CO)_{16}$	$Re_2(CO)_{10}$	140	87	10
	$Rh_6(CO)_{16}$	$Mo(CO)_6$	140	84	8
	$Rh(acac)_3$	$Re_2(CO)_{10}$	160	88	11
	$Rh(acac)_3$	$Mo(CO)_6$	170	85	7
	5% Rh/Al_2O_3	$Re_2(CO)_{10}$	150	80	8
	5% Rh/Al_2O_3	$Mo(CO)_6$	150	83	15
	5% Ru/Al_2O_3	$Re_2(CO)_{10}$	150	89	10
	5% Ru/C	$Re_2(CO)_{10}$	160	81	17
3b	$Rh_6(CO)_{16}$	$Mo(CO)_6$	145	81	17
3c	$Rh_6(CO)_{16}$	$Mo(CO)_6$	160	85	13
3d	$Rh_6(CO)_{16}$	$Mo(CO)_6$	160	91	6
3e	5% Rh/Al_2O_3	$Mo(CO)_6$	165	83	15

[a] All reactions were carried out with substrate (0.5 mmol) and catalyst (0.01 eq.) in DME (1 ml) at given temperature for 16 h.

References and Notes

1) (a) M. Hudlicky, "Reductions in Organic Chemistry", John Wily & Sons: New York, 1984. (b) M. Freifelder, "Catalytic Hydrogenation in Organic Synthesis Procedures and Commentary", John Wiley & Sons: New York, 1978. (c) P. N. Rytlander, "Hydrogenation Methods", Academic Press: New York, 1985.

2) A. J. McAlees and R. McCrindle, *J. Chem. Soc. C,* 2425 (1969).

3) Although similar synergistic effects of Ru, Pd, Pt, or Rh complex with Re_2O_7 have been reported in the reduction of octanoic acid, octyl octanoate is obtained as a main product in addition to octanol. B. C. Trivedi, D. Grote, and T. O. Mason, *J. Am. Oil. Chem. Soc.*, **58**, 19 (1981).

4) L. J. Durham, D. J. McLeod, and J. Cason, *Org. Synth., Coll. Vol.* **4**, 635 (1963).

5) (a) D. C. Sayles and E. F. Degering, *J. Am. Chem. Soc.*, **71**, 3161 (1949). (b) T. Yokota, H. Okino, and M. Takagi, *Eur. Pat. Appl.* EP262,948 (1988); *Chem. Abstr.*, **109**, 128395u (1988).

(*Received in Japan* 12 *September* 1994; *revised* 4 *November* 1994; *accepted* 3 *December* 1994)