CHEMISTRY LETTERS, pp. 5-8, 1991.

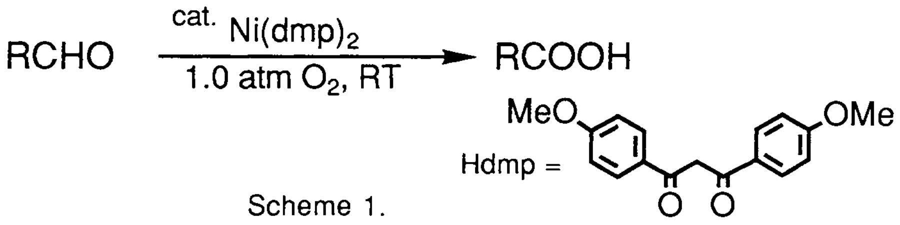
Oxidation of Aldehydes into Carboxylic Acids with Molecular Oxygen Using Nickel(II) Complex Catalyst

Tohru YAMADA, Oliver RHODE, Toshihiro TAKAI, and Teruaki MUKAIYAMA[†]
Basic Research Laboratories for Organic Synthesis,
Mitsui Petrochemical Industries, Ltd.,
Nagaura, Sodegaura-machi, Kimitsu-gun, Chiba 299-02

The oxidation of aldehydes into the corresponding carboxylic acids using a catalytic amount of nickel(II) complex under an oxygen atmosphere at room temperature is described. Bis[1,3-di(*p*-methoxyphenyl)-1,3-propanedionato]nickel(II)(Ni(dmp)$_2$) behaves as an excellent catalyst for the oxidation of aldehydes to afford the corresponding carboxylic acids in good yields.

The oxidation of aldehydes into the corresponding carboxylic acids is one of the important methods in organic synthesis, and many reagents and procedures have been reported for this purpose; for example, $KMnO_4$,1) CrO_3,2) Ag_2O,3) $H_2O_2$4) *etc.* These oxidation reagents contain poisonous metals, such as manganese and chromium, or expensive metal, such as silver, or explosive reagents, such as peroxides, and are employed stoichiometrically against aldehydes. On the other hand, molecular oxygen5, 6) is one of the most available and safe oxidant because of the abundance, cleaness and easiness to handle.

In our previous communication,7) we reported the highly efficient method for epoxidation of olefins catalyzed by bis(1,3-diketonato)nickel(II) complexes with combined use of atmospheric pressure of molecular oxygen and aldehydes at room temperature. Also, the formation of the corresponding carboxylic acid was confirmed by GC analysis after the epoxidation reaction. In this communication, we would like to report a novel method for oxidation of aldehydes into the corresponding carboxylic acids using a catalytic amount of a nickel(II) complex under an atmospheric pressure of oxygen at room temperature.

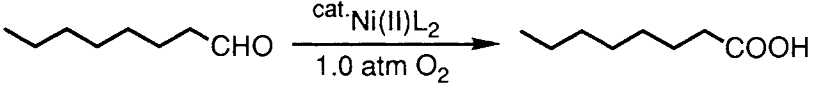


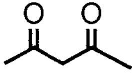
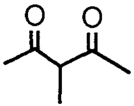
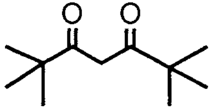
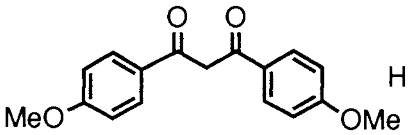
Scheme 1.

[†] Address: Department of Applied Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162.

Based on the results obtained in the epoxidation catalyzed by nickel(II) complex,[7)] we started to study the oxidation of aldehydes with molecular oxygen into the corresponding carboxylic acids according to the following procedure; *n*-octyl aldehyde (2.0 mmol) in 1,2-dichloroethane (2.0 ml) was treated with atmospheric

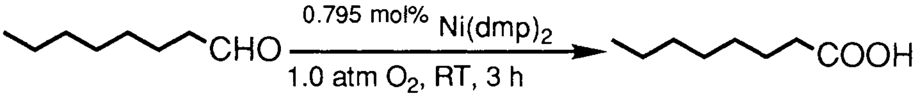
Table 1. Oxidation of *n*-Octyl Aldehyde Catalyzed by Various Nickel(II) Complexes[a)]

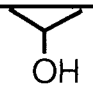
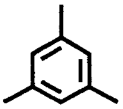
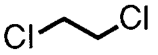
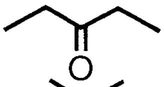
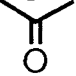
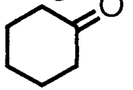


Entry	Ligand (LH)		Conversion / %[b)]	Yield / %[c)]
1		H acac	95.7	78.6
2		H mac	92.8	75.4
3		H dpm	96.5	82.9
4		H dmp	96.9	81.6
5			95.4[d)]	70.4[d)]

a) Reaction conditions: *n*-Octyl aldehyde 2.0 mmol, NiL_2 0.795 mol%, 1.0 atm O_2, in acetone(2.0 ml), RT, 3.0 h. b) Determined by GC analysis. c) After treatment with diazomethane, determined by GC analysis as corresponding methyl ester. d) Carried out in 1,2-dichloroethane (2.0 ml).

Table 2. Oxidation of *n*-Octyl Aldehyde in Several Solvents[a)]



Entry	Solvent	Conversion / %[b)]	Yield / %[c)]
1		85.5	12.1
2	Et_2O	77.7	49.5
3		89.3	72.5
4		95.4	70.4
5	AcOEt	96.4	81.0
6		96.0	81.0
7		96.9	81.6
8		95.9	86.4

a) Reaction conditions: *n*-Octyl aldehyde 2.0 mmol, $Ni(dmp)_2$ 0.795 mol%, 1.0 atm O_2 in 2.0 ml of solvent. b) Determined by GC analysis. c) Determined by GC analysis as the corresponding methyl ester.

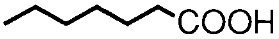
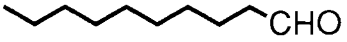
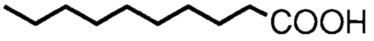
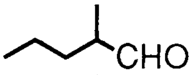
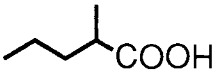
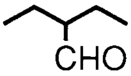
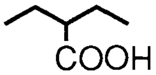
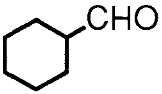
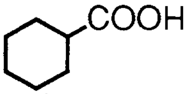
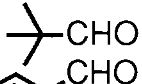
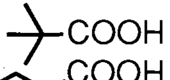
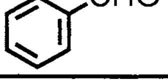
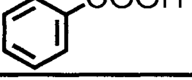
pressure of oxygen at room temperature in the presence of 0.795 mol% of bis[1,3-di(-methoxyphenyl)-1,3-propanedionato]nickel(II)(Ni(dmp)$_2$),[7] and *n*-octanoic acid was obtained as the corresponding methyl ester in 70.4% yield with 95.7% conversion after treatment with diazomethane by an usual manner (Entry 5 in Table 1). And then, several nickel(II) complexes were examined by taking the oxidation of *n*-octyl aldehyde as a model (see Table 1). It was found that nickel(II) complexes having 1,3-diketone-type ligands behave effectively in the present oxidation similar to the epoxidation with combined use of molecular oxygen and aldehydes.[6]

Next, several solvents were screened in the present oxidation (see Table 2). In the case of using alcohol, such as 2-propanol, diethyl ether or aromatic hydrocarbon as a reaction solvent, the corresponding carboxylic acid was obtained only in low yields (Entries 1-3), though aldehyde was almost completely consumed in each case. On the contrary, ketones, such as acetone, diethylketone and cyclohexanone, or ester such as ethyl acetate, were found to be appropriate solvents for the present oxidation(Entries 5-8).

The above procedure was successfully applied to the nickel(II) catalyzed oxidation of various aldehydes. As shown in Table 3, aliphatic aldehydes are oxidized into the corresponding carboxylic acids in good yields (Entries 1-5). The aldehydes having secondary carbon next to carbonyl carbon, such as 2-methylvaleraldehyde, 2-ethylbutyraldehyde, or cyclohexanecaboxaldehyde, are also smoothly oxidized into the corresponding carboxylic acids in good yields (Entries 6-8). And sterically hindered aldehyde, pivalaldehyde, and aromatic aldehyde, benzaldehyde, are converted into pivalic acid and benzoic acid in fairly good yields, respectively (Entries 9 and 10).

Table 3. Nikel(II) Complex-Catalyzed Oxidation of Various Aldehydes[a)]

$$\mathrm{RCHO} \xrightarrow[\text{1.0 atm } \mathrm{O_2}\text{, RT, 3 h}]{\text{0.795 mol\% } \mathrm{Ni(dmp)_2}} \mathrm{RCOOH}$$

Entry	Aldehyde	Carboxylic acid	Yield / %[b)]
1			82.7
2			86.4
3			86.6
4			86.0
5			84.0
6			91.8[c)]
7			87.3[c)]
8			85.7[c)]
9			63.2[d)]
10			78.6[e)]

a) Reaction conditions: Aldehyde 2.0 mmol, Ni(dmp)2 10.0 mg (0.795 mol%) in cyclohexanone (2.0 ml).
b) Determined by GC analysis as the corresponding methyl ester. c) In cyclohexanone (5.0 ml).
d) Carried out at 0 °C for 6.0 h. e) In acetone (2.0 ml).

A typical procedure is described for the oxidation of *n*-dodecyl aldehyde into *n*-dodecanoic acid: A mixture of the aldehyde (5.0 mmol), $Ni(dmp)_2$(25.0 mg, 0.040 mmol, 0.799 mol%) in cyclohexanone (5.0 ml) was stirred at room temperature under an atmosphric pressure of oxygen for 5.0 h. After the reaction, reaction was quenched with aqueous NaOH, and then acidified with aqueous HCl. The crude product was extracted with ether, and purified by vacuum distilation to afford the corresponding carboxylic acid, *n*-dodecanoic acid[9)](879.4 mg, 87.8 % yield).

It is noted that, in the presence of bis[1,3-di(*p*-methoxyphenyl)-1,3-propanedionato]nickel(II), various aldehydes are smoothly oxidized into the corresponding carboxylic acids in good yields under an atmospheric pressure of oxygen.

References

1) J. R. Ruhoff, Org. Synth., Coll. Vol. II, 315,(1943).
2) A. Darapsky and W.Engles, *J. Pract. Chem.*, **146**, 238(1936).
3) I. A. Pearl, *J. Am. Chem. Soc.*, **68**, 429(1946); J. C. Sceeham and C. A. Robinson, *ibid.*, **73**, 1207(1951).
4) J. H. Birkinshaw, H. Raistrick, D. J. Ross, and C. E. Stickings, *Biochem. J. (London)*, **50**, 610(1952).
5) T. J. Wallace and F. A. Baron, *J. Org. Chem.*, **30**, 3520(1965).
6) T. Yamada and T. Mukaiyama, *Chem. Lett.*, **1989**, 519.
7) T. Yamada, T. Takai, O. Rhode, and T. Mukaiyama, *Chem. Lett.*, **1991**, 1.
8) T. Mukaiyama, T. Takai, T. Yamada, and O. Rhode, *Chem. Lett.*, **1990**, 1661.
9) Bp 140°C(bath temp, 5 mmHg); ^1H NMR($CDCl_3$) δ=0.89(3H, tr, J=6.7 Hz), 1.26(16H, m), 1.64(2H, m), 2.35(2H, tr, J=7.3 Hz); IR(neat) 2922, 1705, 1465, 1410, 1298, 938 cm^{-1}.

(Received October 2, 1990)