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The Baeyer-Villiger Oxidation of Ketones Catalyzed by Nickel(II) Complexes with Combined Use of Molecular Oxygen and an Aldehyde

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In the presence of a catalytic amount of a nickel(II) complex coordinated with 1,3-diketone, various cyclic or acyclic ketones are converted into the corresponding lactones or esters by the Baeyer-Villiger oxidation on treatment with an atmospheric pressure of molecular oxygen (oxidant) and an aldehyde (reductant) at room temperature.

The Baeyer-Villiger oxidation is one of the most reliable reactions to convert cyclic ketones into the corresponding lactones, and has been widely used both in degradation work and in synthetic chemistry.1) In the Baeyer-Villiger oxidation, hydrogen peroxide or organic peracid, such as peracetic acid or *m*-chloroperbenzoic acid (*m*-CPBA), are generally used, however, further research on finding safer and simpler oxidant has been expected because they are shock-sensitive and potentially explosive. Recently, several peroxygen products having reasonable thermal stabilities, such as, bis(trimethylsilyl)peroxide2) or magnesium monoperoxyphthalate (MMPP)3) have been proposed as effective oxidants for the Baeyer-Villiger reaction. In our previous communications, we reported much safer and easier method for the efficient epoxidation of olefins4, 5) by combined use of molecular oxygen and aldehydes in the presence of an excellent catalyst of nickel(II) complexes coordinated with 1,3-diketones, such as bis[1,3-di(*p*-methoxyphenyl)-1,3-propanedionato]nickel(II)(Ni(dmp)$_2$) or bis(3-methyl-2,4-pentanedionato)nickel(II)(Ni(mac)$_2$). Similarly, oxygenation of silyl enol ethers into α-hydroxy carbonyl compounds,6) and oxidation of aldehydes into carboxylic acids7) can be carried out according to the above mentioned procedure using the Ni(II) complexes. Concerning the Baeyer-Villiger reaction , several procedures for preparation of ε-caprolactone from cyclohexanone using molecular oxygen and aldehyde catalyzed by transition-metal salts or complexes were shown in patents.8) However, the selectivities of ε-caprolactone described in these patents are not satisfactory (70-86% selectivities) and conversions of cyclohexanone are generally low (3-30% conversions).

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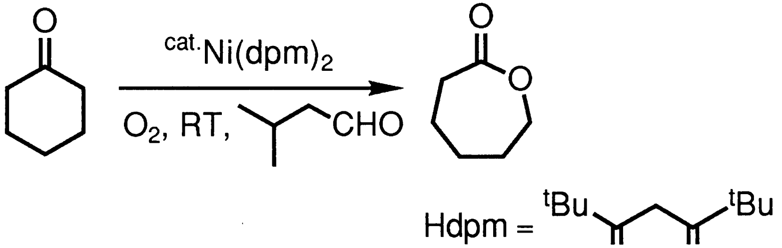
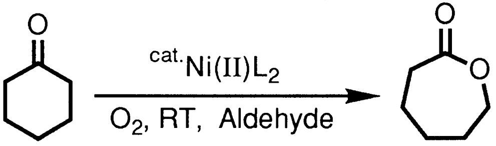
In this communication, we wish to describe the Baeyer-Villiger oxidation of ketones catalyzed by nickel(II) complexes coordinated with 1,3-diketones by combined use of molecular oxygen and aldehydes.

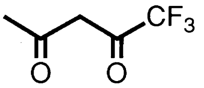
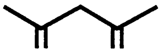
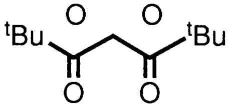


Scheme 1.

In the first place, nickel(II) complexes coordinated with various 1,3-diketones, the catalysts, were examined by taking the Baeyer-Villiger oxidation of cyclohexanone into ε-caprolactone as a model reaction. As shown in Table 1, it was found that nickel(II) complexes of low oxidation potential (E_{OX}), such as bis-(dipivaloylmethanato)nickel(II) (= $Ni(dpm)_2$), behave as effective catalysts in the present oxidation (Entry 3). It is interesting to point out that in the epoxidation of trisubstituted and 1,2-disubstituted olefins[5)] with molecular oxygen using primary alcohols as reductants,[9)] nickel(II) complexes of low oxidation potential also act as

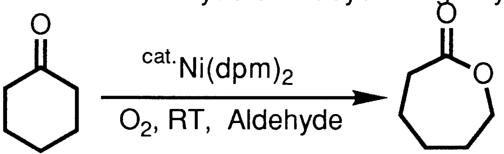
Table 1. Baeyer Villiger-type Oxidation Catalyzed by Various Nickel(II) Complexes[a)]

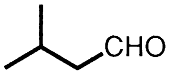
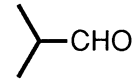
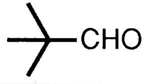


Entry	Ligand (LH)	E_{OX}/V[b)]	Yield / %[c)]
1	 Htfa	1.89	72
2	 Hacac	1.24	88
3	 Hdpm	1.05	91

a) Reaction conditions: Cyclohexanone 1.0 mmol, $Ni(II)L_2$ 1.0 mol%, isovaleraldehyde 3.0 mmol, 1.0 atm O_2, in 1,2-dichloroethane (5.0 ml), RT, overnight. b) E_{OX} were measured in CH_3CN. See Ref. 10. c) Determined by GC.

Table 2. Effect of an Aldehyde on Baeyer Villiger-type Oxidation [a)]



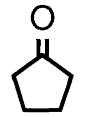
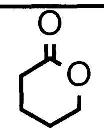
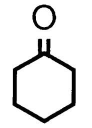
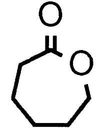
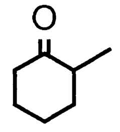
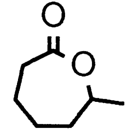
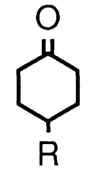
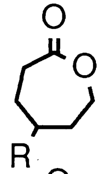
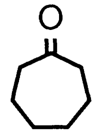
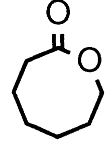
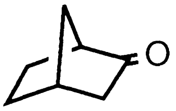
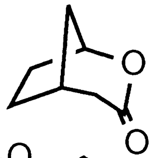
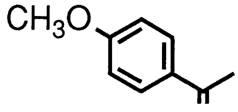
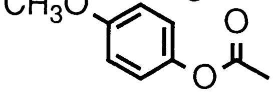
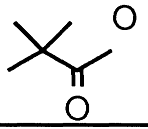
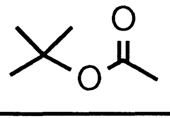
Entry	Aldehyde	Conversion/%[b)]	Yield/%[b)]
1	CH_3CHO	97	70
2		100	91
3		50	40
4		4	4

a) Reaction conditions: Cyclohexanone 1.0 mmol, $Ni(dpm)_2$ 1.0 mol%, Aldehyde 3.0 mmol, 1.0 atm O_2, in 1,2-dichloroethane (5.0 ml), RT, overnight. b) Determined by GC analysis.

effective catalysts. This similarity can be explained by considering that Ni(dpm)2(E_{ox} 1.05 V) and Ni(acac)2(Eox 1.24 V) are more readily oxidized by molecular oxygen to form an active species compared with Ni(tfa)2(E_{ox} 1.89 V).

Next, several aldehydes were examined taking the above reaction as a model. When isobutyraldehyde or pivalaldehyde was employed, both conversion of cyclohexanone and yield of ε-caprolactone were low (Entries 3 and 4 in Table 2), while conversions of cyclohexanone were improved when *n*-alkyl aldehydes, such as acetaldehyde and isovaleraldehyde were used (Entries 1 and 2). Isovaleraldehyde, especially, was found to act as an effective reductant for the present Baeyer-Villiger oxidation to afford ε-caprolactone in 91% yield (Entry 2).

Table 3. Nickel(II) Complex-catalyzed Baeyer-Villiger Oxidation of Various Ketones[a)]

Entry	Ketone	Lactone(Ester)		Yield /%[b)]
1				67
2				84[d)]
3				91
4				93[c)]
5			R=CH_3	96
6			^tBu	95
7			Ph	83
8			Ph	90[d)]
9				33[c,d)]
10				99
11				76
12				56

a) Reaction conditions: Ketone 1.0 mmol, Ni(dpm)$_2$ 1.0 mol%, isovaleraldehyde 3.0 mmol, 1.0 atm O_2, in 1,2-dichloroethane (5.0 ml), RT, overnight. b) Determined by GC analysis. c) Isolated yield. d) Benzaldehyde was employed in the place of isovaleraldehyde.

The above procedure was successfully applied to the nickel(II)-catalyzed Baeyer-Villiger oxidation of various cyclic or acyclic ketones. As shown in Table 3, cyclohexanone and their derivatives (2- or 4-substituted) were oxidized into the corresponding ε-caprolactones in high yields without accompanying any over-oxidized products (Entries 3-8). It is noted that oxidation of 2-methylcyclohexanone afforded ε-heptanoic lactone as a single isomer *via* regio-selective migration of the more substituted carbon atom (Entry 4), whereas that of *m*-CPBA afforded two isomers, ε-heptanoic lactone and 2-methylcaprolactone in the ratio of 10 to 1 (GC analysis). Similarly, the bridged bicyclic ketone was also converted into the corresponding lactone in high yield with high regioselectivity (Entry 10). Oxidation of cyclopentanone or cycloheptanone using isovaleraldehyde as a reductant afforded the corresponding lactones in insufficient yields, whereas yields of the corresponding lactones were improved by using benzaldehyde in the place of alkylaldehydes (Entries 2, 8, and 9). Acyclic ketones were also oxidized into the corresponding esters in good yields (Entries 11 and 12).

A typical procedure is described for the Baeyer Villiger oxidation of 2-methylcyclohexanone into ε-heptanoic lactone; a mixture of 2-methylcyclohexanone (112 mg, 1.0 mmol), $Ni(dpm)_2$ (4.3 mg, 0.01 mmol, 1.0 mol%), isovaleraldehyde (3.0 mmol) in 1,2-dichloroethane (5.0 ml) was stirred at room temperature under an atmosphric pressure of oxygen overnight. Reaction was quenched with aqueous $Na_2S_2O_3$, and the crude product was extracted with dichloromethane. Extraction was successively washed with aqueous Na_2CO_3(10%) and brine. Purification by column chromatography on SiO_2 (Hexane-Ethyl acetate) afforded the corresponding lactone, ε-heptanoic lactone (119.0 mg, 93%yield).[11)]

It is noted that, in the presence of bis(dipivaloylmethanato)nickel(II) ($Ni(dpm)_2$), both cyclic and acyclic ketones are smoothly converted into the corresponding lactones or esters in good to high yields by the combined use of isovaleraldehyde or benzaldehyde as a reductant under an atmospheric pressure of oxygen at room temperature.

References

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5) T. Yamada, T. Takai, O. Rhode, and T. Mukaiyama, unpublished results.
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8) Stamicarbon N. V., JP Patent Tokkosho 46-12456 (1971); Union Carbide Corp., U. S. Patent 3025306 (1962); Knapsack A. G., U. S. Patent 3483222 (1969); Mitsubishi Kasei Co., JP Patent Tokkosho 47-47896 (1972) and Tokkosho 56-14095 (1981).
9) T. Mukaiyama, T. Takai, T. Yamada, and O. Rhode, *Chem. Lett.*, **1990**, 1661.
10) The oxidation potentials (E_{ox}) were measured in acetonitrile solution containing 0.1 mol/l *n*-tetrabutylammonium perchlorate and 0.001 mol/l Ni(II) complex in the cell equipped with a reference electrode (Ag/AgCl), a working electrode (Pt) and an auxiliary electrode (Pt).
11) ^1H NMR($CDCl_3$) δ=1.35(3H, d, J=7.3 Hz), 1.50-2.00(6H, m), 2.55-2.75(2H, m), 4.40-4.45(1H, m); IR(neat) 2938, 1720, 1179, 760 cm^{-1}.

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