SHORT PAPER

J. Chem. Research (S), 2000, 196–197

Nickel (II) and iron (II) / Dowex 50W: an effective catalyst for the Baeyer–Villiger oxidation of ketones using molecular oxygen and benzaldehyde

Mohammed M. Hashemi* and Yousef A. Beni

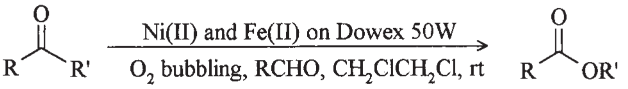
Department of Chemistry, Sharif University of Technology, P.O. Box 11365-9611, Tehran, Iran

A mixture of Ni(II) and Fe(II) supported on Dowex 50W catalyses Baeyer–Villiger oxidation of ketones using molecular oxygen and benzaldehyde

In 1899 Baeyer and Villiger[1] reported on the synthesis of lactones from cyclic ketones by insertion of oxygen into a C–C bond. After one century this is still a widely used method[2] and has been developed by using various reagents, *e.g.* peracids[3], hydrogen peroxide and other peroxides.[4]

In recent years, different catalytic[5] and biocatalytic[6] processes have been developed to perform this reaction. Catalytic oxidation with molecular oxygen and an aldehyde provides an attractive route for the preparation of esters and lactones from ketones via Baeyer–Villiger reaction. In this regard, various catalytic systems such as Ni(II) complexes coordinated with 1,3-diketones[7], Fe_2O_3[8], $Cu(OAc)_2$[9] and Ni_2SiO_2 have been used.[10] Also Baeyer–Villiger reaction can be carried out with molecular oxygen and benzaldehyde in the absence of metal catalyst. In this case the high temperature is needed and yields are not high.

During the course of our systematic study on catalytic oxidation of organic compounds with molecular oxygen,[11] we have found that Ni(II) and Fe(II) supported on Dowex 50W, a macroreticular cation exchanger resin, catalyses effectively Baeyer–Villiger oxidation of ketones with molecular oxygen in the presence of an aldehyde (equation 1).



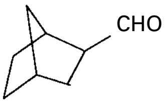
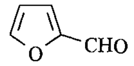
This reaction system was strongly dependent on the aldehydes used, and at first the importance of the aldehyde component in the oxidation system, was examined in Baeyer–Villiger oxidation of 9-fluorenone as a model substrate. Typical results are shown in Table 1.

Table 2 shows the Baeyer–Villiger oxidation of various cyclic and acyclic ketones using molecular oxygen and benzaldehyde in the presence of a 1:1 mixture of Ni(II) and Fe(II) on Dowex 50W. The reactions proceeded smoothly at room temperature to give corresponding esters or lactones in high yields and benzoic acid as a coproduct.

Experimental

Chemicals were purchased from Merck, Aldrich and Riedel de Haen chemical companies and were used without further purification. IR spectra were recorded (KBr) on FT-IR Unicam Mattson 1000 Spectrophotometer. ^{1}H-NMR spectra were recorded on a Brucker AC-80 (80 MHz) spectrometer in $CDCl_3$. All products are known compounds and they were identified by their mp's or bp's, IR and ^{1}H-NMR, spectroscopic properties. All yields refer to pure isolated products.

Table 1 The effect of various aldehydes on Baeyer-Villiger oxidation of 9-fluorenone

Aldehyde	Reaction time (h)	Yield[a] (%)
C_6H_5CHO	4	90
$CH_3(CH_2)_5CHO$	10	45
p-$CH_3C_6H_4CHO$	10	83
$(CH_3)_3CCHO$	10	39
		
$(CH_3)_2CHCH_2CHO$	10	58
$C_6H_5CH_2CHO$	10	48
	10	54
	5	80

[a]Reaction conditions: 9-fluorenone, 5 mmol; aldehyde, 15 mmol; Ni(II) catalyst 5 mol % and Fe(II) catalyst 5 mol %; 1,2-dichloroethane, 35 ml and room temperature.

Preparation of Ni^{2+} and Fe^{2+} supported on cation exchanger resin: 100 g of the sodium form of Dowex 50W, a macroreticular cation exchanger resin containing sulfonate group, was added under stirring to the 500 ml of a saturated solution of $NiCl_2$ and the Ni^{2+} form of the resin was obtained in 3 h. The resin was successively rinsed with deionised water, acetone and methanol and finally dried *in vacuo* at 50°C for 4 h. The capacity of the resin was determined by atomic absorption and the average capacity of the dried resin was 1.65 mmol Ni^{2+} / g of resin. The Fe^{2+} form of the resin was prepared by the same procedure and the average capacity of the dried resin was 2.10 mmol Fe^{2+} / g of resin.

Baeyer–Villiger oxidation of ketones, typical procedure: 9-fluorenone (5.00 mmol) and the dry Ni^{2+} form of the resin (0.15 g, 0.25 mmol), the dry Fe^{2+} form of the resin (0.12 g, 0.25 mmol), and benzaldehyde (15 mmol) were added to 35ml of 1,2-dichloroethane under vigorous stirring and oxygen was bubbled into the stirred solution at room temperature for 3 h. The reaction mixture was filtered through a sintered glass and benzoic acid was removed by successive treatment of the filtrate with saturated $NaHSO_3$ and filtering. Evaporation followed by column chromatography on silica gel (hexane-ethylacetate 3:1) gave the corresponding lactone (4.5 mmol, 90%).

In control experiments reactions using Fe and Ni salts without resin support or with resin alone gave negligible yields.

Received 24 November 1999; accepted 22 March 2000
Paper 99/21

References

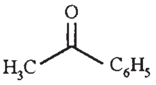
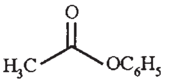
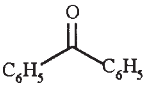
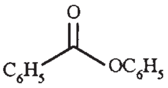
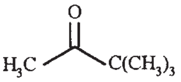
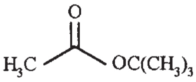
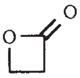
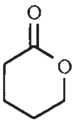
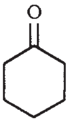
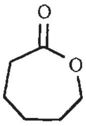
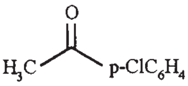
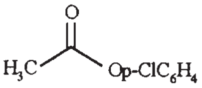
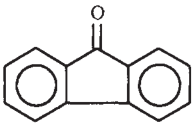
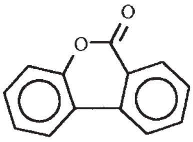
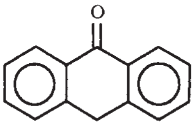
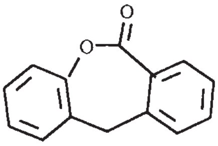
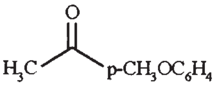
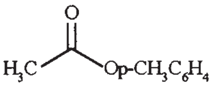
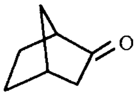
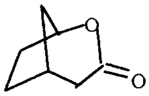
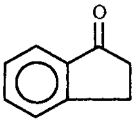
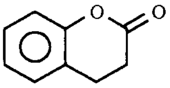
1 Baeyer and V. Villiger, *Ber.*, 1899, **32**, 3625.
2 For reviews, see (a) G.R. Krow, *Organic Reactions*, John Wiley & Sons: New York, 1993,Vol. **45**, 251; (b) M. Hudlicky, *Oxidation in Organic Chemistry*, ACS Monograph 186, Washington DC, 1990.
3 R.R. Sauers and R.W. Ubersax, *J. Org. Chem.*, 1965, **30**, 3939; (a) T. Sugimura, Y. Fujiwara and A. Tai, *Tetrahedron Lett.*, 1997; **38**, 6019.

---

* To receive any correspondence.

† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 2 Baeyer–Villiger oxidation of ketones with molecular oxygen in the presence of benzaldehyde catalyzed by a mixture of Ni(II) and Fe(II) supported on Dowex 50W[a]

Entry	Substrate	Reaction time (h)	Product	Yield[b]
1		8		79
2		6		84
3		15		52
4		15		94
5		5		95
6		5		91
7		11		85
8		3		90
9		5		85
10		7		87
11		3.5		83[c]
12		6.5		88

[a]The reactions was carried out as described in the text. [b]Yields refer to pure isolated products. [c]Benzene was used instead of 1,2-dichloroethane.

4 L. Syper, *Synthesis*, 1989, 167; (b) M. Suzuki, H. Takada and R. Noyori, *J. Org. Chem*., 1982, **47**, 902.
5 C. Mazzini and J. Furstoss, *J. Org. Chem*., 1996; **61**, 8; (b) G. Bolm, G. Schlingloff and F. Bienewald, *J. Mol. Cat., A: Chem*., 1997, **117**, 347.
6 K. Pohelka, M. Gelo-Pujic and E. Guibe-Jampel, *J. Chem. Soc. Perkin Trans. I*., 1998, **1**, 347.
7 Yamada, T. Takai, O. Rhode and T. Mukaiyama, *Chem. Lett*., 1991, 5.
8 I. Murahashi, Y. Oda and T. Naota, *Tetrahedron Lett*., 1992, **33**, 7557.
9 Bolm, G. Schlingloff and K. Weickhardt, *Tetrahedron Lett*., 1993, **34**, 3405.
10 L.H. Yuhi, *New. J. Chem*., 1998, **22**, 81.
11 (a) M.M. Hashemi and D. Ghazanfari, *Iran. J. Chem & Chem. Eng*., 1995, **13**, 77; (b) M.M. Hashemi and Y.A. Beni, *J. Sci. I.R. Iran*, 1998, **9**, 237; (c) M. M. Hashemi and Y.A. Beni, *J. Chem. Res.(S)*, 1998, 138; (d) M.M. Hashemi and Y.A. Beni, *J. Chem. Res.(S)*, 1999, 434; (e) M.M. Hashemi and N. Manuchehri, *Iran. J. Chem. & Chem. Eng*., 1997, **16**, 82 (f) M.M. Hashemi and F. Kalantari, *Synth. Commun*., accepted.