Oxidation of α-hydroxy ketones to diketones by iodic acid supported on alumina

Mohammed M. Hashemi[a]*, Hossein Naeimi[b], Farveh Shirazizadeh[b] and Zahed Karimi-Jaberi[a]

[a]*Department of Chemistry, Sharif University of Technology, P.O.Box 11365 – 9516, Tehran, Iran*

[b]*Department of Chemistry, Kashan University, P.O.Box 87317 – 51167, Kashan, Iran*

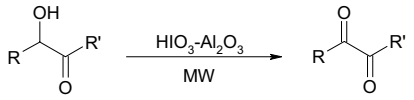
Benzoins are rapidly oxidised to benzils in high yields by iodic acid supported on alumina under solvent-free conditions and microwave irradiation

Keywords: benzoins, benzils, iodic acid

The oxidation of benzoins to benzils has been accomplished by a variety of reagents namely nitric acid,[1] Fehling's solution,[2] thallium(III) nitrate(TTN),[2,3] ytterbium(III) nitrate,[4] ammonium chlorochromat-alumina,[5] ammonium nitrate–copper acetate,[6] nickel acetate,[7] iron(III) chloride,[8] bismuth (III) nitrate–copper(II) acetate.[9] Many of these reagents are highly toxic and contain toxic metallic compounds that generate undesirable materials. Long reaction periods or the use of corrosive acids are disadvantages of some of these methods.

Recently supported reagents and microwave irradiation (MW) have been used to carry out a wide range of organic reactions. These reactions have short reaction times and high conversions and selectivities without solvent.[10] For example, the oxidation of benzoins on zeolite,[11] by oxone[12] or using copper sulfate on alumina[13] occur under microwave irradiation.

Iodic acid is a rather mild inorganic acid (pK_a 0.80) of moderate oxidising power in aqueous acid and of low toxicity to humans, as it has been used in medicine.[14] In continuation of our studies on the application of iodic acid[15-17] we were interested in using this reagent as a suitable catalyst for the oxidation of benzoins to benzils on wet alumina and using microwave irradiation without any solvent.



Iodic acid was supported on wet alumina and used for the oxidation of benzoins under microwave irradiation without solvent. This method offers some advantages in terms of simplicity of performance, the solvent-free conditions, no side product formation and very short reaction times. The results for oxidation of a variety of benzoins to benzils are summarised in Table 1.

Experimental

Products were characterised by comparison of their physical and spectroscopic data with those of authentic samples. All yields refer to isolated products. IR and NMR spectra were recorded on Perkin Elmer 781 and Bruker DPX500 instruments. The progress of the reaction was monitored by TLC.

General procedure for the oxidation of benzoins to benzils: Benzoin (1 mmol), HIO_3 (1 mmol) and neutral alumina (1 g) were mixed thoroughly on a vortex mixer and distilled water (0.1 ml) was added to this mixture. The reaction mixture contained in a glass tube was placed in an alumina bath (heat sink) inside the microwave oven and irradiated for a specified time. Completion of the reaction was ascertained by TLC examination on plates (*n*-hexane/ethyl acetate: 8/1). The product was extracted with methylene chloride (3 × 10 ml). The solvent was removed and the product was recrystallised from ethanol.

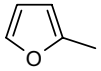
The time of reactions and yields of isolated products are shown in Table 1.

Received 23 May 2005; accepted 27 October 2005
Paper 05/3268

References

1 J.S. Buck and S.S. Jenkins, *J. Am. Chem. Soc*., 1929, **51**, 2163.
2 A. McKillop, B.P. Swann and E.C. Taylor, *Tetrahedron Lett.*, 1970, 5281.
3 A. McKillop, B.P. Swann, M.E. Ford and E.C. Taylor, *J. Am. Chem. Soc*., 1973, **95**, 3641.
4 P. Girara and H.B. Kagan, *Tetrahedron Lett.*, 1975, 4613.
5 G.S. Zhang, Q.Z. Shi, M.F. Chen and K. Cai, *Synth. Commun*., 1997, **27**, 9534.
6 M. Meiss and M. Appel, *J. Am. Chem. Soc*., 1984, **70**, 3666.
7 G.S. Hammond and C.H.S. Mu, *J. Am. Chem. Soc*., 1973, **95**, 8215.
8 Y.M. Zhou, Y.R. Ye and X.Q. Xin, *Synth. Commun*., 1999, **29**, 2229.
9 S.A. Tymonoko, B.A. Nattier and R.S. Mohan, *Tetrahedron Lett.*, 1999, **40**, 7654.
10 A. Loupy, *Microwaves in Organic Synthesis*, Wiley-VCH, Weinheim, 2002.
11 S. Balalaie, M. Golizeh and M.S. Hashtroudi, *Green Chem.,* 2000, **2**, 277.
12 R.S. Varma, R. Dahiya and D. Kumar, *Molecules*, 1998, **2**, 82.
13 R.S. Varma, D. Kumar and R. Dahiya, *J. Chem. Res. (S)*, 1998, 324.
14 N.N. Greenwood and A.A. Earnshaw, *Chemistry of the Elements*; Pergamon Press, Oxford, 1984.
15 M.M. Hashemi and M. Akhbari, *Monatsh. Chem.*, 2003, **134**, 1561.
16 M.M. Hashemi, A. Rahimi and Y. Ahmadibeni, *Acta Chim. Slov.*, 2004, **51**, 333.
17 M.M. Hashemi, A. Rahimi, Z. Karimi-Jaberi and Y. Ahmadibeni, *Acta Chim. Slov.*, 2005, **52**, 86.
18 M.M. Hashemi, M. Bakhtiari and Z. Karimi-Jaberi, *Russ. J. Org. Chem.*, 2005, **41**, In press.

Table 1 Oxidation of α-hydroxy ketones to diketones by iodic acid supported on alumina

Entry	R	R′	Time/min	Yield (%)[a]	m.p./°C	
					Found	Reported
1	Ph	Ph	2	99	92–95	94–96[3]
2	*p*-$CH_3C_6H_4$	*p*-$CH_3C_6H_4$	3	93	131–133	132–134[3]
3	*p*-ClC_6H_4	*p*-ClC_6H_4	3.5	98	195–198	195–197[3]
4	*p*-$CH_3OC_6H_4$	*p*-$CH_3OC_6H_4$	3	97	133–135	132–134[3]
5			2.5	95	161–163	162–164[5]

[a]The yield of isolated product after recrystallisation.

* Correspondent. E-mail: mhashemi@sharif.edu