

## Oxidation of benzoin to benzil using hydroxy-sodalite

Mostafa Nafe<sup>a\*</sup>, Fatemeh Teimouri<sup>a</sup> and Seyed Hadi Khezri<sup>b</sup>

<sup>a</sup> Department of chemistry, Islamic Azad University - Saveh Branch, Saveh, Iran.

<sup>b</sup> Department of Biology, Islamic Azad University -Parand Branch, Parand, Tehran, Iran.

Received: December 2012; Revised: December 2012; Accepted: January 2013

**Abstract:** Benzoin is oxidized to benzil in excellent yields by hydroxy-sodalite ( $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH})_2$ ). Hydroxy-sodalite has the same framework structure as sodalite and consists of the cubic array of  $\beta$ -cages. In this research, a novel method for producing benzil in laboratory conditions is presented. Because of some important features, using hydroxy-sodalite made this procedure a particularly attractive method for oxidation of benzoin.

**Keywords:** Benzoin, Benzil, Hydroxy-sodalite, IR test, Oxidation.

### Introduction

The oxidation of benzoin to benzil has been accomplished by several reagents such as nitric acid [1], Fehling's solution [1], thallium nitrate [2], ammonium nitrate-copper acetate [3], ammonium chlorochromate-alumina [4] and alumina-supported copper(II) sulphate under microwave irradiation [5]. In recent years, the oxidation of benzoin to benzil using bismuth(III) nitrate-copper(II) acetate has been reported [6]. In this research, researchers showed that bismuth(III) nitrate-copper(II) in acetic acid is an excellent reagent for oxidation of benzoin to benzil. It has the advantages of being commercially available, inexpensive and relatively non-toxic [6].

Sodalite is one of the microporous crystalline zeolites which consists of the cubic array of  $\beta$ -cages [7]. Sodalites are microporous tectosilicates with the general composition as  $\text{Na}_8[\text{AlSiO}_4]_6(\text{X})_2$ , where X is a monovalent guest anion as chlorine in the mineral sodalite [8]. Hydroxy-sodalite has a six-membered ring aperture with a pore size of 2.8Å. The pore size of hydroxy-sodalite is smaller than that of the zeolites with an eight-membered ring aperture. Only small

molecules, such as helium, hydrogen and water and so on, can enter the pore of hydroxy-sodalite [9].

From the first researches, scientists showed that benzoin could be oxidized to benzil by the use of chlorine or nitric acid and after years, many other procedures have been developed. One of these, was the use of copper sulphate and pyridine as a modified Fehling solution which may be regenerated by air, is of recent interest [10]. In one research, it is shown that benzoin can be oxidized to the  $\alpha$ -diketone benzil very efficiently by nitric acid or by copper(II) sulfate in pyridine. On oxidation with sodium dichromate in acetic acid, the yield was lower because some material was converted into benzaldehyde by cleavage of the bond between two oxidized carbon atoms that was activated by both phenyl groups [11].

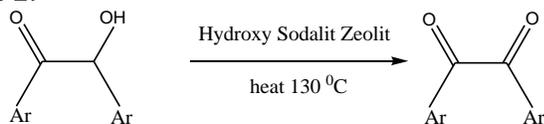
In this research, the oxidation of benzoin to benzil has been carried out using hydroxy-sodalite and dissolving in hot ethanol.

### Results and discussion

Experimental performance for oxidation of benzoin to benzil using hydroxy-sodalite is shown in Table 1. As with all spectroscopic techniques, it can be used to identify and study chemicals. Peaks that are obtained from IR test of the substance produced with proposed

\*Corresponding author. Tel: (+98) 9126517365, E-mail: m.nafe10@yahoo.com

reaction (Figure 1 and entry 4 in Table 1) as shown in Table 2.



**Figure 1:** Schematic view of the reaction.

**Table 1:** Experimental performance for oxidation of benzoin to benzil using hydroxy-sodalite.

Entry	Ar	Time(h)	Yield(%)	M.p(°C)
1	C <sub>6</sub> H <sub>5</sub>	4	95	105 [2]
2	4-Cl <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	4	93	130 [2]
3	2-Cl <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	4	91	135
4	3-NO <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	4	89	135

**Table 2:** Peaks that are obtained from IR test of the substance produced with proposed reaction (Figure 1 and Entry 4 in Table 1) (nm).

511.41	1005.79	1364.19	2346.03	3103.43
663.18	1074.06	1370.16	2364.94	3247.45
669.98	1083.22	1390.54	2427.25	3378.07
792.24	1153.06	1420.13	2504.25	3603.85
826.44	1160.33	1536.55	2862.70	3774.58
906.02	1271.61	1565.76	2939.36	3934.05
934.58	1283.83	1577.79	2962.22	
945.86	1341.66	1601.53	3082.22	

## Experimental

First, a mixture of 0.5 mmol of benzoin and 0.25 gr of hydroxy-sodalite in a small beaker was prepared. Sodalite compounds are attractive candidates for use in benzoin oxidation. The air was naturally occurring oxidant in the whole procedure. Then, the obtained compound was heated in a reflux for about 60 min with an adjusted temperature of 130 °C. In this interval, the compound was ground and properly mixed each 5 min. After 60 min, a Thin Layer Chromatography test (TLC) was carried out on the resulted compound. TLC is a chromatography technique used to separate mixtures. TLC is performed on a sheet of glass, plastic, or aluminium foil, which is coated with a thin layer of adsorbent material, usually silica gel, aluminium oxide, or cellulose (blotter paper). This layer of adsorbent is known as the stationary phase. Results of the TLC test showed that there was no significant difference between the original and obtained substances. At the next level, the obtained compound was heated again in a reflux for about 90 min with an adjusted temperature of 145 °C. After that, another TLC test was carried out on the resulted compound. Results of the second TLC test showed that there were significant differences

between the original and obtained substances. Obtained substance was dissolved in 10 cc of hot ethanol and filtered with a filter paper and transitioned substance began to be crystallized. After evaporating of the third quarter of solvent existing in the obtained substance, it was filtered with a filter paper for the second time. 1 cc of ethanol with ambient temperature was shed on the filter paper to wash the crystals created on the paper. Finally, resulted substance was tested with Infrared spectroscopy (IR) technique.

## References

- [1] Buck, J. S.; Jenkins, S. S. *J. Am. Chem. Soc.* **1929**, *51*, 2163.
- [2] McKillop, A.; Swann, B.; Ford, M. E.; Taylor, E. C. *J. Am. Chem. Soc.* **1973**, *95*, 3641.
- [3] Weiss, M.; Appel, M. *J. Am. Chem. Soc.* **1948**, *70*, 3666.
- [4] Zhang, G.-S.; Shi, Q.-Z.; Chen, M.-E; Cai, K. *Synth. Commun.* **1997**, *27*, 953.
- [5] Varma, R. S.; Kumar, D.; Dahiya, R. *J. Chem. Res.* **1998**, 324.
- [6] Tymonko, S. A.; Nattier, B. A.; Mohan, R. S. *Tetrahedron Lett.* **1999**, *40*, 7657.
- [7] Buhl, J. C.; Lons, J. *J. Alloy. Comp.* **1996**, *41*, 235.
- [8] Buhl, J.C.; Gesing, T.M.; Kerkamm, I.; Gurriss, C. *Micropor. Mesopor. Mater.* **2003**, *65*, 145.
- [9] Xu, X.; Bao, Y.; Song, C.; Yang, W.; Liu, J.; Lin, L. *Micropor. Mesopor. Mater.* **2004**, *75*, 173.
- [10] Kende, A. S.; Freeman, J. P. *Organic Syntheses, Database Online, John Wiley and Sons, Inc.: New York, 2003.*
- [11] Williamson, K. L. *Macroscale and Microscale Organic Experiments, 2nd Ed. Houghton Mifflin, Boston.* **1994.**