

## Alumina and Silica Oxides as Catalysts for the Oxidation of Benzoin to Benzil under Solvent-free Conditions

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**Abstract:** Alumina or silica gel are used as catalysts for a solvent-free oxidation of benzoin to the corresponding benzil. These catalysts are easily recovered after completion of the reactions, which are carried out either by heating in a sand bath or using microwave irradiation. Comparison of the results obtained with both catalysts indicates that all the reactants examined were oxidized faster on alumina than on silica under these conditions.

**Keywords:** Benzoin; benzil; biologically active compounds

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### Introduction

$\alpha$ -Diketones are versatile compounds in organic chemistry that can be utilized for the preparation of a variety of molecules, many of which show a diversity of interesting biological activities [1]. Oxidations of  $\alpha$ -hydroxy ketones to  $\alpha$ -diketones by a wide range of reagents have been reported, including, among others, the dinitrogen tetroxide complex of iron (III) and copper (II) [2], dimethyl sulfide ditriflate [3], peracetic acid in the presence of sodium bromide [4], dimethyl sulfoxide (DMSO)-SbCl<sub>5</sub> [5], thallium (III) nitrate (TTN) [6], a cerium (IV) ammonium nitrate (CAN)-charcoal system [7], nickel acetate [8] and *p*-toluenesulfonic acid in boiling xylene [9]. Alumina and silica gel are both important reagents in industry and in the laboratory and numerous reactions have been carried out using these substances as solid supports. In recent years Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> based reagents have been

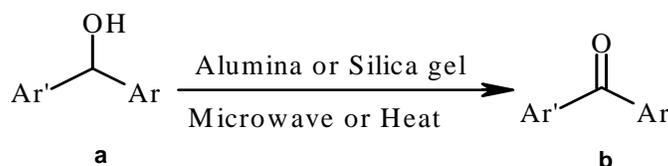
widely used for dehydration or dehydrogenation of alcohols [10-14] and in many oxidation reactions carried out under microwave irradiation or under solid state conditions [15-19].

Benzoin is rapidly oxidized to benzil in high yield by the solid copper (II) sulfate-alumina reagent system under the influence of microwaves [20]. The iodobenzene diacetate-alumina solid reagent system expeditiously and selectively oxidizes sulfides to sulfoxides and alcohols to carbonyl compounds in high yield under the influence of microwaves [21]. A simple and selective method for the oxidation of alcohols to carbonyl compounds using chromium (VI) oxide supported on wet alumina under solvent-free conditions has also been described, again accelerated by microwave irradiation [22]. Other reactions that can be carried out using silica gel as a support include the conversion of epoxides to  $\beta$ -halohydrins with silica gel supported lithium halide [23], the silica gel supported hetero Diels-Alder reaction of quinolinetriones [24], oxidative glycol cleavage with silica gel supported sodium metaperiodate [25], synthesis of benzophenones with Lewis acid catalysts using silica gel [26] and so on. We now report the use of both  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  separately as oxidizing agents in the absence of an additional supported oxidant.

## Results and Discussion

Benzoin is oxidized to benzil in high yield on alumina and silica under solvent-free conditions, under both microwave irradiation assisted conditions and upon heating in a sand bath, without any additional supported oxidant on the alumina or silica gel surface (Scheme 1).

**Scheme 1**



Our results are summarized in Tables 1-4. They show that both alumina and silica gel are suitable oxidants, but that alumina was consistently a better oxidation catalyst than silica gel under the conditions used.

**Table 1.** Solid phase oxidation of benzoin on alumina <sup>a</sup> in a sand bath (140 °C)

Compound	Substituents	Time (min)	Yield (%) <sup>b</sup>
<b>1</b>	Ar' = C <sub>6</sub> H <sub>5</sub> , Ar = C <sub>6</sub> H <sub>5</sub> -CO	10	100
<b>2</b>	Ar' = C <sub>6</sub> H <sub>5</sub> , Ar = 4-Me <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> -CO	60	95
<b>3</b>	Ar' = 4-MeOC <sub>6</sub> H <sub>4</sub> , Ar = 4-MeOC <sub>6</sub> H <sub>4</sub> -CO	180	100
<b>4</b>	Ar' = C <sub>6</sub> H <sub>5</sub> , Ar = 4-MeOC <sub>6</sub> H <sub>4</sub> -CO	65	90
<b>5</b>	Ar' = Ar = C <sub>6</sub> H <sub>5</sub>	N.R. <sup>c</sup>	--
<b>6</b>	Ar' = C <sub>6</sub> H <sub>5</sub> , Ar = H	N.R.	--

a) Activated alumina.

b) Yields based on the products isolated by column chromatography.

c) N.R. = no reaction.

**Table 2.** Solid phase oxidation of benzoin s on alumina under microwave irradiation.

Compound	Time (min)	Yield (%)
1	5	100
2	5	95
3	5	90
4	5	70
5	N.R.	--
6	N.R.	--

**Table 3.** Solid phase oxidation of benzoin s on silica gel <sup>a</sup> in a sand bath (140 °C).

Compound	Time (min)	Yield (%)
1	180	100
2	180	70
3	150	90
4	b	100
5	N.R.	--
6	N.R.	--

a) HF 254(type 60).

b) The reaction time was more than 20 hours.

**Table 4.** Solid phase oxidation of benzoin s on silica gel under microwave irradiation.

Compound	Time (min)	Yield (%)
1	5	95
2	10	95
3	15	85
4	15	70
5	N.R.	--
6	N.R.	--

All of benzoin s examined were readily oxidized but neither diphenyl carbinol (**5a**) nor benzyl alcohol (**6a**) reacted. It seems that an adjacent carbonyl group is necessary for the oxidation of the hydroxyl groups to take place. Naturally, substrates such as **1a- 6a** can be partially oxidized in air after extended exposure to oxygen, but if O<sub>2</sub> played an important role in this oxidation we would expect compounds **5a** and **6a** to have been oxidized too. We attribute the observation that alumina is a better oxidation catalyst than silica to the fact that it is a stronger Lewis acid than silica, although so far we have not proposed a mechanism for this process and at this time we are simply reporting our experimental observations. The reaction times also appear to depend on the temperature, as they are seen to decrease as the temperature increases.

## Conclusions

We report that benzoin is oxidized to benzil in the solid state in good yields under microwave irradiation or in a heated sand bath, using alumina or silica gel as catalysts without added oxidants. The main advantages of these reactions are: (1) easy recovery of the alumina or the silica gel upon completion of the reactions; (2) yields are high and the products contain minimum by-products; (3) no environmental pollution; (4) low cost as no reaction solvents are required.

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## Experimental

### General

Melting points were determined on a Gallenkamp apparatus and are uncorrected. All IR spectra were recorded on a Shimadzu IR-470 spectrometer and  $^1\text{H-NMR}$  spectra were recorded on a Varian EM390 instrument. Chemical shifts ( $\delta$ -scale) are quoted in parts per million and following abbreviations are used: s = singlet; d = doublet; m = multiplet. All the benzoin starting materials were synthesized in our laboratory and were characterized by comparison of their physical data (melting points) with those of authentic samples [27]. All the reported yields refer to isolated products after purification. All products were characterized by comparison of their spectral (IR,  $^1\text{H-NMR}$  and TLC) and physical data (melting points) with those of authentic samples [2, 28]. The apparatus used for the oxidations was either a Samsung domestic microwave oven (2450MHz, 900w) or a sand-bath mortar oven.

### Typical procedure for the oxidation of benzoin to benzil on alumina or silica gel.

Benzoin (0.05 g) was added to  $\text{Al}_2\text{O}_3$  or  $\text{SiO}_2$  (0.5 g, 1:10 w/w), mixed and homogenized in a mortar. The reactions were then allowed to proceed for the times given in Tables 1-4, respectively, either in a sand-bath at 140 °C or under microwave irradiation. Reaction times were monitored and optimized by TLC (checking every 5 minutes under microwave irradiation and every 10 minutes under sand-bath conditions). Upon completion of the reactions the mixtures were washed with a few mL of  $\text{CH}_2\text{Cl}_2$ , filtered, evaporated and the products purified by silica gel column chromatography. The analytical data of two products, **1b** and **3b**, are given as examples: *Benzil (1b)*: light green needle-like crystals, mp 95 °C, (lit. [2,28] 95 °C); IR (KBr): 3100 (C–H, Ar), 1680 (C=O), 1595 (C=C);  $^1\text{H-NMR}$   $\delta_{\text{H}}$  (90 MHz,  $\text{CCl}_4$ ), 7.3 – 7.9 (m, 3H, *m* and *p*-PhH), 8.0 – 8.3 (m, 2H, *o*-PhH); *4,4'-Dimethoxybenzil (3b)*: green solid, mp 133 °C, (lit. [2, 28] 132-134 °C); IR (KBr): 3050(C–H, ar.), 2900(s), 2800 (C–H, aliph.), 1670 (C=O), 1595 (C=C), 1160 (C–O);  $^1\text{H-NMR}$   $\delta_{\text{H}}$  (90 MHz,  $\text{CDCl}_3$ ,  $\text{CCl}_4$ ); 4.0 (s, 3H,  $\text{CH}_3$ ), 7.2 (d,  $J = 9\text{Hz}$ , 2H, *m*-PhH), 8.2 (d,  $J = 9\text{Hz}$ , 2H, *o*-PhH).

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