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# Microwave assisted oxidation of benzoin on alumina using chromium based oxidants

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**ABSTRACT:** Chromium based oxidants like pyridinium chlorochromate, benzimidazolium fluorochromate, pyridinium fluorochromate, piperdinium chlorochromate and ammonium chlorochromate supported on alumina has been found to be an effective reagent for the oxidation of benzoin under microwave irradiation. Alumina acts as a catalyst as well as solid support in the reaction and increases the yield of product. The time of the reaction also get reduced considerably. The durability, easy work up and efficiency of chromium based oxidants are considerably increased by using alumina as a solid support.
**Key Words:** Benzoin, Benzil, Chromium based oxidants, Alumina, Microwave.

## INTRODUCTION

α- Diketones are versatile compounds in organic chemistry that can be utilized for the preparation of a variety of molecules. Many of these show a diversity of intresting biological activities (1). Oxidation of α-hydroxy ketone to α-diketone by a wide range of reagent has been reported. The oxidative transformation of benzoins to benzils have been accomplished by a variety of reagents namely nitric acid, Fehling's solution(2), thallium(III) nitrate(TTN)(3-4), ytterbium(III) nitrate(5), clayfen(6).

Chromium (VI) compounds have been reported as versatile oxidants for many type of substrates varying from metal ions to naturally occurring organic compounds. These oxidants have a wide range of applications spamming the synthesis of sulphur nanoparticals(7), and the determination of biological oxygen demand in organic polluted water. Cr(VI) chromate or dichromate are highly soluble and are reported to be highly toxic also(8).There researchers are continue for the development of new chromium (VI) reagent for the effective and selective oxidation of organic substrates, under mild condition. Therefore, the search for newer oxidizing agents is of interest to synthetic organic chemist. Many such reagents have been developed recently with some success (9).

Some of the important entries in the list of reagents are pyridinium fluorochromate(PFC)(10), Caffinilium chlorochromte (11), quinolinium fluorochromate(12), triphenylemethylphosphonium chlorochromate(13), pyridinium dichromate(14), quinolium chloromate(15), isoquinolinium chlorochromate(16), chromium trioxide 3-5-Dimethylepyrozole complex $CrO_3$3.5-DMP(17), tributyle .ammonium chlorochromate(18),prolinium chlorochromate(19), tripropylammonium fluorochromate(20), Use of supported reagents such as $CrO_3$-supported on resin(21), graphite(22), silica gel(23), QFC on alumina(24) etc are also worth mentioning. Alumina is important reagent in industry and in the laboratory and numerous reactions has been carried out

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using as solid support. Recently, $Al_2O_3$ supported reagent have been widely used for dehydration and dehydrogenation of alcohols (25-26).

**EXPERIMENTAL SECTION**

**General:** Melting points of all products were taken in open capillary tubes and are therefore uncorrected. Purity of the compounds was checked on silica gel G TLC plates of 2 mm thickness using n-hexane and ethyl acetate as solvent system. The visualization of spot was carried out in an iodine chamber. The IR spectra were recorded on Simadzu IR-470 spectrometer. The $^1$H NMR spectra were scanned on a Bruker DRX-300 MHz. spectrometer (300 MHz) in CDCl3/DMSO-d6 using TMS as internal standard and chemical shifts are expressed in δ ppm. IR (KBr); 3100(C-H, Ar), 1680(C=O), 1595(C=C); $^1$H-NMR δ H (90 MHz, $CCl_4$), 7.3-7.9(m; 3H, m and p-PhH), 8.0-8.3(m, 2H, o-PhH).

**Typical procedure for the oxidation of benzoin:** chromium based oxidant mixed with alumina through pestle and mortar by grinding. Then benzoin were added to it and homogenized in a mortar. The reaction mixture was then allowed to proceed for the time in given in table I under microwave irradiation. Reaction time were monitored and optimized by TLC. After the completion of the reaction product is separated by dichloromethane and after separation, evaporated dichloromethane to get product.

**RESULTS AND DISCUSSION**

We report here in the use of chromium based oxidants supported on alumina and its reactivity towards benzoin. We have used here different type of chromium based oxidants for the oxidation of benzoin .All the oxidants show a good oxidation towards benzoin and conversion to benzyl in good yield under microwave irradiation table (I). We have compared here the reactivity of these oxidants supported on alumina in microwave and we found that pyridinium fluorochromate is better oxidant when it is supported on alumina then other oxidants table (II).

In summary we have extended successfully the application of chromium based reagent supported on alumina in microwave irradiation for the oxidation of benzoin. This methods offers some advantage in terms of simplicity of perform, solvent free condition, high yield and short reaction time.

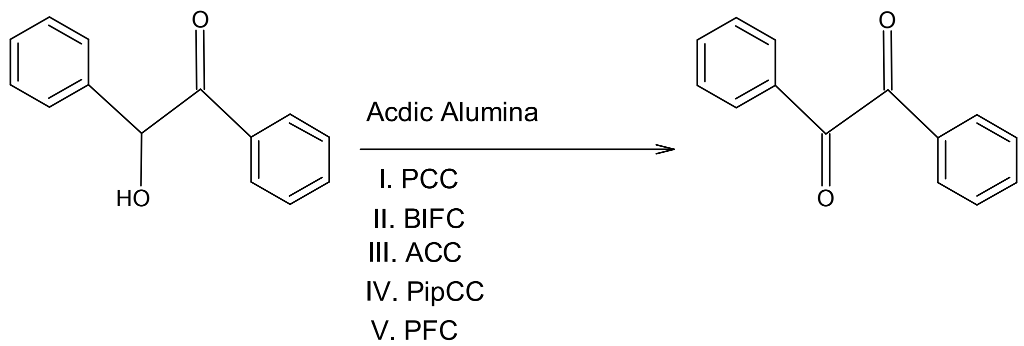


**Table 1: Oxidation of benzoin using various chromium based oxidant supported on alumina under microwave irradiation.**

| S.No. | Chromium based oxidant | Time in min | Yield % |
|---|---|---|---|
| 1. | Pyridinium chlorochromate | 1.0 | 98 |
| 2. | Benzimidazolium fluorochromate | 2.0 | 92 |
| 3. | Pyridinium fluorochromate | 1.5 | 100 |
| 4. | Piperdinium chlorochromate | 1.2 | 90 |
| 5. | Ammonium chlorochromate | 3.0 | 80 |

**Table 2: Comparison of Oxidation of benzoin using various chromium based oxidant supported on alumina under microwave irradiation.**

| S.No. | Chromium based oxidant | Time in min | Yield % |
|---|---|---|---|
| 1. | Pyridinium chlorochromate | 1.0 | 98 |
| 2. | Benzimidazolium fluorochromate | 1.0 | 70 |
| 3. | Pyridinium fluorochromate | 1.0 | 100 |
| 4. | Piperdinium chlorochromate | 1.0 | 80 |
| 5. | Ammonium chlorochromate | 1.0 | 60 |

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