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OVERVIEW ON MICROWAVE – ASSISTED OXIDATION OF α-HYDROXY KETONE UNDER SOLVENT FREE CONDITIONS

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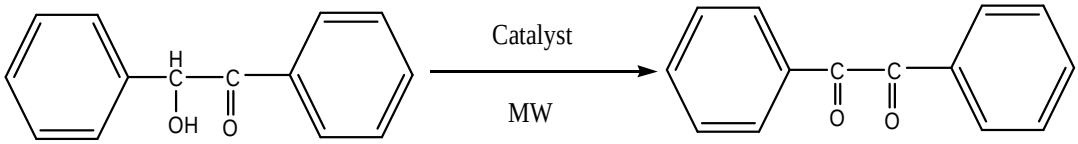
ABSTRACT

In oxidation of α-Hydroxy ketone the conversation of activated hydroxyl group to carbonyl is one of importantmethod of preparation of benzils. The use of microwave for the oxidation of benzoins under solvent-free conditions result benzil in high yield, short reaction time and without use toxic oxidant agents.

Keywords: Benzoins; benzyls and Microwave.

INTRODUCTION

Benzils have gotten a lot of considerationin organic chemistry because it can be used as photosensitive, synthetic reagents , photo initiators for radical polymerization, and for the preparation of a variety heterocyclic compounds, many of which are show a diversity of interesting in pharmaceutical chemistry such as: 5,5-diphenylhydantoin[2], pyrazine derivatives[3].The oxidation of benzoins to benzils has been accomplishedby a variety of reagents such as TTN (thallium (III) nitrate) [McKillop et al., 1973], nitric acid[4], bismuth nitrate—copper acetate[5], Clayfen/n-C_6H_{14}[6], bismuth oxide and bismuth nitrate, iron (II) thiolate, oxone, etc. Many of these reagents limited used for oxidation of benzoins because its highly toxic, and contain toxic metallic compounds that produce unwanted materials. In resent year microwave irradiation and supported reagents are used for oxidation reaction of benzoin to benzil (Scheme.1), these reaction have low time of reaction, high yield and free solvent conditions[7].



Scheme 1: Oxidation of benzoin reaction

Typical procedures for the oxidation of benzoins to benzils under MW

1. The benzoin (2.33 mmol), N-bromosuccinimide (4.67 mmol) and (1.5g) neutral Al_2O_3were blended in a porcelain mortar for 10 min. The subsequent homogenized solid was exchanged to a 50 mL beaker. The beaker was submerged in a neutral Al_2O_3 bath and irradiated in microwave oven (using 100% of 900 W) for (2.5 min). when the reaction was completed the mixture cooled and the solid was extracted with ethyl acetate. The combined ethyl acetate extract was dried over anhydrous $MgSO_4$, filtered, and vanished on a Büchi evaporator. After drying under vacuum[8].
2. Benzoin (0.05g) was added to (0.5g, 1:10 w/w) Al_2O_3 or SiO_2, mixed and homogenized in a mortar. The reaction mixture was irradiated under microwave oven for (10 min). Upon completion of the reactions the mixture was washed with a few mL of CH_2Cl_2 the benzilwas filtered, evaporated and purified by column chromatography[9].
3. Benzoin (1mmol) and $CuSO_4$-Al_2O_3 (1.5g, 0.85mmol of $CuSO_4.5H_2O$) or oxone (2.5 mmol) were mixed by using pestle and mortar. The reaction mixture contained in glass tube was placed in alumina bath inside microwave oven and irradiated for (2min). On complete of the reaction the product was extracted in to methylene chloride and recrystallization from an appropriate solvent to afford nearly quantitative yield of benzil[10].
4. In a 100 mL beaker covered with watch glasses, benzoin (7 mmol) and (5 g) of claycop or clayfen were mixed. The mixture was irradiated in microwave irradiation at (500W) for (3 min) when used claycop and at (300W) for (10min) when used clayfen. When the reaction was completed the beaker of the reaction was allowed to cool to room temperature. The products were extracted by washing the solid support with ethanol, filtered and the solvent was removed under vacuum. The product was recrystallized with CCl_4 to give benzil[11].
5. 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 (2 min). The product was extracted and the product was recrystallized from ethanol[12].
6. A mixture of benzoin (1.0mmol), sodium nitrate (0.085g, 1.0mmol), and p-toluenesulfonic acid monohydrate (0.380g, 2.0 mmol) was thoroughly mixed with 2 mL of acetonitrile. After evaporation of acetonitrile, the residue was placed in a 50 mL of glass tube and the reaction mixture was inserted in an alumina bath inside a domestic microwave oven and irradiated (850 W) one to ten times for a period of 30 sec with 10 sec intervals. After completion of the reaction, the product was extracted and washed. The organic layer was dried with $MgSO_4$ and concentrated in vacuo. Purification of residue with silica gel flash column chromatography[13].
7. One gram silica gel was added to the solution of (1 mmol) of an appropriate benzoin and (0.4g) $Bi(NO_3)_3.5H_2O$ in CH_2Cl_2 (5ml) at room temperature. The reaction mixture was thoroughly mixed, and the adsorbed material was dried and placed in the microwave oven operating at medium to high power for (1 min), Then the resulting crude product was extracted with (3×20 cm^3) of CH_2Cl_2. The solvent was evaporated. The residue was recrystallized from ethanol to give pure benzil[14].
8. A powdered mixture of the oxidant was prepared by grinding (10 mmol) of $KMnO_4$ with(10mmol) of $CuSO_4.5H_2O$ until the complete homogenization. Benzoin (1mmol) and the oxidant mixture were placed in a closed glass container. The mixture was submitted to microwave irradiation at (300W) for (21 min). The product was extracted by washing with dichloromethane. The organic layer was dried with $MgSO_4$, filtered and the solvent was removed under vacuum. The product was recrystallized with CCl_4[15].
9. (4 g) crude benzoin mixed with (20 ml) conc. HNO_3 was taken in a RBF and the mixture was irradiated in microwave oven at 80 ^{0}C temperature and (155 W) for (2 min 30 s). The reaction mixture was poured into

(50 ml) cold water for complete crystallization. A solid obtained was later recrystallized from ethanol to obtain the pure benzil[16].

10. Alumina (2.5 g) and calcium hypochlorite (143 mg, 1 mmol, 1.0 equivalents) were mixed thoroughly in a mortar. Then the benzoin (2 mmol) and H_2O (36 mg, 2 mmol) were added and mixed well. The reaction mixture was transferred to a 25 cm^3 beaker and irradiated in a conventional microwave oven (900 W) for 75 min. The reaction mixture was extracted with (20 ml) diethyl ether . The combined organic extracts were dried over Na_2SO_4, and the solvent was removed with a rotary evaporator[17].
11. Benzoin (2 mmol) and zeolite A (2 g) were mixed thoroughly in a mortar and the mixture was transferred to a beaker and irradiated in microwave oven for 6 min. The mixture was extracted into methylene chloride and then filtered. The solvent was removed under reduced pressure to afford pure benzil. Further purification was carried out by column chromatography (CH_2Cl_2-light petroleum, 80:20, v/v) and crystallization in EtOH[18].
12. Benzoin (1mmol) and $Fe(NO_3)_3{\cdot}9H_2O$ (1g) was mixed thoroughly and then irradiated in a microwave oven for 0.5–1 min. Acetone (10mL) was added to the crude mixture, then mixed thoroughly. After that, 30 mL of cold water was added and faint yellow products were precipitated. The products were isolated by filtration, recrystallized with methanol, and dried under vacuum[19].

RESULT AND DISCUSSION

Microwave heating is playing important rule in organic synthesis. The main advantages of the oxidation reaction of benzoin to benzyl under microwave irradiation are: high yield and the by-products are minimum, rapid oxidation, use free solvent conditions and ability to replace the toxic oxidizing agents with mild, inexpensive oxidants.

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