

Microwave assisted solvent free oxidation of hydrobenzoins, benzoins and alcohols with NBS - Al₂O₃

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Abstract

A simple and efficient protocol for microwave-assisted solvent-free oxidation of hydrobenzoins to benzoins or benzils, benzoins to benzils, and alcohols to the corresponding aldehydes or ketones, using *N*-bromosuccinimide – neutral alumina is reported.

Keywords: Oxidation, carbonyl compounds, diols, hydrobenzoins, microwave irradiation.

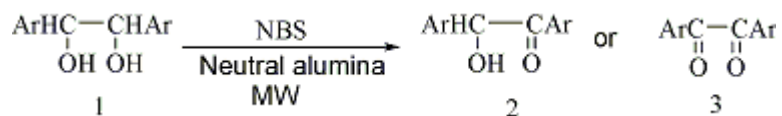
Introduction

Oxidation of alcohols to the carbonyl moiety can be achieved by an array of reagents.¹ Recently other reagents e.g., cobalt(II) complexes,² *m*-iodosylbenzoic acid/RuCl₃,³ IBX/*n*-Bu₄N⁺Br⁻/CH₂Cl₂-H₂O,⁴ DABCO/Br₂,⁵ DMSO/N₂H₄.H₂O/I₂/H₂O/CH₃CN,⁶ have also been reported. Hydrobenzoins and benzoins have also been oxidized with Bi(NO₃)-Cu(OAc)₂,⁷ RuCl₃/Bromamine-T,⁸ the Burgess reagent,⁹ NBS/CCl₄/pyridine,¹⁰ etc. Many of these reagents lack generality for oxidation of alcohols, benzoins and hydrobenzoins, besides being expensive, and giving low yields and undesirable side products. Microwave-assisted solvent-free chemical reactions on inorganic solid supports have drawn attention recently.¹¹ NBS is an economical and convenient oxidant and has been used in a variety of oxidation reactions.^{10,12} We have investigated the oxidation of hydrobenzoins, benzoins and alcohols with NBS–Al₂O₃ in solvent-free conditions expedited by microwave irradiation.

Results and Discussion

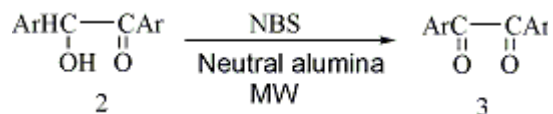
We report herein a simple and efficient solvent-free protocol for the microwave- accelerated oxidation of hydrobenzoins, benzoins and alcohols with *N*-bromosuccinimide–neutral alumina. The reaction conditions were optimized by carrying out reactions of hydrobenzoin (**1a**) as a model substrate and changing the molar ratios of NBS and Al₂O₃ besides variable microwave

irradiation. It was observed that hydrobenzoin (**1a**) could be selectively oxidized to give benzoin (99 %) when exposed to microwaves for 20 sec or to give benzil (**3a**) in quantitative yields when exposed to microwaves for 2 min using a 1:2 molar ratio of **1a**: NBS and a 1:3 w/w ratio of **1a**: neutral Al₂O₃. Other hydrobenzoin, namely *p,p'*-dichlorohydrobenzoin (**1b**) and *o,o'*-dichlorohydrobenzoin (**1c**) could also be oxidized selectively under these reaction conditions (Scheme 1).

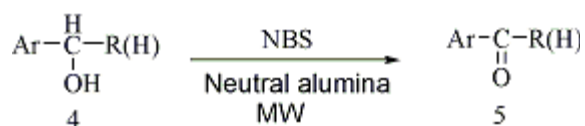


Scheme 1

Similarly, benzoin (**2**) could be quantitatively oxidized to the corresponding benzil (**3**) with NBS–Al₂O₃ when exposed to microwaves (Scheme 2). Both primary and secondary alcohols (**4**) underwent oxidation under these conditions to give the corresponding aldehydes or ketones (**5**) in quantitative yields (Scheme 3). Aldehydes obtained from primary alcohols did not undergo subsequent oxidation to give carboxylic acids, as has been confirmed by an independent reaction. The reactions were clean and rapid and atom economy was observed. The oxidations were complete in 20 sec – 6 min of microwave exposure. These results are summarized in Table 1.

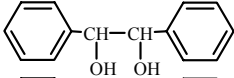
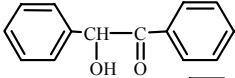
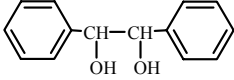
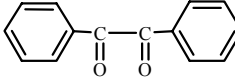
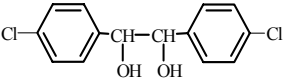
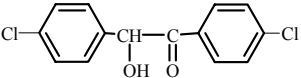
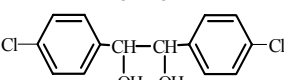
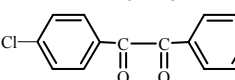
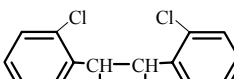
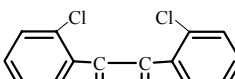
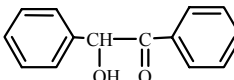
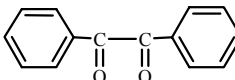
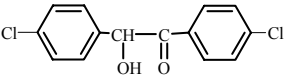
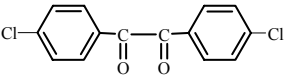
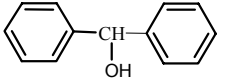
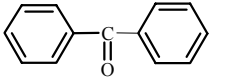
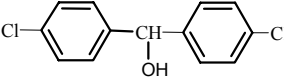
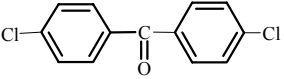
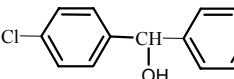
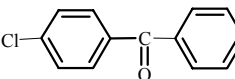
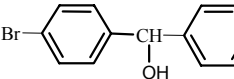
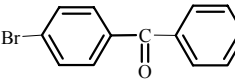
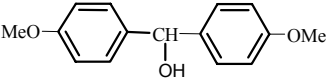
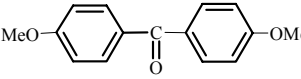
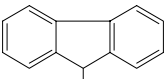
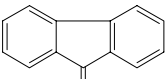
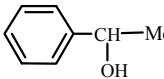
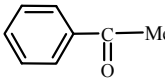
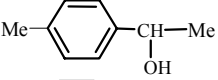
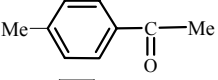
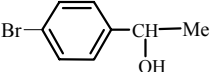
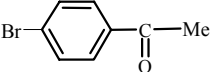


Scheme 2



Scheme 3

Table 1. Microwave-assisted solvent free oxidation of hydrobenzoin, benzoin and alcohols using NBS–neutral alumina^a

Entry	Substrate (S)	Microwave exposure time	Product	Yield (%)
1.		20 sec		99
2.		2 min		99
3.		20 sec		99
4.		2.5 min		99
5.		3 min		98
6.		2.5 min		99
7.		2 min		99
8.		2 min		99
9.		6 min		99
10.		2 min		99
11.		4 min		99
12.		2 min		99
13.		2.5 min		99
14.		20 sec		99
15.		30 sec		97
16.		20 sec		97

17.		20 sec		98
18.		1 min		99
19.		30 sec		98
20.		20 sec		96
21.		50 sec		97

^a Substrate: NBS, molar ratio = 1: 2; substrate: neutral Al₂O₃, w/w ratio = 1: 3.

The oxidations were incomplete with lower molar ratios of substrate: NBS. The oxidations were also attempted on other inorganic solid supports such as silica gel, acidic alumina, and basic alumina, but in all these reactions, a mixture of products was obtained. Benzoin and alcohols did not undergo any oxidation with *N*-chlorosuccinimide–alumina (NCS–Al₂O₃) instead of NBS–Al₂O₃ under identical conditions.

Conclusions

We conclude that oxidation of hydrobenzoin, benzoin and alcohols to the corresponding benzoin, benzil, and carbonyl compounds can be achieved by NBS–neutral Al₂O₃ under microwave irradiation. Synergism of the microwave methodology and solvent-free conditions makes this oxidation an attractive and facile synthetic protocol for the oxidation of hydroxyl group.

Experimental Section

General Procedures. All the melting points were recorded on a Tropical Labequip apparatus and are uncorrected. IR spectra were recorded on Perkin-Elmer FT-IR SPECTRUM-2000. NMR spectra were recorded on a Hitachi FT-NMR model R-600 (60 MHz) with TMS as internal standard. The products were identified by co-TLC, m.p., mixed m.p. (wherever applicable), IR and NMR spectra.

General experimental procedure. In a typical procedure, the hydrobenzoin (0.5 g, 2.33 mmol), *N*-bromosuccinimide (0.83 g, 4.67 mmol) and neutral Al₂O₃ (1.5 g) were mixed thoroughly in a

porcelain mortar for 10 min. The resulting homogenized solid was transferred to a 50 mL beaker. The beaker was immersed in a neutral Al_2O_3 bath and irradiated with microwaves in a domestic microwave oven (using 100% of 900W) for 20 sec. The completion of the reaction was monitored by TLC using petroleum: ethyl acetate (90:10, v/v) as eluent. The reaction mixture was cooled and extracted with ethyl acetate (3×10 mL). The combined ethyl acetate extract was dried over anhydrous MgSO_4 , filtered, and evaporated on a Büchi evaporator. After drying under vacuum, a white solid was obtained which was identified as benzoin by m.p. and spectroscopic data.

Acknowledgements

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