

HEXAMETHYLENETETRAMINE-BROMINE ON WET ALUMINA : RAPID OXIDATION OF ALCOHOLS TO CARBONYL COMPOUNDS IN SOLVENTLESS SYSTEM USING MICROWAVES

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ABSTRACT: *In an environmentally benign solventless system, alcohols are rapidly oxidized to carbonyl compounds using hexamethylenetetramine-bromine on wet alumina under microwave irradiation.*

KEY WORDS: *Alcohol, Oxidation, Microwave assisted, Alumina support, Solventless, hexamethylenetetramine-bromine.*

In recent years, the organic reactions on, solid supports [1,2] and assisted by microwaves [3,4] in particular have gained special attention because of their enhanced selectivity, milder conditions and associated ease of manipulation. In spite of these waves of interest, oxidation reactions are less considered under the microwave irradiation due to unsafe and uncontrollable experimental conditions [5].

The oxidation of alcoholic group to a carbonyl functionality is an important reaction in organic synthesis and several methods are available to accomplish this conversion under a variety of reaction conditions [6-9].

In continuation of our ongoing program to develop environmentally benign reactions using solid acids [10] and under solvent free conditions using microwaves [11] we explored the oxidation of neat alcohols

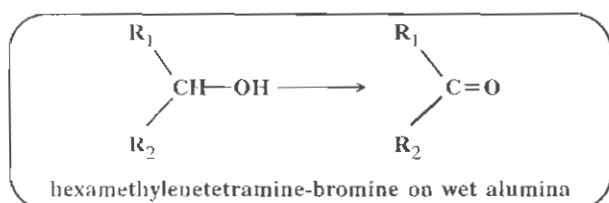
with wet alumina supported hexamethylenetetramine-bromine that results in rapid formation of syrupy thick liquids upon exposure to microwaves with rapid consumption of the starting alcohols. The analysis of the products obtained after work up revealed the formation of carbonyl compounds.

The hexamethylenetetramine-bromine complex was prepared by addition of bromine to a chloroform solution of amine following the reported procedure [12]. This reagent in an aprotic solvent that oxidizes primary and secondary alcohols. However, under inert atmosphere these reactions require 0.4-4 h for completion [12]. To work in a solventless system we mixed the above reagent with neat alcohol and observed a very sluggish conversion. To decrease the time of reaction the above mixture was placed under microwave irradiation but partial decomposition of the

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reagent was observed. Moreover, the isolation of products from the ensuing residue rendered difficult and the oxidation was accompanied by the formation of minor contaminants. In view of our earlier success of MW reactions on solid supports [11] which normally afford cleaner products, we examined various mineral supports such as clay, silica and alumina and found that wet alumina provides the best result in terms of pure products. Also the yields obtained are comparable to those reported for related reaction [12]. We discovered that the reactions with dry alumina are slow in the absence of moisture and considerable amounts of alcohols remain unchanged.

Wet alumina was prepared by shaking neutral aluminium oxide with distilled water. The reagent was prepared by mixing hexamethylenetetramine-bromine with wet alumina using a pestle and mortar. This reagent oxidizes various alcohols to carbonyl compounds under microwave irradiation almost immediately (Table 1). No overoxidation to carboxylic acids observed in the case of primary alcohols. Cinammyl alcohol was converted to cinammyl aldehyde showing carbon-carbon double bonds are not prone to cleavage with this method.



EXPERIMENTAL

products were characterized by GLC and by direct comparison with authentic samples. Yields are based on GLC analysis. Hexamethylenetetramine-bromine was prepared according to the literature [12].

Preparation of hexamethylenetetramine - bromine supported onto wet alumina

Neutral aluminium oxide (13.8 g, Aldrich, Brockmann I \approx 150 mesh) was shaken with distilled water (3 mL). To this mixture hexamethylenetetramine-bromine (4.6 g, 10 mmol) was added and mixed using a pestle and mortar to give an intimate mixture.

Oxidation of benzyl alcohol, Typical procedure

Benzyl alcohol (0.108 g, 1 mmol) was added to the above supported reagent (0.92 g) in a beaker using a spatula. The beaker was placed in a household microwave oven (National) at 900 W for the time indicated in Table 1. The crude was taken on CH_2Cl_2 and filtered. The solvent was evaporated to dryness and the crude passed through a pad of silica gel using hexane, EtOAc, 8:2 to afford pure benzaldehyde.

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Table 1: Oxidation of alcohols to carbonyl compounds by hexamethylene tetramine- Br_2 supported onto wet alumina under microwave irradiation.

Alcohol	Time (Sec)	Product	Yield
Benzyl alcohol	20	Benzaldehyde	96
4-Methylbenzyl alcohol	20	4-Methylbenzaldehyde	96
2-Methyl-5-nitrobenzyl alcohol	20	2-Methyl-5-nitrobenzaldehyde	95
Benzhydrol	30	Benzophenone	92
Benzoin	30	Benzil	93
Cyclohexanol	60	Cyclohexanone	90
2-Ethylcyclohexanol	60	2-Ethylcyclohexanone	89
1-Octanol	60	Octanal	89
2-Ethylhexanol	60	2-Ethylhexanal	88
Menthol	60	Menthone	80

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