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Microwaves-promoted Kornblum oxidation of benzyl halides to benzaldehydes using Mg-Al hydrotalcite as catalyst

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ABSTRACT

Microwaves were found to accelerate the Kornblum oxidation of benzyl halides to benzaldehydes using DMSO in the presence of Mg-Al hydrotalcite (Mg/Al = 3) as a heterogeneous basic catalysts.

Keywords: Benzyl halides, Aldehydes, Hydrotalcite, Dimethyl sulfoxide, Kornblum oxidation, Microwaves.

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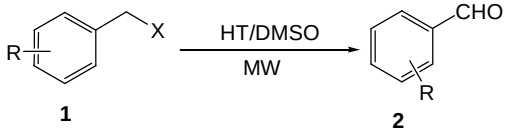
INTRODUCTION

Oxidation of primary halides to aldehydes is well known transformation in organic synthesis [1]. The most convergent and well establish classical approach for the preparation of aldehydes is Kornblum oxidation [2]. In Kornblum reaction, a benzyl halide is refluxed in DMSO along with a base, like sodium bicarbonate to give the corresponding aldehyde.

Recently, we have reported catalysis of Kornblum oxidation using heterogeneous Mg-Al Hydrotalcite [3]. In this case, special advantages were that, good yield of product as compared to the classical catalysts, operational simplicity and reusability of catalyst. The limitation of the methodology was long reaction time, which was needed for the complete consumption of the reactants. To reduce the reaction time substantially we thought of using microwaves.

Microwaves have been employed in organic chemistry to reduce the reaction time from hours to minutes and to increase the yield and selectivity [4]. Recently, the Kornblum oxidation has been attempted under microwave irradiation, using classical catalysts such as $NaHCO_3$, Na_2CO_3, K_2CO_3, KH_2PO_4, and K_3PO_4 [5]. Heterogeneous catalysts have often been proved to be advantages over classical catalysts, because of their unique properties such as reusability, ease of handling and environmentally friendliness. To couple the advantages of heterogeneous catalysts with microwaves acceleration, we investigated Kornblum oxidation of benzyl chlorides to benzaldehydes in the presence of Mg-Al hydrotalcite in the presence of microwaves. (Scheme 1).

A series of benzyl halides was reacted with DMSO in the presence of Mg-Al HT (Mg/Al = 3) as heterogeneous basic catalyst. The reaction was studied both under microwave irradiation as well as conventional heating (Table 1). The striking feature was that the reaction under microwave irradiation was considerably accelerated as compared to that under classical conditions using bases like NaOH, $NaHCO_3$, Na_2CO_3, and K_2CO_3, as well as the one using HT without microwaves. Time of microwave reaction was optimized for 100 % conversion of benzyl halides.



1 **2**

R = X, NO_2, OMe

Scheme 1

In conclusion, the present study is the first application of hydrotalcite as heterogeneous catalysts for the Kornblum oxidation of benzyl halides under microwave irradiation. This method offers a very efficient and convenient modification to Kornblum oxidation.

EXPERIMENTAL

Biotage monomode microwave reactor was used. The Mg-Al hydrotalcite (Mg/Al = 3) was prepared by the reported procedure [6].

Typical reaction procedure

Benzyl chloride (0.252 g, 2 mmol), Mg-Al HT (0.1 g, 40 % w/w of benzyl chloride) and dimethyl sulfoxide (DMSO) (1 ml) were taken in the microwave vial. The solution was subjected to microwave irradiation at 140 °C for appropriate time. The solution was allowed to cool at room temperature, filtered and the catalyst was washed with ethyl acetate (2 x 5 mL). Distilled water (10 mL) was added to the filtrate to remove the un-

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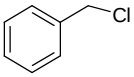
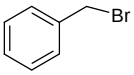
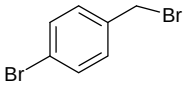
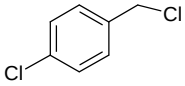
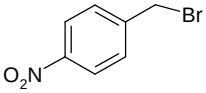
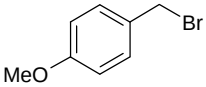
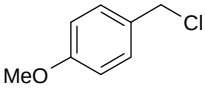
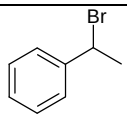
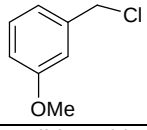
reacted dimethyl sulfoxide. The ethyl acetate layer was dried on anhydrous Na_2SO_4 and concentrated under reduced pressure. The product was purified by column chromatography on silica gel (60-120 mesh) using pet-ether (60 – 80 °C) as an eluent.

Table1. Mg-Al hydrotalcite catalyzed conversion of benzyl halides to benzaldehydes

Entry	Substrate	Yield of benzaldehydes (%)	
		Microwave [a] (min)	Conventional [b] (h)
1		83(20)	80 (10)
2		87(15)	82 (6)
3		90(10)	78(3.5)
4		94(10)	89 (3)
5		77(20)	70 (15)
6		94(5)	92 (1)
7		97(5)	96 (1.5)
8		61(30)	60 (12)
9		88(20)	80 (7)

Reaction conditions: (a) Benzyl halide (2 mmol); DMSO (1 ml); HT 40% w/w of benzyl halide; temperature: 140 °C. The products were characterized by GC-MS and FT-IR. a- microwave irradiation; b- conventional heating.

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