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Mg–Al hydrotalcites as the first heterogeneous basic catalysts for the Kornblum oxidation of benzyl halides to benzaldehydes using DMSO

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Abstract

Mg–Al hydrotalcites (Mg/Al = 2, 3, 5) act as efficient heterogeneous base catalysts for the conversion of benzyl halides to the corresponding benzaldehydes using DMSO as an oxidant.

Keywords: Benzyl halides; Aldehydes; Hydrotalcite; Dimethyl sulfoxide

1. Introduction

Aromatic aldehydes can be prepared by the direct introduction of a formyl group onto an aromatic nucleus through reactions such as the Gatterman–Koch reaction,[1] the Reimer–Tiemann reaction[2] and the Vilsmeier reaction.[3] Moreover, the formyl group can be generated from an appropriate precursor group such as a hydroxymethyl, an acid chloride, a halomethyl or a methyl group, attached to the aromatic ring. However, the preparation of aromatic aldehydes from benzyl alcohols can be difficult, due to over-oxidation. The conversion of primary halides into aldehydes is a well-known method in organic synthesis although the oxidation of aliphatic halides to aldehydes is far more difficult than the oxidation of benzylic halides.

Benzylic halides can be prepared easily through the photohalogenation of aromatic methyl groups[4] or by the Blanc chloromethylation reaction.[5] The preparation of aromatic aldehydes from benzylic halides, therefore, is an attractive route to aromatic aldehydes and several methods have been developed to carry out this conversion. One reaction is the Sommelet reaction using hexamine as a reagent.[6] In this process, the first step is the reaction of hexamine with the alkyl halide to form a quaternary salt, which on hydrolysis gives a primary amine, formaldehyde and ammonia (the Delepine reaction). The primary amine on reaction with the aldimine, derived from formaldehyde and ammonia, forms the corresponding aromatic aldimine, which on hydrolysis gives the aldehyde. This reaction is generally possible with active halides such as benzylic halides, allylic halides, α-halo ketones and primary iodides.[7]

Reagents that convert benzyl halides to benzaldehydes include 2-nitropropane–NaOEt in EtOH,[8] mercury-ethanolic alkali,[9] pyridine followed by *p*-nitrosodimethylaniline and water (the Krohnke reaction),[10] $NaIO_4$–DMF[11] and IBX.[12] Primary halides can also be oxidized to aldehydes using trimethylamine oxide,[13] 4-dimethylaminopyridine-N-oxide,[14] other amine oxides,[15] pyridine N-oxide under microwave irradiation[16] and K_2CrO_4 in HMPA in the presence of a crown ether.[17]

It is known that DMSO acts as a good oxidizing agent in many organic transformations.[18] In the Kornblum reaction, benzyl halides are refluxed in DMSO along with sodium bicarbonate to give the corresponding aldehydes.[19] In this reaction, the nucleophilic oxyanion of DMSO attacks the benzylic halide in an S_N2 reaction and displaces the halide to form an alkoxysulfonium salt. The base often

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abstracts a benzylic proton to form the aldehyde. The reaction has recently been attempted under microwave irradiation.[20]

Heterogeneous catalysts, with stable and well-defined surface active sites, are currently receiving considerable attention because of their unique properties such as reusability, ease of handling and separation with their environmental friendliness. Hydrotalcites (HTs) possess strong surface basicity and are useful catalysts for selective oxidation reactions. HTs and modified HTs have been used for epoxidation of olefins and α,β unsaturated ketones using hydrogen peroxide,[21,22] oxidation of alcohols[23] and Bayer–Villager reaction using peracids.[24]

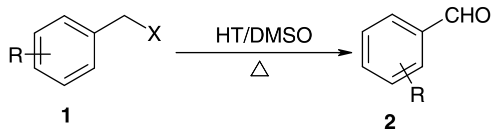
In the present Letter, we describe the use of Mg–Al hydrotalcites (varying mole ratio of Mg and Al) as heterogeneous catalysts for the oxidation of benzyl halides **1** to benzaldehydes **2** using DMSO. This is the first report of Kornblum reaction, using a heterogeneous catalyst (Scheme 1).

Mg–Al hydrotalcites with a Mg/Al mole ratio of 2, 3 and 5 were prepared by the reported procedures[25] and were characterized by XRD and FT-IR. From their XRD spectra, it was seen that the basal spacing at 7.87 Å corresponded to the HT phase. In the FT-IR of Mg/Al hydrotalcite, the absorption at 3581 cm^{-1} corresponded to the H-bonding stretching vibration of the OH group in the brucite layer. A shoulder present at around 3000 cm^{-1} was due to the H-bonding between H_2O and the anions in the interlayer.

The conversion of benzyl chloride to benzaldehyde was taken as a model reaction for optimization. The reaction was carried out at different temperatures. It was found that with increase in reaction temperature above 140 °C, there was a decrease in selectivity, whilst with a decrease in temperature (140–80 °C) the rate of reaction decreased.

The reaction was carried out using different HTs as well as classical bases at 140 °C (Table 1). The uncalcined HTs (Mg/Al = 2, 3, 5) gave better yields as compared to the classical catalysts. The reaction with sodium hydroxide resulted in the formation of dibenzyl ether and benzoic acid as a side products, whilst with sodium carbonate, benzyl alcohol was the major product. In the presence of sodium bicarbonate, the reaction was sluggish.

The Lewis basicity of hydrotalcite increases, whilst the Bronsted basicity decreases on calcination at high temperature. The catalytic activity of calcined HT was lower than that of the corresponding uncalcined hydrotalcite (entry 8). The reaction did not take place in the absence of hydrotalcite (entry 9). For further reaction the $Mg_6Al_2(OH)_{24}CO_3$ HT was used.



R = X, NO_2, OMe

Scheme 1.

Table 1
Conversion of benzyl chloride to benzaldehyde catalyzed by different bases

Sr. no.	Catalyst	Yield (%)
1	$Mg_{10}Al_2(OH)_{24}CO_3$	74
2	$Mg_6Al_2(OH)_{24}CO_3$	80
3	$Mg_4Al_2(OH)_{24}CO_3$	78
4	MgO	40
5	NaOH	30
6	Na_2CO_3	10
7	$NaHCO_3$	54
8[a]	$Mg_6Al_2(OH)_{24}CO_3$	45
9	Without catalyst	NR

Reaction conditions: Benzyl chloride (10 mmol); DMSO (2 ml); HT 40% w/w of benzyl halide; temperature: 140 °C; time: 10 h; NR: no reaction.

[a] Hydrotalcite calcined at 450 °C.

The hydrotalcite is a heterogeneous catalyst and could easily be separated from reaction mixture by filtration. The recovered catalyst was used for successive runs to test its reusability (Table 2). Under the optimized conditions, various benzyl halides were reacted with DMSO to obtain the corresponding benzaldehydes (Table 3). Simple aliphatic halides, for example, propyl bromide and octyl chloride, did not undergo the oxidation under these conditions.

In the present scheme, we are not using any separate oxidizing agent such as hydrogen peroxide, peracid, periodate and IBX, but the DMSO was used in excess.

In conclusion, HT and DMSO provide an effective combination for the oxidation of benzylic halides to benzaldehydes.

2. Experimental

2.1. Preparation of Mg/Al hydrotalcite

The Mg/Al hydrotalcites were prepared by the reported procedure.[25]

2.2. Typical reaction procedure

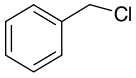
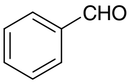
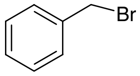
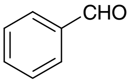
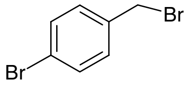
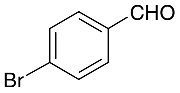
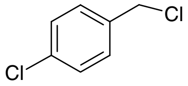
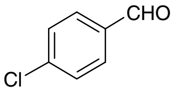
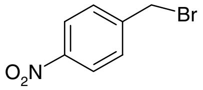
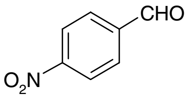
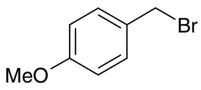
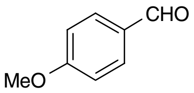
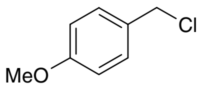
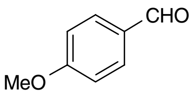
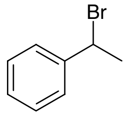
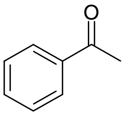
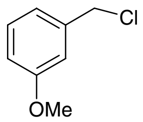
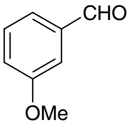
To a 100 ml two-neck round-bottomed flask, fitted with a water condenser, benzyl chloride (1.26 g, 10 mmol), Mg–Al HT (0.50 g, 40% w/w of benzyl chloride) and dimethyl sulfoxide (DMSO) (2 ml) were added and the solution

Table 2
The reusability of $Mg_6Al_2(OH)_{24}CO_3$HT in the reaction of benzyl chloride with DMSO

Run	Yield of **2** (%)
1	80
2	77
3	77
4	74

Reaction conditions: Benzyl chloride (10 mmol); DMSO (2 ml); HT 40% w/w of benzyl halide; temperature: 140 °C; time: 10 h.

Table 3
Mg–Al hydrotalcite catalyzed conversion of benzyl halides to benzaldehydes

Sr. no.	Substrate	Product	Time (h)	Yield (%)
1			10	80
2			6	82
3			3.5	78
4			3	89
5			15	70
6			1	92
7			1.5	96
8			12	60
9			7	80

Reaction condition: Benzylic halide (10 mmol); DMSO (2 ml); HT 40% w/w of benzylic halide; temperature: 140 °C. The products were characterized by GC–MS and FT-IR.

heated at 140 °C for 10 h and the reaction was monitored by TLC. The solution was cooled to room temperature, filtered and the catalyst was washed with ethyl acetate (2 × 5 ml). Distilled water (20 ml) was added to the filtrate. The ethyl acetate layer was concentrated under reduced pressure and the product purified by column chromatography on silica gel (60–120 mesh).

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