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Short Communication

Debenzylation by Ni–Al alloy

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Abstract

Nickel-aluminum alloy in aqueous sodium hydroxide-ethanol medium brings about facile hydrogenolysis of benzyl ether function in substrates carrying a vicinal methoxy group. Simplicity of the reaction conditions and cheapness of the reagent are some of the advantages of the procedure. *Additionally, carbonyl functions when present are untouched and alkaline medium of the reaction* makes it compatible with the presence of acid-sensitive groups.

Key words : Ni-Al alloy, benzyl ether cleavage, hydrogenolysis, debenzylation.

1. Introduction

Introduced by Schwenk and co-workers[1–6] nickel-aluminium alloy[7] (1 : 1) in aqueous alkali has proved to be quite useful in several reduction reactions because of cheapness of the reagent and operational simplicity of the reaction. α, β-Unsaturated acids with[5, 8, 9] and without[5, 6, 10, 11] aryl substitution, γ-aryl-β, γ-unsaturated acids[12–15] chlorinated polyene acids[16] and neutral substrates like benzyl alcohols[2], aldehydes and ketones[2, 6, 17], aromatic halides[4, 18], nitroaromatics[3], oximes[19] and nitriles[20] have been reduced by Ni–Al alloy essentially under aqueous conditions. Displacement of some groups (sulphonic acid and alkoxy groups) was also encountered in some cases[4].

2. Discussion

Our recent finding of facile hydrogenolysis of benzyl ethers with vicinal methoxy function constitutes a useful addition to the above list of applications of Ni–Al alloy in

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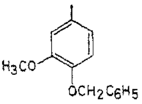
organic synthesis. Thus 3-methoxy-4-benzyloxytoluene (I), 3-methoxy-4-bezyloxybenzaldehyde (II) and 3-(2′-methyl-4′-methoxy-5′-benzyloxybenzoyl) propanoic acid (III) underwent debenzylation in excellent yield on stirring with Ni–Al alloy powder in ethanolic sodium hydroxide to afford the corresponding hydrogenolysis products IV, V and VI respectively. The hydrogenolysis of compounds II and III is particularly noteworthy in that the carbonyl functions are left in tact, whereas literature records reduction of the carbonyl group, in most cases, to the carbinol or to the methylene stage, depending on reaction temperature[2, 6, 17].

Recently Kametani *et al*[21] reported cleavage of benzyl ethers with sodium bis (2-methoxyethoxy) aluminium hydride in refluxing xylene. Thus benzyl vanillin afforded (i) a mixture of the phenol (IV) and the alcohol (VII) (reaction time 6 hr) and (ii) exclusively the phenol (IV) (reaction time 10 hr), the aldehyde function in either case reduced partially or completely depending on the length of time of the reaction. On the other-hand Ni–Al alloy, as found by us, does not reduce the carbonyl function while cleaving the benzyl ether (II → V; III → VI). However, as observed by Kametani *et al*[21], a vicinal methoxy function appears to be essential for debenzylation in the case of Ni–Al alloy too, as shown by the complete recovery of 4-benzyloxytoluene under identical experimental conditions. Subject to this limitation, Ni–Al alloy seems to score an advantage over some of the alternate catalytic[22], metal hydride[23], and alkoxy metal hydride[21] debenzylation techniques, as the reagent (Ni–Al alloy) is accessible even to a low-budget laboratory. It also demands no special handling (except for keeping the pyrophoric nickel wet till disposal) and storage precautions and the reaction is conducted in alkaline aqueous ethanolic medium, compatible with acid sensitive functions.



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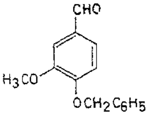

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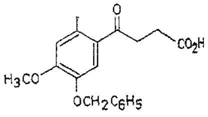

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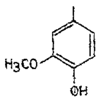

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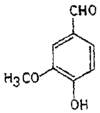

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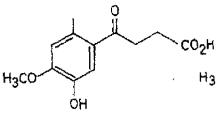

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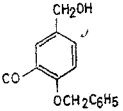

VII

3. Typical experimental procedure

To a solution of the benzyl ether (I/II/III) (0·01 mol) dissolved in ethanolic sodium hydroxide [NaOH (1 g) dissolved in minimum amount of water and the volume made up to 10 ml with ethanol] and maintained at gentle reflux, Ni–Al alloy powder (1 : 1, 1 g) was added under stirring in small lots, keeping the frothing under control by adjusting the rate of addition of the alloy. After completion of addition, the reaction mixture was stirred for 6 hr, allowed to cool and the nickel was filtered off, taking care to see that it is maintained wet. Most of the ethanol from the filtrate was distilled off under suction and the residue was acidified with dilute hydrochloric acid (1 : 1). The product was thoroughly extracted with ether and the extract was washed with brine and dried over anhydrous sodium sulphate. Removal of solvent furnished the debenzylated products IV (95%), V (60%), VI (95%) yield, identified by L.I. and spectral comparison (i.r. and p.m.r.) with authentic materials[11].

4. Acknowledgement

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