

Oxidative Removal of Acetal Protection by the Action of KHSO_5 and AlCl_3 under Mild Heterogeneous Conditions*

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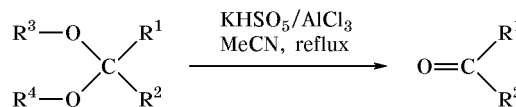
Received January 23, 2002

Protection [1] and deprotection [2] of carbonyl functionalities are key problems in organic chemistry. Numerous methods for removal of acetal protection are known. These are based mostly on acid-hydrolysis of the acetal moiety in aqueous medium [3]. Less common nonaqueous procedures utilize phosphorus triiodide and diphosphorus tetraiodide [4], iodotrimethylsilane [5], chlorotrimethylsilane-sodium iodide [6], K10 montmorillonite [7], cobalt and manganese salts in the presence of oxygen [8], cerium(III) chloride [9], triphenylphosphine and CBr_4 [10], as well as oxidative systems, e.g. cerium ammonium nitrate [11], $\text{Fe}(\text{NO}_3)_3 \cdot 1.5\text{N}_2\text{O}_4$ [2], and $\text{Cu}(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4$ [2]. We recently showed that heterogeneous systems are considerably more advantageous than homogeneous, for they are characterized by experimental simplicity, mild reaction conditions, and minimal wastes [12–17]. To our knowledge, Oxone (potassium peroxymonosulfate, $\text{KHSO}_4 \cdot 2\text{KHSO}_5 \cdot \text{K}_2\text{SO}_4$, $\text{p}K_a \sim 1$) is a widely used oxidant [18] which has never been applied to deprotect acetals.

In the present work various acetals (compounds **Ia–Ik**, see table) were subjected to deacetalization in the presence of Oxone and AlCl_3 in acetonitrile under reflux. According to the TLC data, the conversion of the initial acetal and the yield of the corresponding carbonyl compound were quantitative.

Deacetalization of compounds **I** was carried out in various solvents, such as acetonitrile, tetrahydrofuran, and methylene chloride. The most appropriate solvent was acetonitrile. We also examined the possibility of catalytic action of Oxone and AlCl_3 or at least

of using them in smaller than stoichiometric amounts. However, high yields of carbonyl compounds were obtained only when the ratio Oxone: AlCl_3 :substrate was 1:3.8:6. Thus we have found that Oxone is an effective reagent ensuring fast removal of acetal protection.



Carbonyl compounds, ethylene glycol, aluminum chloride, and acetonitrile were purchased from Fluka, Merck, and Aldrich. Commercial potassium peroxy-monosulfate was used ($\text{KHSO}_4 \cdot 2\text{KHSO}_5 \cdot \text{K}_2\text{SO}_4$, from Merck). Acetals and 5,5-bis(hydroxymethyl)-2-norbornene were synthesized by the procedure described by us in [1]. The deacetalization products were identified by comparing their spectral (IR and ^1H NMR) and TLC data and physical properties with those of authentic samples.

Deacetalization of compound **Ig to 4-hydroxy-3-methoxybenzaldehyde (typical procedure).** A mixture of 0.07 g (0.25 mmol) of compound **Ig**, 0.3 g of Oxone, and 0.2 g of AlCl_3 in 5 ml of acetonitrile was refluxed for 60 min. The precipitate was filtered off and washed with methylene chloride, and the filtrate was evaporated under reduced pressure. Addition of ethanol and water to the residue gave 4-nitrobenzaldehyde in quantitative yield.

The authors are grateful to the Reserach Departments at the University of Yazd (Yazd, Iran) and Bu-Ali Sina University (Hamadan, Iran) for the financial support of this work.

* The original article was submitted in English.

Deacetalization with Oxone and AlCl_3 in acetonitrile

Comp. no.	Formula	Product	Comp. no.	Formula	Product
Ia			Ig		
Ib			Ih		
Ic			Ii		
Id			Ij		
Ie			Ik		
If					

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