

An Efficient and Selective Solvent-free Oxidation of Alcohols by Shaking with Chromium Trioxide Supported on Aluminium Silicate

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Abstract: A selective oxidation of primary alcohols to the corresponding aldehydes by shaking with chromium trioxide supported on aluminium silicate at room temperature under solvent free conditions is reported. This new procedure can also oxidise secondary alcohols.

Keywords: Alcohols; Oxidation; Chromium trioxide; Solvent free; Shaking.

Introduction

Recently considerable attention has been paid to the solvent free reactions [1]. These are not only of interest from an ecological point of view, but in many cases they also offer considerable synthetic advantages in terms of yields, selectivity and simplicity of the reaction procedures. These factors are especially important in industry. Therefore, some the traditional organic synthetic methods, which have long been carried out in solvents, may be modified to more modern, elegant, and safe versions.

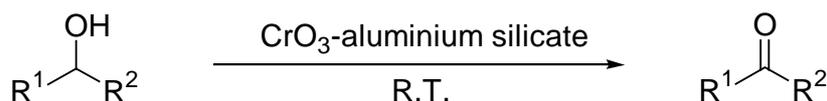
One of the most important reactions of alcohols, which have long been the objective of many research papers, is their oxidation to the corresponding carbonyl compounds. Chromium (VI)-based reagents have been extensively used in organic synthesis [2-4]. The utility of chromium (VI) reagents in the above oxidative transformation is compromised due to their inherent toxicity, cumbersome preparation, and potential danger in terms of product isolation and waste disposal. The introduction of

reagents on solid supports [5] has circumvented some of these problems and provided an attractive alternative in organic synthesis in view of the selectivity and associated ease of manipulation. Therefore, it is not surprising that a large number of chromium (VI)-based oxidants impregnated on solid supports have been explored [6-19], however, almost all of these procedures are performed under heterogeneous conditions, or assisted by microwave irradiation.

Results and Discussion

We have described a new reagent, chromium trioxide (CrO_3) supported on aluminium silicate, for the heterogeneous selective oxidation of primary alcohols [16]. In connection with our recent work [20-22] we now report a novel oxidation of primary alcohols to the corresponding aldehydes using this supported reagent under solvent free conditions by shaking at room temperature without microwave irradiation (Scheme 1). This is the first time a shaking machine has been employed for this reaction, and its performance is very simple. We find that using shaking is much more effective than using a stirrer for this kind of solvent-free reactions. Some previous methods required the reactions to be heated, but in the present work, heating is unnecessary, and the reaction times are also quite reduced.

Scheme 1



The present method has several procedural advantages over heterogeneous oxidations [16], for instance, the reaction conditions are milder, the reaction times are shorter, and the work-ups are easier. In addition, compared to the few existing CrO_3 -based reagents used under solvent free conditions, such as chromium trioxide on wet alumina [23], and chromium trioxide with HZSM-5 zeolite [24], an important benefit of the present method is that there is no need to use microwave irradiation, an additional energy input. Furthermore, owing to the fact that the reaction takes place under solvent free conditions, the risk of combustion, the toxicity, and environmental pollution of solvents are reduced. In addition, the present method has been extended to oxidation of secondary alcohols.

In the present method, a 1.5 to 1 molar ratio of CrO_3 to substrate is employed. First, the oxidant is carefully added to the substrate and the mixture is shaken mechanically at room temperature. The progress of the reaction is monitored by TLC. In general, the oxidations are completed within 60 min. The residue is then washed with dichloromethane or diethyl ether. Purification of the residue gives a product that is of acceptable purity for most purposes. As can be seen in Table 1, this method is generally applicable to a wide range of alcohols, and gives the corresponding aldehydes and ketones in good yields, thus comparing favourably with some traditional CrO_3 -based oxidation methods [25].

Conclusions

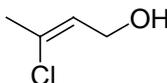
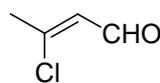
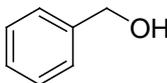
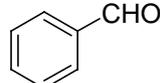
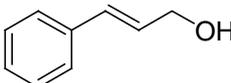
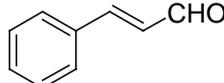
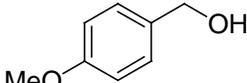
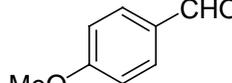
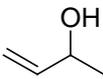
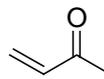
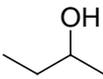
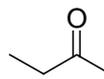
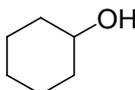
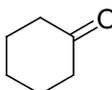
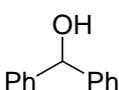
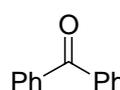
In conclusion, solvent free oxidation of primary and secondary alcohols using CrO_3 supported on aluminium silicate at room temperature by shaking is a new and efficient method for the preparation of corresponding aldehydes and ketones.

Experimental

Typical Procedure: Oxidation of Benzyl Alcohol to Benzaldehyde:

A mixture of benzyl alcohol (108 mg, 1 mmol) and CrO₃-aluminium silicate reagent [16] (750 mg) is shaken mechanically (Horizontal oscillator, Model HY-2, Zhengji Instrument Co. Ltd.) at room temperature for 20 min. The progress of the reaction is monitored by TLC (aluminum-backed silica gel Merck 60 GF₂₅₄ plates) using hexane-ethyl acetate (8:2) as eluent. The reaction mixture is then washed with CH₂Cl₂ (3 × 5 mL). The combined filtrates are evaporated to give crude product, which is purified by preparative TLC (hexane-ethyl acetate 8:2) to afford benzaldehyde (97 mg, 92%).

Table 1. Solvent free oxidation of alcohols with CrO₃ supported on aluminium silicate

Substrate	Reaction time (min)	Product ^a	Yield (%)
<i>n</i> -C ₄ H ₉ -CH ₂ -OH	60	<i>n</i> -C ₄ H ₉ -CHO	65
<i>n</i> -C ₈ H ₁₇ -CH ₂ -OH	60	<i>n</i> -C ₈ H ₁₇ -CHO	72
	30		86
	20		92
	20		90
	20		90
	30		87
	30		80
	40		85
	20		95

^a All the products are known compounds and were identified by comparison of their IR spectra or by the IR spectra and melting points of their 2,4-dinitrophenylhydrazones with literature values [26].

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Sample Availability: Contact the authors.