

Ammonium Chlorochromate Adsorbed on Montmorillonite K-10: Selective Oxidation of Alcohols under Solvent-free Conditions†

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A simple and selective oxidation of alcohols to carbonyl compounds on clay supported ammonium chlorochromate under solventless conditions is expedited by microwave irradiation.

Prompted by stringent environment protection laws in recent years, there has been increasing emphasis on the use and design of environmentally friendly solid acid–base catalysts to reduce the amount of toxic waste and by-products arising from the chemical processes.¹

The oxidation of alcoholic groups to carbonyl functionalities continues to receive attention from chemists in search of newer and selective methods of oxidation.²

Chromium-based reagents have extensively been used in organic synthesis.³ The utility of chromium(vi) reagents in oxidative transformation is compromised due to their inherent toxicity, cumbersome preparation and potential danger (ignition or explosion) in terms of product isolation and waste disposal. Introduction of reagents⁴ on solid supports 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-based oxidants impregnated on solid supports have been explored.⁵ These supported reagents in solvents oxidize primary and secondary alcohols.⁶

Organic solvents are not only expensive, but are often flammable, toxic and environmentally hazardous. Consequently, there is scope for the development of rapid and solventless methods that have manipulative advantages over heterogeneous reactions. In continuation of our investigations on organic reactions in solventless systems,^{7,8} we now report a facile and selective oxidation of alcohols to carbonyl compounds using ammonium chlorochromate adsorbed on montmorillonite K-10 under solvent-free conditions that is accelerated in most cases by exposure to microwaves.

The reagent is easily prepared by addition of a weighed amount of montmorillonite K-10 to a solution of ammonium chlorochromate⁹ in water and rotary evaporating

to dryness. The reaction is conducted by mixing finely ground supported reagent with neat alcohols. In the absence of the clay the reactions are slow and considerable amounts of alcohols are recovered unchanged at room temperature or even upon microwave irradiation for an extended period. As an example the reaction of 5-methyl-2-nitrobenzyl alcohol with ammonium chlorochromate results in the formation of only 30% of 5-methyl-2-nitrobenzaldehyde, whereas the yield increases to almost to quantitative in the case of the clay-supported reagent. In a few cases, the reactions are completed upon simple mixing; gentle warming by microwaves accelerates some others (Table 1). The reactions are relatively clean with no tar formation typical of many CrO₃ reactions.

Primary alcohols were oxidized to the corresponding aldehydes and an overoxidation of aldehydes to the corresponding acid derivative was not observed even after prolonged irradiation and with excess of supported chromium reagent. On the other hand the oxidations of aryl-substituted unsaturated alcohols were less than satisfactory. The carbon–carbon double bond was partially cleaved under the above conditions. Cinnamaldehyde for example was obtained in only 61% yield along with 39% of benzaldehyde in the oxidation of cinnamyl alcohol.

In conclusion, oxidation with ammonium chlorochromate supported on montmorillonite K-10 under solvent-free conditions is a rapid, manipulatively simple and selective protocol which avoids the drastic conditions usually employed.

Experimental

All products are known compounds and their physical data were essentially identical with those of authentic samples. Microwave irradiations were carried out in a National oven, Model 5250 at 900 W.

Table 1 Oxidation of alcohols to carbonyl compounds using ammonium chlorochromate adsorbed on montmorillonite K-10

Entry	Alcohol	Product	Yield (%) ^a
1	Benzyl	Benzaldehyde	92 (85)
2	4-Methylbenzyl	4-Methylbenzaldehyde	93 (85)
3 ^b	5-Methyl-2-nitrobenzyl	5-Methyl-2-nitrobenzaldehyde	90 (81)
4 ^b	4-Nitrobenzyl	4-Nitrobenzaldehyde	95 (83)
5 ^b	Salicyl	Salicylaldehyde	95 (82)
6	α -Phenylethyl	Acetophenone	94 (88)
7	Benzhydrol	Benzophenone	90 (81)
8 ^b	Benzoin	Benzil	90 (80)
10 ^b	Cyclohexanol	Cyclohexanone	88 (72)
11 ^b	2-Methylcyclohexanol	2-Methylcyclohexanone	85 (75)
12 ^b	(–)-Menthol	Menthone	85 (74)

^aYields are based on GLC analysis; figures in parentheses refer to isolated yields. ^bReaction completed under microwave irradiation.

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Preparation of Ammonium Chlorochromate/Montmorillonite K-10.—To a solution of chromium trioxide (40 g, 0.4 mol) in water (100 mL) was added ammonium chloride (21.4 g, 0.4 mol) within 15 min at 40 °C. The mixture was cooled until a yellow-orange solid

formed. Reheating to 40 °C gave a solution. Montmorillonite K-10 (200 g) was then added with stirring at 40 °C. After evaporation in a rotary evaporator, the orange solid was dried in vacuum for 2 h at 70 °C. It can be kept for several months in air at room temperature without losing its activity.

Oxidation of Alcohols in the Solventless System.—The above reagent (1.7 g, 2.6 mmol) was added to an appropriate neat alcohol (1.3 mmol). This mixture was thoroughly mixed using a pestle and mortar. An exothermic reaction ensued with darkening of the orange reagent and was complete almost immediately as confirmed by TLC (hexane–AcOEt, 8:2). The product was extracted into CH₂Cl₂ and passed through a small bed of silica gel (1 cm) to afford the corresponding pure carbonyl compounds (Table 1).

Oxidation of Alcohols under Microwave Irradiation and Solvent-free Conditions (General Procedure).—The above reagent (1.7 g, 2.6 mmol) was added to an appropriate neat alcohol using a beaker and mixed thoroughly by a spatula. The reaction mixture was placed in a beaker inside a microwave oven and irradiated for 1 min. On completion of the reaction (TLC; hexane–ethyl acetate, 8:2) the crude product was directly charged onto a silica gel column. Elution with hexane–ethyl acetate afforded the pure carbonyl compound (Table 1).

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