SHORT PAPER

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Oxidation of alcohols and primary aliphatic amines to carbonyl compounds using sodium hypochlorite adsorbed on montmorillonite K10[†]

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NaClO adsorbed on montmorillonite K10 converts alcohols and primary aliphatic amines into corresponding carbonyl compounds.

Solid phase organic synthesis for preparation of various molecules has provide an attractive option for organic synthesis.[1–4] Modification of the activity and product selectivity are the characteristics of this method.

Montmorillonite clays have a great impact in organic synthesis and offer a major breakthrough for the fine chemicals manufacturing industry.[3,5]

The oxidation of primary and secondary alcohols to the corresponding carbonyl compounds is an important reaction in organic synthesis and the newer oxidative protocols are welcome in spite of the availability of several methods to accomplish this objective.[6]

Sodium hyphochlorite is a readily available and inexpensive oxidant and has been used for the oxidation of a variety of compounds. Unfortunately the traditional NaClO oxidation methods are limited by the very low solubility of NaClO in most organic solvents. In order to overcome this limitation, milder NaClO oxidation methods such as oxidation under phase-transfer catalysis[8] have been developed. However, these methods possess disadvantages, *e.g.*, long reaction time, high temperature and the use of expensive polar aprotic solvents.

This communication reports our finding that NaClO adsorbed on montmorillonite K10 is an effective oxidizing agent for the rapid oxidation of alcohols and primary aliphatic amines to aldehydes and ketones.

Alcohols are rapidly converted into carbonyl compounds at room temperature by stirring with a NaClO / montmorillonite K10 reagent. This reagent is prepared by mixing weighed amounts of 5% aqueous NaClO (commercial home bleach) and K10 clay. The oxidation reactions are carried out simply by adding 1.2 eq. of the NaClO / K10 clay reagent to the stirred solution of an alcohol in dichloromethane. Aliphatic primary alcohols are oxidized to the corresponding aldehydes, and secondary alcohols to the corresponding ketones. The results are summarized in Table 1.

A variety of oxidizing reagents *e.g.* Na_2SO_3,[9] $NaNO_2$,[10] K_2FeO_4,[11,12] $KMnO_4$,[13] and NaClO under phase transfer catalyst[8] have been used for the transformation of amines to carbonyl compounds. Most of the reported reagents require vigorous conditions.[8] Some of these reagents involved tedious solvent removal[9,10], low yields[11–13] and a long reaction time[8,10].

Our reagent is a cheap alternative for oxidation of aliphatic

Table 1 Oxidation of alcohols to carbonyl compounds by NaClO / K10 clay

Alcohol	Time (min.)	Product	Yield (%)
4-hydroxy-3-methoxybenzaldehyde	25	Vanilin	96
2,4,6-trimethylbenzyl alcohol	30	2,4,6-trimethyl benzaldehyde	93
4-chlorobenzyl alcohol	20	4-chlorobenzaldehyde	98
9-fluorenole	35	9-fluorenone	98
4-nitrobenzyl alcohol	20	4-nitrobenzaldehyde	95
Cyclohexanol	30	Cyclohexanone	97
Cinamyl alcohol	25	Cinamaldehyde	89[a]
Furfuryl alcohol	25	2-furaldehyde	97

[a]Yield of 2,4-dinitrophenylhydrazone derivative.

Table 2 Oxidation of primary amines to carbonyl compounds by NaClO / K10 clay

Amine	Product	Time (min)	Yield (%)
Ethyl amine	Acetaldehyde	30	85
N-buthyl amine	*n*-buthylaldehyde	25	88
Benzyl amine	Benzaldehyde	30	93
Isopropyl amine	Acetone	65	82[a]
Cyclohexyl amine	Cyclohexanone	55	90
2-phenylethyl amine	Phenyl acetaldehyde	60	89
4-methylbenzyl amine	4-methylbenzaldehyde	35	96 [a]
3-phenylpropyl amine	Dihydrocinnamaldehyde	50	91
3-chlorobenzyl amine	3-chlorobenzaldehyde	45	86
4-chlorobenzyl amine	4-chlorobenzaldehyde	50	90

[a]Yield of 2,4-dinitrophenylhydrazone derivative.

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

as well as benzylic primary amines with total selectivity and good yields to corresponding aldehydes and ketones (Table 2).

In conclusion, mild reaction conditions, high yields, ease of work-up, stability and reusability of support are the most significant aspects of this method.

Experimental

Chemicals were purchased from Merck, Aldrich and Riedel dehaen AG chemical companies and were used without further purification. All products are known compounds and they were identified by comparison of their 2,4-dinitrophenylhydrazones' melting points, IR and ^{1}H-NMR, spectra with those reported in the literature. All yields refer to pure isolated products.

Preparation of montmorillonite K10 supported sodium hypochlorite: This reagent is prepared by co-grinding NaClO (150 ml, 5% commercial home bleach solution, 100 mmol) and montmorillonite K10 (150 g, surface 200 m^2/g, Fluka) in an agate mortar. A white paste is obtained which must be used immediately.

Oxidation of alcohols to aldehydes and ketones: typical procedure: Cyclohexanone (200 mg, 2mmol), K10 clay supported NaClO (9.00 g, NaClO content; 3 mmol) and dichloromethane (30 ml) were vigorously stirred in a round bottom flask at room temperature for 30 minutes. The heterogeneous mixture was then filtered through a sintered glass funnel, and the insoluble material was thoroughly washed with hot solvent. Rotary evaporation of the combined filtrate *in vacuo* followed by passage through a short column filled with silica gel gave 190 mg (97%) of cyclohexanone, bp 154-156 °C, lit 155.6 °C.

Oxidation of primary amines to aldehydes and ketones: typical procedure: Benzylamine (214 mg, 2mmol), K10 clay supported NaClO (9.00 g, NaClO content; 3 mmol) and dichloromethane (30 ml) were vigorously stirred in a round bottom flask at room temperature for 30 minutes. The solvent was washed with 2N HCl solution to remove any unreacted amines. After work-up and purification as above, 198 mg (93%) of benzaldehyde was obtained, bp 176–178 °C, lit 179 °C.

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