J. Chem. Research (S), 1999, 560–561†

Regeneration of Aldehydes from Bisulfite Addition Products in the Solid State using Montmorillonite KSF Clay under Microwave Irradiation†

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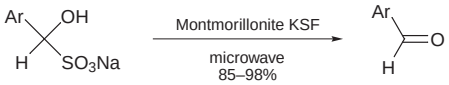
Microwave irradiation of bisulfite addition products with montmorillonite KSF clay under solvent-free conditions provides a fast, efficient and simple method for regeneration of aldehydes in excellent yields.

Protection of aldehydes as bisulfite addition products is of great interest to organic chemists as they are easily prepared by treatment with sodium bisulfite.[1] The bisulfite addition products are extensively used for purification of aldehydes. Although the regeneration of the aldehyde can be performed by treatment of the addition product with mineral acid[2] or base,[3] these methods are hazardous. Such reagents are also corrosive and detrimental to the environment.

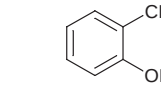
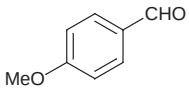
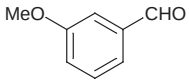
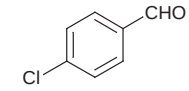
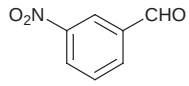
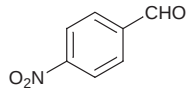
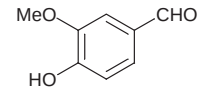
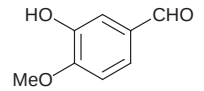
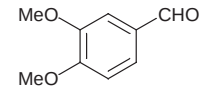
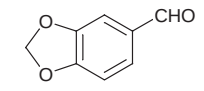
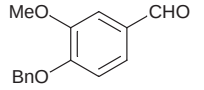
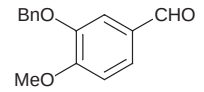
The use of inorganic supports as reaction media in organic synthesis is increasingly widespread owing to improved efficiency of many surface bound reagents.[4] Further, with the advent of microwave dielectric heating, the rate of several reactions can be promoted to afford faster and cleaner conversion.[5] Microwave heating techniques in solvent-free organic reactions have been developed recently. Thus, by the choice of suitable solid supports such as silica, alumina or clays, several organic reactions are carried out successfully in the solid state in an ordinary domestic microwave oven.[6]



Scheme 1

Montmorillonite KSF clay has been extensively used in various organic reactions *viz*. alkylation,[7] acylation,[8] Beckmann rearrangement[9] *etc*. and also under microwave irradiation in Fischer indole synthesis,[10] ortho-ester Claisen rearrangement,[11] acetal formation,[12] anhydride formation,[13] *etc*. In continuation of our ongoing programme to develop synthetic protocols utilising microwave irradiation under solvent-free conditions,[14] we report a simple synthetic procedure for regeneration of aldehydes from bisulfite addition products in the solid state using montmorillonite KSF clay (Scheme 1). The reaction proceeds efficiently in excellent yields at ambient pressure within a few seconds (Table 1). To the best of our knowledge, this is the first report of the regeneration of aldehydes from their bisulfite addition products using montmorillonite KSF under microwave irradiation. The reaction remains incomplete if the amount of clay used is less than the optimum amount found experimentally or if the reaction is carried out at room temperature for several hours. Montmorillonite KSF was regenerated easily by washing with ethanol, followed by drying at 110 °C for 12 h, and could be reused.

Table 1 Microwave-assisted regeneration of aldehydes from bisulfite addition products using montmorillonite KSF clay

Entry	Aldehyde	*t*/s	Yield[a](%)
1		10	96
2		14	95
3		12	90
4		15	92
5		18	87
6		20	85
7		5	97
8		15	96
9		9	95
10		10	92
11		16	98
12		11	97

[a] Yields refer to pure products.

Experimental

The IR spectra were run on Perkin-Elmer 782 spectrometer. ^{1}H NMR spectra were recorded in $CDCl_3$ solution on a Bruker AM 300L NMR spectrometer operating at 300 MHz using

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† This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

tetramethylsilane as the internal standard. Montmorillonite KSF was purchased from Aldrich. The reactions were carried out in a domestic microwave oven (BPL-SANYO, BMO-700T, 1200 W).

General Procedure.—A mixture of bisulfite addition product (1 mmol) and montmorillonite KSF (300 mg) was taken in a 25 ml Erlenmeyer flask and kept over an alumina bath (heat sink) inside a domestic microwave oven and irradiated for 5–20 s and the reaction was monitored by TLC. The product was extracted with ethyl acetate (2×5 ml), washed with brine and dried over anhydrous sodium sulfate. Evaporation of the solvent afforded the products in excellent yield (Table 1). All the products were characterised by ^{1}H NMR spectroscopy and by comparison with IR spectra of authentic samples.

In conclusion, we have developed a solvent-free method for the facile regeneration of aldehydes from their bisulfite addition products in the solid state using montmorillonite KSF clay under microwave irradiation.

We thank the CSIR, the UGC, New Delhi and the University of Calcutta for financial support.

Received, 11th January 1999; Accepted, 1st June 1999
Paper E/9/00309F

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