An eco-friendly regeneration of aldehydes exploiting ammonium acetate under microwave irradiation

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A number of bisulphite addition products and diacetates are deprotected separately to the corresponding aldehydes exploiting a green reagent, ammonium acetate in solvent-free conditions under microwave irradiation by a rapid, clean, efficient and high yielding method under environmentally benign conditions.

Keywords: ammonium acetate, solvent-free, microwave irradiation

Green chemistry emphasises the design and use of environmentally friendly reagents in chemical reactions without any organic solvent, as most of these are generally toxic.[1] It also involves the development and optimisation of reaction conditions that can help to maximise product yield and minimise energy consumption. The most convenient methods for purification and protection of aldehydes are the formation of bisulfite addition products and diacetates as they are easily prepared[2]. Consequent regeneration is also an important process. Bisulfite addition products are generally deprotected using mineral acids[3] or bases[4] which are detrimental to the environment and also corrosive. In the light of environmental concerns, we have previously reported[5] an environmentally benign process for the regeneration of aldehydes from bisulphite addition products using montmorillonite KSF-clay. Some of the methods reported earlier for deacetylation involve the use of Al_2O_3[6], zeolite[7], clayan[8]. In continuation of our attempt[9] to make chemical practices more environmentally friendly, we have chosen ammonium acetate as the reagent. In the last decade the growing interest in microwave-irradiated chemical reaction enhancement[10] is due to the combined effects of high reaction rates with the formation of cleaner products minimising the side reactions. Solvent-free reactions[11] under microwave irradiation are especially focused an providing environmentally safer reaction conditions.

As part of our ongoing programme[5,9,12] for the development of synthetic routes utilising microwave irradiation (MW) under solvent-free conditions, we now report the solid state regeneration of aldehydes from bisulfite addition products (Scheme 1) and diacetates

(Scheme 2) exploiting wet ammonium acetate under microwave irradiation .The reactions provide aldehydes in high yields (70–98 %) from bisulphate addition products within a very short time (6–180 s) (Table 1). Diacetates are also deprotected within 15–60 s with high yields (74–94%) (Table 2). Only aromatic aldehydes (including 3-phenylprofenal) are regenerated from their corresponding diacetates. Both the reactions were carried out at atmospheric pressure.

Ammonium acetate is an environment-friendly, inexpensive and useful reagent in organic synthesis[9,13]. To the best of our knowledge, ammonium acetate is reported here for the first time as a deprotecting agent for bisulfite addition products as well as diacetates of aldehydes under microwave irradiated solvent-free condition. Ammonium acetate is moistened as water absorbs heat efficiently as it is highly microwave active. The optimum ratio of the substrate to reagent has been found to be 1:1 (mol/mol). The reactions remain incomplete if carried out at room temperature for several hours. The reaction does not take place in the absence of ammonium acetate.

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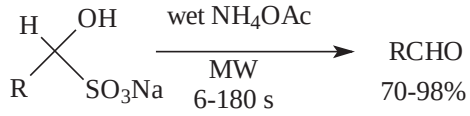
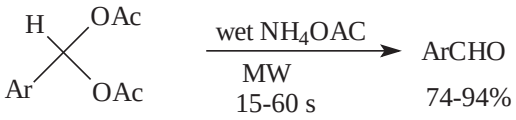


Scheme 1



Scheme 2

In conclusion, we have illustrated a fast, efficient and environmentally friendly method for the facile deprotection of bisulphite addition products and diacetates to the corresponding aldehydes exploiting an environmentally-safe reagent, ammonium acetate, under microwave irradiation and under solvent-free conditions.

Experimental

General procedure

A mixture of bisulfite addition product / diacetate of aldehyde (1 mmol), ammonium acetate (0.077 g, 1 mmol) and water (0.5 ml) was taken in a 25 ml Erlenmeyer flask placed in an alumina bath (heat sink) inside a domestic microwave oven (BPL, 800T / MM 261 EEP) and irradiated for specified time at a power level of 700 W. The reaction was monitored by TLC. The product was extracted with ethyl acetate (2x5 ml), washed with brine (5 ml) and dried over anhydrous sodium sulfate. Evaporation of the solvent afforded the products which after chromatographic purification on a short silica gel column (ethyl acetate:hexane 2:98),were characterised by ^{1}H NMR spectroscopy and by comparison with IR spectra of authentic samples.[2,14]

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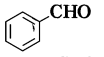
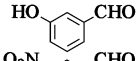
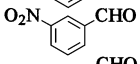
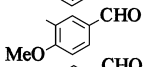
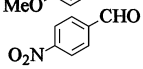
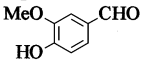
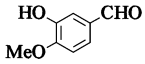
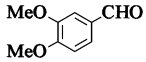
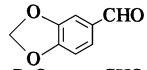
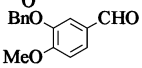
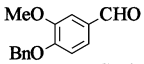
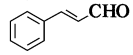
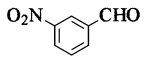
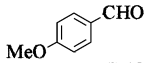
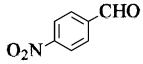
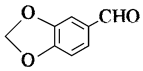
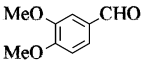
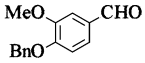
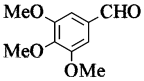
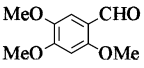
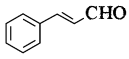
Table 1 Results of regeneration of aldehydes from bisulfite addition products.

Entry	Aldehyde	Time/s	Yield*/%	Obs.m.p. or b.p./mm/°C	Lit.m.p. or b.p./mm[2,1]/°C
1		9	98	178/760mm	179/760mm
2		11	96	197/760mm	197/760mm
3		120	72	105	180
4		180	75	58	58
5		6	93	135/10mm	248/760mm
6		45	80	105	106
7		9	96	81	81
8		38	93	113	115
9		15	89	158/8mm	281/760mm
10		40	85	150/8mm	264/760mm
11		56	70	62	–
12		12	97	64	–
13		15	80	140/10mm	252/760mm
14	*n*-butyraldehyde	135	75	158/760mm	162/760mm
15		12	78	75/760mm	75/760mm
16	Citral	19	82	120/10mm	229d/760mm

*Isolated yield.

Table 2 Results of regeneration of aldehydes from diacetates.

Entry	Aldehyde	Time/s	Yield*/%	Obs.m.p. or b.p./mm/°C	Lit.m.p. or b.p./mm[2,15]/°C
1		39	94	178(760mm)	179(760mm)
2		55	76	58	58
3		44	89	136(10mm)	248(760mm)
4		15	92	105	106
5		29	88	150(8mm)	264(760mm)
6		35	80	158(8mm)	281(760mm)
7		60	74	64	–
8		15	85	73	75
9		45	77	114	114
10		54	90	140(10mm)	252(760mm)
11	*n*-butyraldehyde	60	0	-	–
12	Citral	12	0	-	–

*Isolated yield.

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