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Note

Solvent free diacetylation of aldehydes using a solid acid under microwave irradiation and a simple route to their regeneration

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A simple solvent-free microwave mediated procedure for the selective protection of aldehydes by conversion to their 1,1-diacetates is reported. The resultant diacetates were deprotected to generate the aldehyde using aqueous formic acid in the presence of a surfactant in high yield.

Keywords: Protection, deprotection, aldehydes, 1,1-diacetates, solid state reaction, surfactant

Solid state organic synthesis is an active area of research[1]. Popular among the techniques used is the solvent-free synthesis under exposure to microwave irradiation or by simple heating. This method is an essential facet of green chemistry. Solvent free reactions eliminate the use of toxic solvents, helps in scaling down reaction vessels and work-up is considerably simple. Besides reducing handling costs, enhanced selectivity and reactivity are also observed [2-5]. In a similar manner, organic reactions conducted in aqueous media in the presence of surfactants have also been receiving importance in the field of organic synthesis because of mild and environmentally benign reaction conditions[6-8].

Selective protection of the aldehydes *vis-a-vis* the ketones have been the topic of investigations for quite sometime and several methods have been reported. Conversion of aldehydes to the diacetates is a procedure which has assumed importance particularly because the diacetates are stable and can be easily isolated and characterized[9,10]. It is also known that ketones do not give the diacetates easily. Hence conversion to the diacetates is a method of choice for selective protection of the aldehydes when both functional groups are present particularly so when the conversion can be carried out under solvent free condition. 1,1-diacetates are also reported to be important precursors to the synthesis of acetoxydienes and dihalovinylacetates[11,12]. There are several methods reported for the selective protection of the aldehydes by conversion to the diacetates and notable among them are the use of β-zeolites[13], montmorillonite KSF[14], graphite[15], surfurated zirconia[16], poly(vinylchloride)/$FeCl_3$ (Ref.17), $InCl_3$ (Ref.18), acidic alumina (Ref.19) besides others.

Herein a simple solvent free synthesis of 1,1-diacetate from aldehyde using a solid acid a catalyst under microwave irradiation is reported. The procedure precludes the use of toxic solvents and the solid acid catalyst is environmentally benign. Sulfurated silica gel is used as the solid acid catalyst and the method of synthesis involved the preparation of an intimate mixture of the aldehyde, acetic anhydride and the solid acid and then exposing the mixture to microwave irradiation for varying period of time (**Table I**).

Further, deprotection of the diacetate was also carried out with the aim of regenerating the parent aldehyde in hydrated media using aqueous formic acid solution in the presence of aqueous surfactant. Results obtained from deprotection is given in **Table II**. The general scheme of the conversions is shown in **Scheme I**.

The products, namely the 1,1-diacetates and the aldehydes were identified by comparing the melting points reported in literature and also by comparing the m.p. with authentic sample and finally confirmed by recording the ^{1}H NMR, IR and mass spectral data and CHN-analysis.

Experimental Section

Melting points were determined in a melting point apparatus from Scientific devices, India, Type MP-D in open capilliaries and are uncorrected. ^{1}H NMR spectra were recorded on a Jeol FT 300 MHz spectrometer in $CDCl_3$ solvent using TMS as the internal standard, IR spectra recorded in KBr pallets on Perkin-Elmer 1600 FT IR spectrometer. Microwave irradiation was done using domestic microwave oven operating at 750 W.

Preparation of the solid acid: A 500 mL RB Flask was charged with silica gel (100 g) and CH_2Cl_2 (50 mL). To this was added chlorosulfonic acid (58.3 g, 5 mole) with vigorous stirring. After

Table I—Conversion of aldehyes to diacetates using solid acid

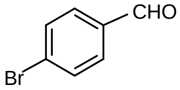
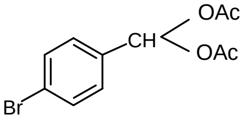
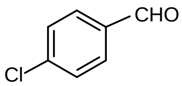
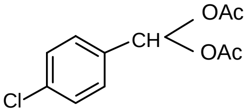
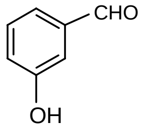
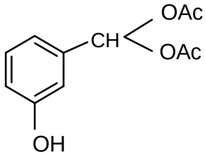
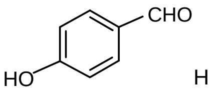
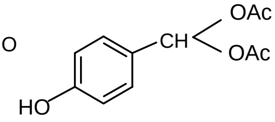
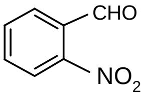
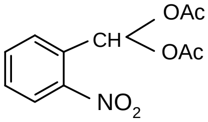
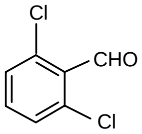
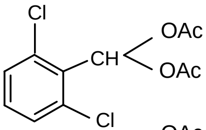
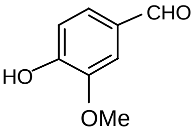
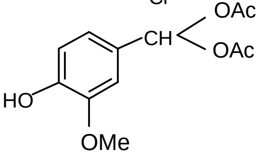
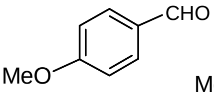
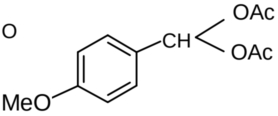
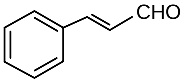
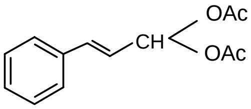
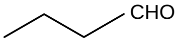
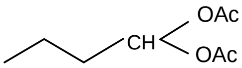
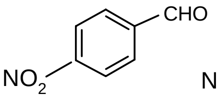
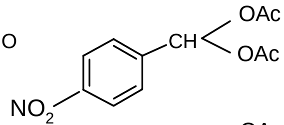
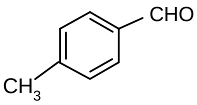
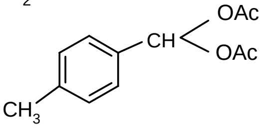
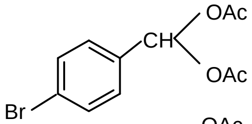
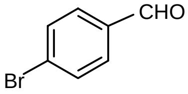
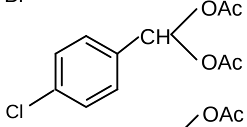
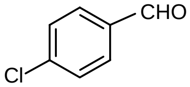
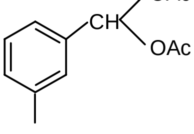
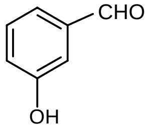
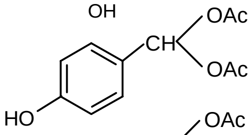
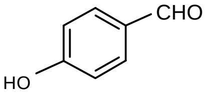
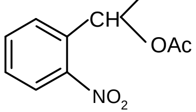
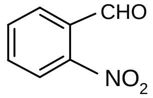
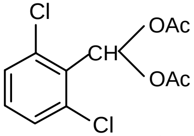
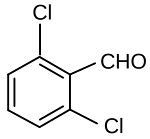
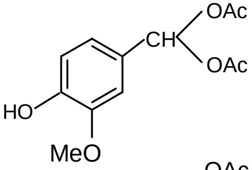
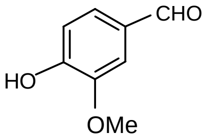
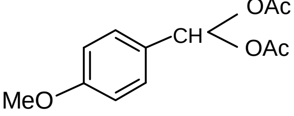
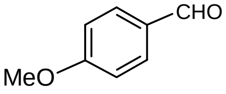
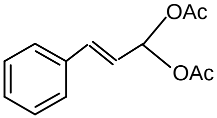
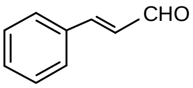
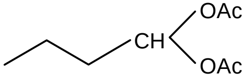
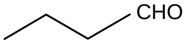
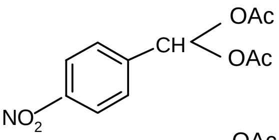
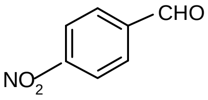
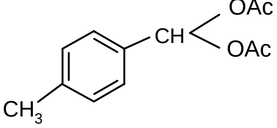
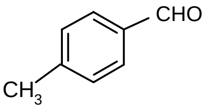
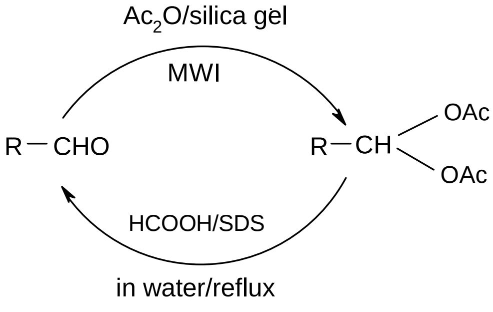
Entry	Substrate	Product	time(Sec)	m.p (^{0}C)		yield
				obs	lit	
1			120	89		92
2			60	79	79 (ref 21)	94
3			60	67		89
4			60	91	90(ref 21)	90
5			30	82	85(ref 21)	85
6			70	83		90
7			240	91		60
8			420	oil		80
9			300	oil		65
10			150	oil		70
11			120	121	124 (ref 21)	90
12			60	82	80-81 (ref 22)	85

Table II — Deprotection of 1,1-dicaetates to the aldehydes using formic acid/SDS

Entry	Substrate	Product	Reaction condition %SDS,% HCOOH	reflux time hrs	yield %
1			20,20	4	70
2			20,20	3	75
3			20,30	4	80
4			20,50	5.5	85
5			20,60	4	90
6			20,30	5	83
7			20,80	7	65
8			20,40	7.5	60
9			20,40	8	65
10			20,80	5	45
11			20,30	4.5	80
12			20,30	4	85

yields of liquid aldehydes (entry 7,8,9) ascertained by GC



Scheme I

completion of the addition, the mixture was stirred for 30 min. The solvent DCM and HCl were removed under reduced pressure to obtain a free flowing white solid which was stored in a vacuum desiccator[20].

General procedure for the conversion of the aldehyde to the 1,1-diacetate: To a homogeneous mixture of the aldehyde (5 mmole) and the solid catalyst (5 g) was added 15 mmole of acetic anhydride. The reaction mixture was exposed to microwave irradiation. After completion of the reaction as indicated by TLC, the mixture was extracted with ether (2×20 mL) and the ether layer was washed with 5% HCl (10 mL), 5% $NaHCO_3$ (10 mL) and brine (2×20 mL) successively and dried over sodium sulfate. After removal of the ether, the crude product was purified by column chromatography in silica gel using ethylacetate:petroleum ether (40-60°C) 1:9 as the eluent.

General procedure for the conversion of 1,1-diacetate to the aldehyde: A mixture of the diacetate (0.001 mole) in 10 mL of 20% aqueous SDS and varying percentage of aqueous formic acid taken in a RB flask fitted with a reflux condenser. The solution was refluxed. After completion of the reaction indicated by TLC, the reaction solution was poured into a large excess of water resulting in the precipitation of the aldehyde which was recovered and purified by recrystallization. The aldehydes were obtained in high yield. The products were identified by comparing the m.p. ^1H NMR, IR and mass spectral data with those observed for the authentic samples.

Selective spectral analysis of some representative compounds:

4-bromobenzal-1,1-diacetate: ^1H NMR(300 MHz $CDCl_3$): δ 2.1(s,6H), 6.8(d,2H,J=7.2) 7.2 (d,2H, J=8Hz), 7.6(m,1H); IR(KBr): 1820 cm^{-1} (-CO-).

2-chlorobenzal-1,1-diacetate: ^1H NMR(300 MHz, $CDCl_3$): δ 2.2(s,6H), 6.8(d,2H, J=7.2) 7.3(d,2H, J=8Hz), 7.8(m,1H); IR(KBr): 1790 cm^{-1} (-CO-).

2-hydroxybenzal-1,1-diacetate: ^1H NMR(300 MHz, $CDCl_3$): δ 2.3(s,6H), 7(m,1H), 7.9(m,4H); IR(KBr): 1810 cm^{-1} (-CO-).

2-nitrobenzal-1,1-diacetate: ^1H NMR(300 MHz, $CDCl_3$): δ 2.1(s,6H), 7.3(m,1H), 7.8(m,4H); IR(KBr): 1808 (-CO-), 1550 and 1320 cm^{-1} (-NO_2).

4-methoxybenzal-1,1-diacetate: ^1H NMR(300MHz, $CDCl_3$): δ 2.3(s,6H),7.1(d,2H J=6.5 Hz),7.3 (d, 2H, J=6.5 Hz), 3.3 (s,3H); IR(KBr): 1785 cm^{-1} (-CO-).

4-methylbenzal-1,1-diacetate: ^1H NMR(300MHz, $CDCl_3$): δ 2.1(s,6H), 7.3(d,2H J=7 Hz),7.1 (d,2H, J=6.5 Hz),2.4(s,3H); IR(KBr): 1820 cm^{-1} (-CO-).

Cinnamaldehyde-1,1-diacetate: ^1H NMR(300MHz, $CDCl_3$): δ 2.1(s,6H),7.1(5H aromatic), 7.7(d,1H J=11.5 Hz), 8.4(d,1H J=11.5 Hz); IR(KBr): 1800 cm^{-1} (-CO-).

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