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## Nickel boride mediated chemoselective deprotection of 1,1-

#### diacetates to aldehydes and deprotection with concomitant

reduction to alcohols at ambient temperature

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#### ABSTRACT

A variety of 1,1-diacetates have been chemoselectively and efficiently deprotected to the corresponding aldehydes as well as deprotected and concomitantly reduced to the corresponding alcohols in high yields at ambient temperature with nickel boride generated *in situ* using different molar ratios of sodium borohydride and nickel (II) chloride in methanol at room temperature. Deprotection and reduction of a variety of aromatic, aliphatic and heterocyclic acylals have been

achieved efficiently. Mild reaction conditions, easy work-up, high yields and chemoselectivity demonstrate the efficiency of this new method.



#### **GRAPHICAL ABSTRACT**

KEYWORDS: 1,1-diacetates, alcohol, aldehyde, deprotection, nickel boride, reduction

#### Introduction

The selective protection and deprotection of functional groups is of vital importance in synthetic organic chemistry. 1,1-Diacetates have been employed as suitable protecting groups for aldehydes<sup>[1]</sup> as they show remarkable stability in neutral, basic<sup>[2a]</sup> as well as acidic media.<sup>[2b]</sup> They can also be chemoselectively synthesized in presence of ketonic group and serve as important precursors for the synthesis of valuable intermediates of Diels-Alder reaction.<sup>[3,4]</sup> Different methodologies have been developed for the deprotection of acylals to corresponding aldehydes. These include the use of sulphuric acid,<sup>[5]</sup> hydrochloric acid,<sup>[6]</sup> expensive graphite,<sup>[7]</sup> zeolite,<sup>[8]</sup>

montomorillonite clays,<sup>[9]</sup> layered zirconiumsulfophenyl phosphonate,<sup>[10]</sup> Envirocat EPZG,<sup>[11]</sup> boron triiodide-N,N-diethylaniline complex,<sup>[12]</sup> ceric ammonium nitrate coated on silica gel,<sup>[13]</sup> neutral alumina under microwave irradiation,<sup>[14]</sup> CeCl<sub>3</sub>.7H<sub>2</sub>O/NaI,<sup>[15]</sup> CBr<sub>4</sub>,<sup>[16]</sup> [NO<sup>+</sup>-Crown H(NO<sub>3</sub>)<sub>2</sub><sup>-</sup>],<sup>[17]</sup> AlCl<sub>3</sub>,<sup>[18]</sup> zirconium(IV) chloride,<sup>[19]</sup> BiCl<sub>3</sub>,<sup>[20]</sup> Sc(OTf)<sub>3</sub>,<sup>[21]</sup> 2,6-dicarboxypyridiniumchlorochromate.<sup>[22]</sup> Some of the methods suffer from one or more drawbacks such as long reaction time, tiresome work up procedures, long reaction time for catalyst preparation, large amount of solid supports, lack of selectivity, expensive reagents or requirement of a microwave oven.

Nickel boride can be generated *in situ* from nickel(II) chloride and sodium borohydride in different solvents and has been used as an efficient reagent in various organic reactions. It is superior to many other metal catalysts due to its low cost, ease of preparation and handling, non-pyrophoric nature and easy removal. It is used as a reducing agent without need of any external hydrogen source as it contains adsorbed hydrogen.<sup>[23]</sup> Our research group has reported a number of transformations with nickel boride.<sup>[24]</sup> Recently, we had reported chemoselective deprotection and deprotection with concominant reduction of 1,3-dioxolanes, acetals and ketals using nickel boride.<sup>[25]</sup> Therefore, we decided to investigate the reactions of 1,1-dacetates (acylals) which are also employed as protecting groups of aldehydes with nickel boride.

#### **Result and Discussion**

In this paper, we report a simple, rapid and convenient procedure for the deprotection of a variety of 1,1-diacetates to the corresponding aldehydes (eq. 1) and also deprotection with concomitant reduction of 1,1-diacetates to the corresponding alcohols (eq. 2) with nickel boride generated *in situ* using different molar ratios of nickel (II) chloride and sodium borohydride. The

appropriate conditions for chemoselective deprotecion of 1,1-diacetates were investigated using 4-chlorobenzaldiacetate (**1a**) as the model substrate. The activity of nickel boride is known to depend on the method of its preparation, source of metal used, solvents etc.<sup>[23]</sup> Therefore, parameters had to be set out by carrying out reactions of **1a** with nickel boride generated *in situ* by changing molar ratios of nickel chloride and sodium borohydride and solvents.

Initially, reactions of 1a were carried out with NiCl<sub>2</sub>.6H<sub>2</sub>O and NaBH<sub>4</sub> in 1:3:9 and 1:4:12 molar ratio of 1a: nickel chloride: sodium borohydride in THF at room temperature. There was no reaction at all (entries 1-2, Table 1). Similarly, there was no reaction in DMF using 1:4:12 ratio of 1a: nickel chloride: sodium borohydride (entry 3, Table 1) whereas reactions carried out in CH<sub>3</sub>CN and DCM using 1:5:15 molar ratio of 1a: NiCl<sub>2</sub>.6H<sub>2</sub>O: NaBH<sub>4</sub> were incomplete and mixtures of products was formed (entries 4-5, Table 1). The reaction carried out using 1:4:12 molar ratio of **1a**: NiCl<sub>2</sub>.6H<sub>2</sub>O: NaBH<sub>4</sub> in methanol at ambient temperature showed formation of two products which were seperated after 4 h and identified as 4-chlorobenzaldehyde 2a (34%) and 4-chlorobenzyl alcohol 3a (56%) (entry 6, Table 1). The above reaction was repeated using 1:3:9 molar ratio (1a: NiCl<sub>2</sub>.6H<sub>2</sub>O: NaBH<sub>4</sub>) in methanol and was complete in 2 h. After work up, 88% of 4-chlorobenzaldehyde (entry 7, Table 1) was obtained. Reaction carried out with still lower ratio 1:2:6 of 1a: NiCl<sub>2</sub>.6H<sub>2</sub>O: NaBH<sub>4</sub> was incomplete even after 4 h and gave only 51% of 4chlorobenzaldehyde (entry 8, Table 1). The reaction of 1a with only sodium borohydride in 1:9 molar ratio in methanol at ambient temperature was incomplete even after 12 h (entry 9, Table 1) whereas 1a was left unreacted when treated with NiCl<sub>2.6</sub>H<sub>2</sub>O in 1:3 molar ratio in methanol even after 12 h (entry 10, **Table 1**). Therefore, it can be inferred that the reduction was proceeding due to in situ formation of nickel boride.

Subsequently, reactions of different 1,1-diacetates were carried out with nickel chloride and sodium borohydride in methanol at room temperature. All the reactions were complete in 2-3 h by changing the molar ratios and gave the corresponding aldehydes (eq. 1) in high yields (entries 1-14, **Table 2**). The results are listed in **Table 2**.

It can be inferred from above results that 1,1-diacetaes showed remarkable selectivity to give the corresponding aldehydes. It is also clear that halo groups (entries 1 and 5-6, **Table 2**), methoxy group (entries 3-4, **Table 2**) and heterocyclic moieties (entries 9-10, **Table 2**) remained unaffected under these conditions. Aliphatic 1,1-diacetaes could also be deprotected under these conditions (entries 12-14, **Table 2**).

The reaction of **1a** was then attempted using higher molar ratio 1:5:15 of 1a: NiCl<sub>2</sub>.6H<sub>2</sub>O: NaBH<sub>4</sub>. The reaction was complete in 3 h and gave 90% of 4-chlorobenzyl alcohol (**3a**). When the progress of the above reaction was monitored, formation of 4-chlorobenzaldehyde was distinctly observed. Therefore, it can be inferred that 4-chlorobenzal diacetate is undergoing deprotection with concomitant reduction using higher molar ratio of substrate: NiCl<sub>2</sub>.6H<sub>2</sub>O: NaBH<sub>4</sub>. Subsequently, reactions of a variety of 1,1-diacetates were carried out using 1:5:15 molar ratio in methanol at room temperature. All the reactions were complete in 2-4 h and gave the corresponding alcohols (eq. 2) in high yields. The results are summarized in **Table 3**.

$$R \xrightarrow{OAc} \underbrace{NaBH_{4}, NiCl_{2}.6H_{2}O}_{MeOH, r.t} \qquad R \xrightarrow{H}_{O} \qquad ...(1)$$

$$R = Aryl, Heteroaryl, Aliphatic$$

The halo substituents as well as hetroaryl groups remained unaffected under these conditions. A probable mechanism has been given in Scheme 1.

R = Aryl, Heteroaryl, Aliphatic

The reaction involves initial coordination of acetoxy group with nickel boride followed by hydrogenolysis of O-CO bond to give a gem-diol which loses water to give the aldehyde. Aldehyde undergoes subsequent reduction to alcohols using higher molar ratios of substrate to nickel boride. The nickel boride generated *in situ* is reported to contain absorbed hydrogen.<sup>[26]</sup> The mechanism is in agreement with our observations as no traces of 4-xylene or 4-trifluromethyl toluene were detected in the reactions of substrate **1f** and **1g** (entries 6-7, **Table 3**) with nickel boride. The aldehyde formed undergoes subsequent reduction to give corresponding alcohols when the reaction was carried out in higher molar ratios.

#### Conclusion

In conclusion, we have reported an efficient procedure for the deprotection of various 1,1diacetaes to corresponding aldehydes and deprotection with concomitant reduction to corresponding alcohols. Nickel boride generated *in situ* under non-acidic and protic conditions at room temperature afforded products in excellent yields. Chemoselective reaction, easy workup and no undesirable side-products are the advantages of this methodology.

# Experimental

All chemicals were of analytical grade. HPLC grade methanol (S.D. Fine) was used for the reactions. Sodium borohydride (S.D. Fine) and nickel chloride hexahydrate (S.D. Fine) were used as such. All 1,1-diacetaes were prepared by standard synthetic methods.<sup>[27]</sup> Melting points were recorded on a Tropical Labequip apparatus and are uncorrected. IR spectra were recorded on

Perkin Elmer FT-IR SPECTRUM-2000. NMR spectra were recorded on JEOL at 400 MHz using TMS as internal standard. All products are reported compounds and were identified by co-TLC with authentic samples wherever applicable, and by m.p., IR and <sup>1</sup>H NMR spectra.

# General Procedure for chemoselective reduction of 1,1-diacetaes to

#### corresponding aldehydes

In a typical experiment 4-chlorobenzaldiacetate (2.0 mmol, 0.5 g), methanol (10 mL) and NiCl<sub>2</sub>.6H<sub>2</sub>O (6.0 mmol, 1.469 g) were placed in a 100 mL round-bottomed flask fitted with a reflux condenser, a CaCl<sub>2</sub> guard tube and mounted over a magnetic stirrer. NaBH<sub>4</sub> (9.0 mmol, 0.7 g) was added cautiously and formation of black precipitate of nickel boride was observed immediately. The reaction mixture was stirred vigorously at room temperature and its progress was monitored by TLC using ethyl acetate: petroleum ether (10: 90) as eluent. TLC showed complete disappearance of the starting material after 2 h. The reaction mixture was quenched with methanol (20 mL) and filtered through a celite pad (~1 inch). The celite residue was washed with methanol (2 x 5 mL). The filtrate was concentrated to nearly half volume on rotavapor and diluted with water (20 mL). It was extracted with diethyl ether (3 x 10 mL). The combined ether extract was dried over anhyd. MgSO<sub>4</sub> and concentrated on a Buchi rotavapor to give 4-chlorobenzaldehyde (**2a**) as a pale yellow solid in 88% yield, m.p. 45 °C (lit.<sup>[28]</sup> m.p. 47 °C) and was also identified by IR and <sup>1</sup>H NMR spectra.

# General procedure for chemoselective reduction of 1,1-diacetaes to corresponding benzyl alcohols

In a typical experiment, 4-chlorobenzaldicetate (2.0 mmol, 0.5 g), methanol (10 mL) and NiCl<sub>2</sub>.6H<sub>2</sub>O (10.0 mmol, 2.440 g) were placed in a 100 mL round-bottomed flask fitted with a

reflux condenser, a CaCl<sub>2</sub> guard tube and mounted over a magnetic stirrer. NaBH<sub>4</sub> (30.0 mmol, 1.169 g) was added cautiously and formation of black precipitate of nickel boride was observed immediately. The reaction mixture was stirred vigorously at room temperature and its progress was monitored by TLC using ethyl acetate: petroleum ether (10: 90) as eluent. TLC showed complete disappearance of the starting material after 3 h. The reaction mixture was quenched with methanol (20 mL) and filtered through a celite pad (~1 inch). The celite residue was washed with methanol (2 x 5 mL). The filtrate was concentrated to nearly half volume on rotavapor and diluted with water (20 mL) and extracted with diethyl ether (3 x 10 mL). The combined ether extract was dried over anhyd. MgSO<sub>4</sub> and concentrated on a Buchi rotavapor to give 4-chlorobenzyl alcohol (3a) as white crystalline solid in 90% yield, m.p. 74 °C (lit.<sup>[28]</sup> m.p. 75 °C) and was also identified by IR and <sup>1</sup>H NMR spectra.

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S.No.	Solvent	1a:NiCl <sub>2</sub> .6H <sub>2</sub> O:NaBH <sub>4</sub>	Time (h)	Yield (%) (2a)
1.	THF	1:3:9	4	_a
2.	THF	1:4:12	4	_a
3.	DMF	1:5:15	4	_a
4.	CH <sub>3</sub> CN	1:5:15	4	_b
5.	DCM	1:5:15	8	_b
6.	MeOH	1:4:12	4	34(56) <sup>c</sup>
7.	MeOH	1:3:9	2	88 <sup>d</sup>
8.	MeOH	1:2:6	4	51
9.	MeOH	1:0:9	12	_b
10.	МеОН	1:3:0	12	_a

**Table 1.** Optimization of reaction conditions for deprotection of 4-benzachlorodiacet ate (1a) asmodel substrate.

<sup>a</sup>No reaction.

<sup>b</sup>Incomplete reaction and mixture of products.

<sup>c</sup>Yield in bracket is of 4-chloro benzyl alcohol.

<sup>d</sup>Average isolated yield of two runs.

**Table 2.** Chemoselective deprotection of 1,1-diacetates to corresponding aldehyde using nickel boride in methanol at ambient temperature.

S.No.	R	a: NiCl <sub>2</sub> .6H <sub>2</sub> O: NaBH <sub>4</sub>	Time (h)	Producta	Yield
					(%)
1.	4-ClC <sub>6</sub> H <sub>4</sub> (1a)	1:3:9	2	2a	88
2.	C <sub>6</sub> H <sub>5</sub> (1b)	1:4:12	2.5	2b	84
3.	4-(OCH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> (1c)	1:4:12	2	2c	86
4.	3,5-(OCH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (1d)	1:4:12	2	2d	90
5.	$4-BrC_{6}H_{4}$ (1e)	1:3:9	2.5	2e	87
6.	2,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (1f)	1:3:9	2.5	2f	84
7.	4-(CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub> (1g)	1:4:12	2	2g	82
8.	$4-(C_2H_5)C_6H_4$ (1h)	1:4:12	2.5	2h	86
9.	2-Thienyl (1i)	1:3:9	2.5	2i	88
10.	2-Furanyl (1j)	1:3:9	2	2ј	90
11.	PhCH <sub>2</sub> (1k)	1:3:9	3	2k	80
12.	2-(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> (11)	1:4:12	3	21	78

13.	n-CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> (1m)	1:3:9	3	2m	84
14.	n- CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> (1n)	1:4:12	3.5	2n	86

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<sup>a</sup>Yield of isolated products.

S.No.	R	1a: NiCl <sub>2</sub> .6H <sub>2</sub> O:	Time (h)	Product <sup>a</sup>	Yield (%)
		NaBH <sub>4</sub>			
					4
1.	$4-ClC_{6}H_{4}$ (1a)	1:5:15	3	3a	90 <sup>b</sup>
2.	$C_{6}H_{5}(1b)$	1:5:15	3	3b	84
3.	$4-(OCH_3)C_6H_4$ (1c)	1:5:15	3.5	3c	86
4.	$4-BrC_{6}H_{4}$ (1d)	1:5:15	2	3d	84
5.	$2,4-(Cl)_2C_6H_3$ (1e)	1:5:15	2	3e	88
6.	$4-(CH_3)C_6H_4$ (1f)	1:5:15	3	3f	84
7.	$4-(CF_3)C_6H_4$ (1g)	1:5:15	3	3g	90
8.	3,4,5-(OCH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>2</sub> (1h)	1:5:15	2.5	3h	88
9.	3,4-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> (1i)	1:5:15	3	3i	78
10.	$4-(C_{2}H_{5})C_{6}H_{4}(1j)$	1:5:15	3	3ј	80
11.	PhCH <sub>2</sub> (1k)	1:5:15	4	3k	80
12.	(CH <sub>3</sub> ) <sub>2</sub> CH(11)	1:4:12	3.5	31	80
13.	n-CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> (1m)	1:5:15	3	3m	84
14.	n-CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> (1n)	1:5:15	3.5	3n	86
15.	2-Thienyl (10)	1:4:12	4	30	88
16.	2-Furanyl (1p)	1:4:12	4	3р	86
987.11 C.	1 / 1 1 /				

**Table 3.** Chemoselective reduction of substituted 1,1-diacetate to corresponding alcohols using nickel boride in methanol at ambient temperature.

<sup>a</sup>Yield of isolated product.

<sup>b</sup>The progress of the reaction was monitored by TLC which showed the formation of 4-chlorobenzaldehyde during the course of reaction.

**Scheme 1.** Probable mechanism for nickel boride deprotection of 1,1-diacetates into aldehydes and alcohols.

