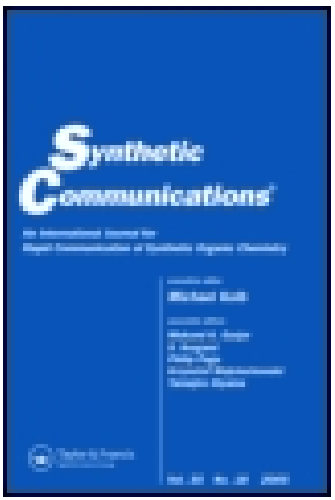

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Exclusive 1,2-Reduction of Functionalised Conjugated Aldehydes with Sodium Triacetoxyborohydride

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EXCLUSIVE 1,2-REDUCTION OF FUNCTIONALISED CONJUGATED ALDEHYDES WITH SODIUM TRIACETOXYBOROHYDRIDE

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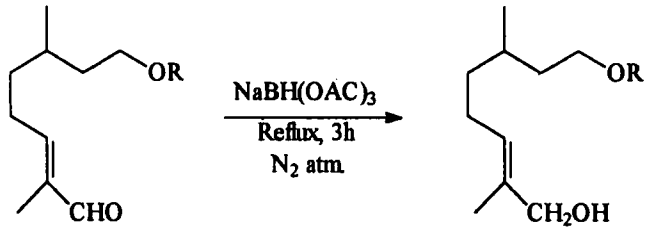
Abstract : Functionalised α,β-unsaturated aldehydes were exclusively reduced to allylic alcohols with sodium-triacetoxyborohydride. Neither saturated alcohol nor saturated aldehydes are obtained. Conjugated ketones are not reduced.

Selective reduction of one functional group in the presence of other reducible functionalities, though a simple and mild operation, is a challenging problem in organic synthesis. Sodium borohydride although is a reagent of choice for the reduction of aldehydes and ketones but unsaturated aldehydes[1] give substantial amounts of saturated alcohol and under special measures esters are also reduced[2]. Marshall and Johnson[3] reported that a combination of sodium borohydride and acetic acid can effectively reduce steroidal dienamines to γ, δ-unsaturated amines. Tetra-n-butylammonium triacetoxyborohydride[4] and sodium

triacetoxyborohydride[5] effectively reduces aldehydes in the presence of ketones. Regioselective 1,2-reduction of conjugated enones and enals has also been studied with sodium monoacetoxy borohydride[6].

Now we have found that sodium triacetoxyborohydride prepared from sodium borohydride and glacial acetic acid is highly useful for 1,2-reduction of conjugated aldehydes containing other reducible and acid sensitive functionalities (Table) to get allylic alcohols, whereas conjugated ketones fail to react under these conditions.

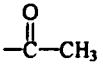
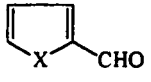
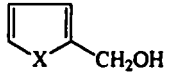
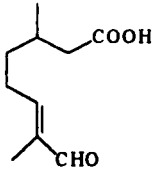
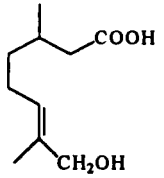
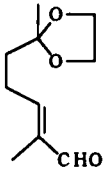
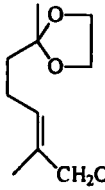
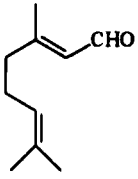
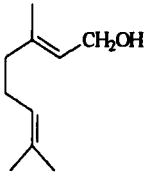


1 (a - e) 2 (a - e)

Experimental Procedure

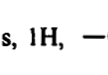
Sodium triacetoxyborohydride was prepared according to the literature procedure.[5] A dry 100 mL three-necked round-bottomed flask was equipped with magnetic stir bar, septum and reflux condenser purged with nitrogen. Glacial acetic acid (16.32g, 0.272mol) was added to benzene (dry) suspension of sodium borohydride (12g, 0.3348mol) and the reaction mixture was refluxed. After 15 min. when the initial rapid gas evolution subsided, a clear solution of sodium triacetoxyborohydride (0.0022 mol) was obtained. 2,6-Dimethyl-8-hydroxyoct-2-enal (substrate 1a, 0.1g, 5.88×10^{-4}mol) in 5mL of dry benzene was added to it dropwise. After 3h of refluxing, the extraction was done with diethyl ether (3x25 mL), washed with water and brine, dried (anhydrous Na_2SO_4), evaporated under vacuo and purified by column chromatography over silica gel to furnish the pure product 2a (0.0849g, 84%).

Table

Entry	Substrate	Product	Yield(%)
1.	1a R = H	2a	84
2.	1b - THP	2b	92
3.	1c -Ts	2c	90.5
4.	1d 	2d	93.7
5.	1e $-C_2H_5$	2e	93.7
6.	 6(a-b)	 6(c-d)	
	6a X = O	6c	89.2
	6b X = S	6d	92.5
7.	 7a	 7b	82.9
8.	PhCH = CH-CHO 8a	PhCH=CH-CH_2OH 8b	88.6
9.	 9a	 9b	89.6
10.	 10a	 10b	92.0

a) Purity of compounds was determined by TLC analysis.
b) All products were characterised by spectral (^{1}H-NMR, IR) analysis.

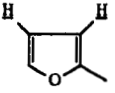
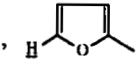
2a ^{1}H-NMR (δ/ppm): 1.0(d, J=6Hz, 3H, -CH-C$\underline{H}_3$), 1.3(m, 5H, -$\underline{H}_2$C-C$\underline{H}$(CH_3)C$\underline{H}_2$-), 1.7(s, 3H, C$\underline{H}_3$-C=C-), 2.2(m, 2H, -C$\underline{H}_2$-C=), 3.5(t, J=7Hz, 2H, -CH_2C$\underline{H}_2$OH), 3.8(s, 2H, =C(CH_3)C$\underline{H}$OH), 3.9(bs, 2H, 2x-OH, D_2O exchangeable), 5.2(t, J=6Hz, 1H, -C$\underline{H}$=C-).

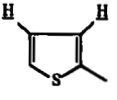
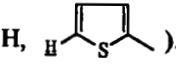
2b ^{1}H-NMR (δ/ppm): 1.0(d, J=6Hz, 3H, C$\underline{H}_3$CH-), 1.5(bs, 14H, C$\underline{H}_2$C$\underline{H}$(CH_3)C$\underline{H}_2$-, ring protons and C$\underline{H}_3$-C=C-), 2.3(m, 2H, -C$\underline{H}_2$C=), 3.3(bs, 1H, -OH, D_2O exchangeable), 3.5(m, 4H, 2x-OC$\underline{H}_2$-), 3.8(s, 2H, -C$\underline{H}_2$OH), 4.9(s, 1H, ), 5.2(t, J=6Hz, 1H, -C$\underline{H}$=C).

2c ^{1}H-NMR (δ/ppm): 1.0(d, J=6Hz, 3H, C$\underline{H}_3$-CH-), 1.3(m, 5H, C$\underline{H}_2$C$\underline{H}$(CH_3)C$\underline{H}_2$-), 1.7(s, 3H, C$\underline{H}_3$C=C-), 2.3(m, 2H, -C$\underline{H}_2$C=), 2.5(s, 3H, ArC$\underline{H}_3$), 4.0(m, 4H, -C$\underline{H}_2$OTs and -C$\underline{H}_2$OH), 4.1(s, 1H, -OH, D_2O exchangeable), 5.2(t, J=6Hz, 1H, -C$\underline{H}$=C-), 7.3(d, J=6Hz, 2H, Ar$\underline{H}$), 7.6(d, J=6Hz, 2H, Ar$\underline{H}$).

2d ^{1}H-NMR (δ/ppm): 1.0(d, J=6Hz, 3H, C$\underline{H}_3$-CH-), 1.3(m, 5H, C$\underline{H}_2$C$\underline{H}$(CH_3)C$\underline{H}_2$-), 1.8(s, 3H, C$\underline{H}_3$-C=C-), 2.2(m, 5H, -C$\underline{H}_2$C= and -COC$\underline{H}_3$), 3.0(bs, 1H, -OH, D_2O exchangeable), 4.1(m, 4H, -C$\underline{H}_2$OCOCH_3 and -C$\underline{H}_2$OH), 5.2(t, J=6Hz, 1H, -C$\underline{H}$=C-).

2e ^{1}H-NMR (δ/ppm): 1.0(t, J=6Hz, 3H, OCH_2-C$\underline{H}_3$), 1.2(d, J=6Hz, 3H, -CHC$\underline{H}_3$), 1.4(m, 5H, -C$\underline{H}_2$C$\underline{H}$(CH_3)C$\underline{H}_2$-), 1.7(s, 3H, C$\underline{H}_3$-C=C-), 2.2(m, 2H, -C$\underline{H}_2$C=), 3.4(m, 4H, -C$\underline{H}_2$-OC$\underline{H}_2$$CH_3$), 3.8(s, 2H, -C$\underline{H}_2$OH), 4.0(bs, 1H, -OH, D_2O exchangeable), 5.2(t, J=6Hz, 1H, -C$\underline{H}$=C-).

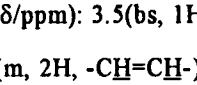
6c ^{1}H-NMR (δ/ppm): 3.8(bs, 1H, -OH, D_2O exchangeable), 4.6(s, 2H, -C$\underline{H}_2$OH), 6.3(m, 2H, ), 7.3(d, J=6Hz, 1H, ).

6d ^{1}H-NMR (δ/ppm): 3.5(bs, 1H, -OH, D_2O exchangeable), 4.5(s, 2H, -C$\underline{H}_2$OH), 6.1(m, 2H, ), 7.1(d, J=6Hz, 1H, ).

7b ^{1}H-NMR (δ/ppm): 1.0(d, J=6Hz, 3H, C$\underline{H}_3$CH-), 1.5(m, 3H, -C$\underline{H}$C$\underline{H}_2$-),

1.8(s, 3H, C$\underline{H}_3$C=C-), 2.2(m, 4H, -C$\underline{H}_2$C= and -C$\underline{H}_2$COOH), 3.1(bs, 1H, -OH, D_2O exchangeable), 3.8(s, 2H, -C$\underline{H}_2$OH), 5.2(t, J=6Hz, 1H, -C$\underline{H}$=C-), 8.5(s, 1H, -COOH, D_2O exchangeable).

8b ^{1}H-NMR (δ/ppm): 3.5(bs, 1H, -OH, D_2O exchangeable), 4.8(d, J=6Hz, 2H, -C$\underline{H}_2$OH), 6.8(m, 2H, -C$\underline{H}$=C$\underline{H}$-), 7.1(s, 5H, Ar$\underline{H}$).

9b ^{1}H-NMR (δ/ppm): 1.2(s, 3H, J=6Hz, ), 1.6(s, 3H, C$\underline{H}_3$-C=C-), 2.3(m, 4H, -C$\underline{H}_2$C(CH_3)- and -C$\underline{H}_2$C=), 3.0(bs, 1H, -OH, D_2O exchangeable), 4.0(s, 6H, -OC$\underline{H}_2$C$\underline{H}_2$O- and -C$\underline{H}_2$OH), 5.2(t, J=6Hz, 1H, -C$\underline{H}$=C-).

10b ^{1}H-NMR (δ/ppm): 1.6 and 1.7(2s, 9H, =CC$\underline{H}_3$ and =C(C$\underline{H}_3$)$_2$), 2.0(m, 4H, =C(C$\underline{H}_2$)$_2$), 3.5(bs, 1H, -OH, D_2O exchangeable), 4.1(d, J=7.5Hz, 2H, -C$\underline{H}_2$OH), 5.1(t-like, 1H, =C$\underline{H}$CH_2OH), 5.5(t, J=6Hz, 1H, -CH_2C$\underline{H}$=C-).

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