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CHEMOSELECTIVE REDUCTION OF CARBONYL COMPOUNDS WITH PMHS - ZnCl₂

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Abstract: An inexpensive and safer reagent system comprising of PMHS and ZnCl₂ has been developed for the selective reduction of carbonyl compounds to corresponding alcohols.

Polymethylhydrosiloxane (PMHS), an inexpensive and air stable siloxane polymer in combination with bis (tributyltin) oxide produces Bu₃SnH which has been extensively used for the reduction of organic functional groups especially in Barton - McCombie deoxygenation¹ and free radical mediated transformations². However, PMHS alone is exploited to a very limited extent, owing to its inertness as a hydride source on its own. Very recently Buchwald et. al have successfully demonstrated that this reagent in combination with titanocene reduces esters³ and lactones⁴. Prior to this, some occassional reports have been documented for the activation of PMHS using fluorides⁵, Pd(0) catalysts⁶, and DBATO⁷, albeit requiring high temperatures, polar solvents and/or high pressures. Our interest

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in finding new procedures for reduction⁸ of organic functionalities using *combination of reagents* has prompted us to take up a study and identify a readily available reagent which can effectively allow PMHS to liberate hydride for efficient reduction. To this end, herein we report our latest findings on the conversion of carbony1 functionalites to alcohols using stoichiometric amounts of PMHS and ZnCl, (equation 1).

$$R^{1} = alkyl, aryl, H$$

In our initial studies, we have found that, when to an ethereal solution of $ZnC1_2$ and PMHS, benzaldehyde (Table 1 entry 1) was added and stirred at ambient temperature for 24h, a clean formation of benzyl alcohol was observed after a standardised workup. This result has prompted us to extend this reaction procedure to various carbonyl bearing substrates, (Table 1) and we observed that all of them have produced the expected alcohols in practical yields⁹.

A characteristic of this reaction protocol has been that the conjugated aldehyde (entry 3) has undergone a regioselective 1,2 reduction and double bond remained untouched. Similarly the ester group (entry 4) remained intact unlike in the case of titanocene activated reaction, wherein ester moiety also underwent a reduction to furnish corresponding diol. Also aromatic nitro group (entry 5) survived the reaction conditions, however an acid labile - THP ether (entry 6) underwent hydrolytic cleavage with the concomitant reduction of aldehyde.

In summary, we have demonstrated that PMHS in combination with $2nCl_2$ has been utilised for the regio and chemo-selective reduction of carbonyl functionalities. The use of air stable and cost effective PMHS as a safer hydride

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OMe	Ŧ	24	68
	о́Ме <u>2</u> а		
О сно	Отон За	24	69 (82)
0G-(CH ₂)9- CHO	Me00C- (CH2)g-CH2C)H 24	70
	4a OH N ⁰ 2 <u>5</u> a	20	65 (85)
0H2C-(CH2)8-CH	0 HO-CH ₂ -(CH ₂) ₈ -CH ₂ <u>6</u> a	OH 20	80
Осно	—————————————————————————————————————	20	72
OL	OH Sa Ba	40	52
	ос-(СН2)9- СНО СНО NO2 NO2 ЮН2С-(СН2)8-СНО ОС-СНО СНО СНО СНО СНО	$OC-(CH_2)_{9}-CHO \qquad OH \qquad 3a$ $OC-(CH_2)_{9}-CHO \qquad MeOOC-(CH_2)_{9}-CH_2C$ $CHO \qquad 4a \qquad OH \qquad 0H \qquad 0H$ $NO_2 \qquad NO_2 5a$ $OH_2C-(CH_2)_{8}-CHO HO-CH_2-(CH_2)_{8}-CH_2 \qquad 6a$ $OH \qquad 7a \qquad 0H \qquad 0H \qquad 8a$ $OH \qquad 0H \qquad 8a$ $Ids in parenthesis based on res$	OC-(CHQ) OH 24 $3a$ $OC-(CHq)g-CHO MeOOC-(CHq)g-CHQOH 24$ $4a$ OH OH OH CHO CHO OH CHO OH CHO OH CHO OH CHO OH CHO CHO OH CHO CHO OH CHO CHO CHO OH CHO C

Table 1 Reduction of carbonyl groups with PMHS-ZnCl₂

source, and relatively simpler reaction conditions i.e., ambient reaction temperatures at which the reaction is run, deserves some experimental advantages. Attempts to identify similar combination of reagents for reduction of other organic functional

Typical Experimental Procedure:

To Polymethylhydrosiloxane (2ml) in a 50ml flask fitted with a septum inlet and magnetic stir bar was added freshly fused $ZnCl_2$ (1.36g, 10mmole) followed by phenyl propanaldehyde (entry 7, 1.34g, 10mmole) in 25ml dry ether. The reaction mixture was allowed to stir at room temperature for 24h, at which time 10ml of 1N NaOH solution was added and stirred for further 1h. The reaction mixture was extracted with ether (3x50ml), washed with 5% HCl (1x25ml), brine (1x25ml) and dried over sodium sulphate. The solvent was removed under reduced pressure and the pure product is isolated by simple column chromatography (1:10 ethyl acetate - petroleum ether as eluent) to furnish phenyl propanol 7a (0.97g, 72%).

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- All compounds gave satisfactory spectral data (¹H/¹³C NMR, IR, Mass) and are identical with authentic samples.

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