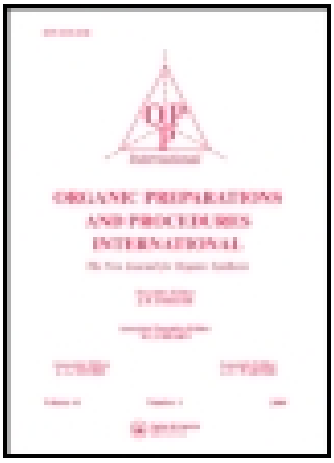

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MILD AND SELECTIVE METHOD FOR THE OXIDATIVE CLEAVAGE OF ACETALS AND THIOACETALS

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MILD AND SELECTIVE METHOD FOR THE OXIDATIVE CLEAVAGE OF ACETALS AND THIOACETALS†

Submitted by (12/26/97)

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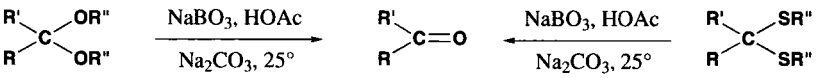
The protection and deprotection of functional groups are often necessary in the synthesis of multifunctional organic molecules. Aldehydes and ketones are frequently protected as acetals and thioacetals. Various catalysts have been utilized for the acetalization and thioacetalization of aldehydes and ketones.[1] Acetals are used not only as protecting groups but also as efficient chiral auxilary groups for enantioselective syntheses.[2] Thioacetals are often employed as acyl anion equivalents[3] and intermediates in the reductive transformation of carbonyl compounds into corresponding hydrocarbons[4] or olefins.[5] Thus, although there is considerable interest in the formation and cleavage of acetals and thioacetals, their use is sometimes hampered by the lack of efficient procedures for the regeneration of the original carbonyl groups. We now report $NaBO_3.4H_2O$, sodium perborate (SPB) as a safe, efficient, and inexpensive agent for the mild deprotection of acetals and thioacetals.

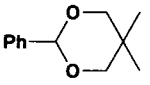
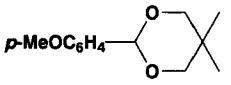
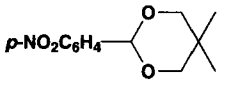
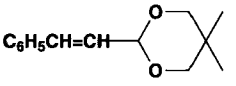
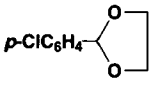
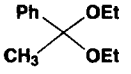
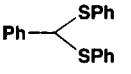
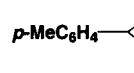
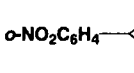
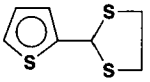
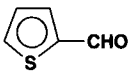
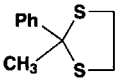
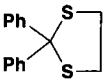
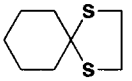
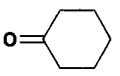
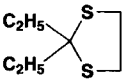
When acetals or thioacetals are treated with SPB in glacial acetic acid in the presence of sodium carbonate at 25°, the carbonyl compounds are produced in good yields even in the presence of other functional groups such as OMe, NO_2, Cl and Me (entries 2, 3, 5, 8, 9 and 10). One α, β-unsaturated acetal (entry 4) and the acetal of an aliphatic ketone (entry 15) also undergo smooth deprotection by SPB under these experimetal conditions. The present procedure is general for oxidative cleavage of aliphatic, aromatic, heteroaromatic, cyclic acetals and thioacetals. It should be noted, however, that SPB oxidizes aromatic amino and nitrile groups into azo, azoxy[6] or nitro[7] and amido[8] groups respectively. A special feature of this method is that α-β-unsaturated acetal (entry 4) underwent cleavage to



Scheme

the parent carbonyl compound without the double bond being affected. Even the sterically hindered acetal (entry 6) and thioacetals (entries 12, 13) were successfully deprotected in good yields. The most noteworthy advantage is that no acid was formed due to over-oxidation of regenerated aldehyde (entries 1-5 and 7-11). The present method is also effective for deprotection of cyclic dithioacetal derivatives (entries 11-14) which are more resistant to the action of a variety of reagents.[9]

TABLE 1 . Cleavage of Acetals and Thioacetals using SPB at 25°

Entry	Compd.	Product	Yield (%)	Time (hrs)	mp.(bp.) Observed	(°C) lit.
1		PhCHO	98	1	(177)	(179)[12]
2		*p*-$MeOC_6H_4CHO$	88	4	(245)	(248)[12]
3		*p*-$NO_2C_6H_4CHO$	89	2	105	106[12]
4		C_6H_5CH=CHCHO	98	8	(244)	(248)[12]
5		*p*-ClC_6H_4CHO	93	2	46	47[12]
6		$PhCOCH_3$	86	0.5	(197)	(202)[12]
7		PhCHO	87	2	(177)	(179)[12]
8		*p*-MeC_6H_4CHO	97	2	(200)	(204)[12]
9		*p*-$MeOC_6H_4CHO$	85	1	(242)	(246)[12]
10		*o*-$NO_2C_6H_4CHO$	80[a]	3	43	44[12]
11			82	1	(158)	(55/17mm)[12]
12		$PhCOCH_3$	93	0.5	(198)	(202)[12]
13		PhCOPh	97	0.5	50	49[12]
14			88	2	(152)	(156)[12]
15		$C_2H_5COC_2H_5$	85	4	(101)	(102)[12]

a) Reaction was carried out at reflux temp.

This procedure can be easily scaled up and, given the inexpensive cost of SPB coupled with its non-toxic nature, ease of handling and absence of effluent or by-product problems, could well prove to be the oxidizing method of choice.[10]

EXPERIMENTAL SECTION

All reactions were conducted in oven-dried flasks. Solvents were distilled before use. All acetals and thioacetals were prepared from corresponding aldehydes and ketones by using recently published procedures.[11] SPB was obtained from S.D. Fine Chemicals, Mumbai. As far as we are aware, it is a safe oxidizing agent and no special precaution is required regarding its use.

General Procedure for the Cleavage of Acetals and Thioacetals.- A mixture of acetal/ thioacetal (1 mmol), SPB (2 mmol), sodium carbonate (40 mg) in glacial acetic acid (10 mL) was stirred at 25° for the specified period (Table), the reaction was monitored by TLC. After completion of the reaction, the regenerated carbonyl compound was extracted with ether (3x10 mL) and the ethereal layer was washed with aqueous sodium bicarbonate and water and was dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure gave regenerated carbonyl compound in good yield. Products were characterised by comparison with authentic samples (IR, ^{1}H NMR, physical constants and tlc).

Acknowledgement.- Mr. Sameer Kulkarni thanks Principal Dr. P. S. Gunjal and S. S. Pandit for their encouragement.

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† This paper is dedicated to Prof. M. S. Wadia (University of Pune) on occasion of his 60th birthday and it is part 10 in the series of synthetic methods. For part 9, see B. P. Bandgar and N. J. Nigal, *Synth. Commun.*, **28**, 3225 (1998).

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THE SYNTHESIS OF 3-AMINO-2-DIALKYLAMINOPYRIDINES

Submitted by A. D. Dunn
(04/28/98)

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While compounds of type **3** are readily available from the reaction of amines with 2-halo-3-nitropyridines (1)[1] followed by reduction, the latter compounds (1) are relatively expensive or require considerable time for synthesis and purification. Recently we have found that **3a-c** may be prepared directly from the reaction of secondary cyclic amines with 3-amino-2-chloropyridines (2), which are readily obtained by halogenation of 3-aminopyridines.[2,3] In these reactions, the amine is used in slightly greater than a three-fold excess and acts as reactant, solvent and halogen halide acceptor; this