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SELECTIVE REDUCTION OF ALDEHYDES WITH SODIUM TRIARYLOXYBOROHYDRIDES

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Sodium tris-(3,5-dimethyl-, and 3,5-di-t-butylphenoxy)borohydrides soluble in tetrahydrofuran have been prepared. These stable hydride complexes exhibit an excellent chemoselectivity for the reduction of aldehydes in the presence of ketones.

Chemoselective reduction of aldehydes in the presence of ketones with various hydride reagents has been the subject of much study.[1] Although modification of sodium borohydride (1) with acyloxy[2] or alkoxy[3] functions has been reported to afford effective complexes with high chemo- or stereoselectivity, no attempt was made to modify 1 with aryloxy group. It is expected that introduction of various aryloxy functionalities with different electronic or steric effect to 1 may change the activity and the effective steric bulk of the complex resulting the formation of the reagent with different chemo-, stereo-, or regioselectivity.

In this communication, we wish to report a preparation of sodium tris-(3,5-dimethyl-, and 3,5-di-t-butylphenoxy)borohydrides and an efficient chemoselective reduction of aldehydes with these reagents.

To a stirring suspension of 1 (128 mg, recrystallized from diglyme[4]) in anhydrous THF (12 ml) was added 3,5-dimethylphenol (1.22 g, 3 mol equivalent) and the mixture was kept at 65°C. After 2 h, calculated amount of hydrogen (3 mol eq.) has evolved giving a transparent homogeneous solution (complex A). Heating was continued for 3 h. In the case of 3,5-di-t-butylphenol as modifying reagent (complex B), the complex formation proceeds more slowly (~5 h) than that of the complex A. The active species in these solutions are considered to be $NaBH(OAr)_3$ from the following reasons: (1) One molar eq. of hydrogen was evolved by adding excess 2 M HCl to each complex solution, and (2) no evolution of hydrogen was observed when the complexes were heated with additional 1 mol eq. ArOH, indicating that disproportionation of these complexes does not occure. These reagents can be stored more than six month at room temperature without any loss of their activities.

A mixture of PhCHO (1 mmol) and $PhCOCH_3$ (1 mmol) was added dropwise to the stirred, standardized THF solution of complex A (1 mmol) at 0°C. At appropriate intervals, a small amount of the reaction mixture was withdrawn and quenched with CH_3CHO aq. solution or dil HCl. The ether extract of the organic layer was washed with dil NaOH and H_2O successively, and then analysed by GLC. Most of the reductions completed within 3 h except for the case of entry 2, where the reduction is considerably sluggish. Results are summarized in the Table. As can be seen from the Table,

these reagents exhibit excellent chemoselectivity for the reduction of aldehydes in quantitative conversions. While there has been reported few reagents[5] which have the ability to distinguish between an aliphatic aldehyde and an unhindered cyclohexanone, the present complexes are also effective for such cases. In addition to the chemoselective property equal to or greater than the reagents previously reported, there are several advantages that they are economical, stable, and easy to prepare and to handle. Further investigation to explore the selectivity of these reagents is in progress.

Table Selective Reduction of Aldehydes with Complex A and B in the Presence of Equimolar Amount of Ketones

	Substrate	Extent of Reduction (%)[a] Aldehydes		Ketones		Conversion(%) (RCH_2OH + RR'CHOH)		Ratio RCH_2OH/RR'CHOH	
1	PhCHO; $PhCOCH_3$	95	(96)[c]	3	(2)	98	(98)	97/3	(98/2)
2	p-$MeOC_6H_4CHO$; $PhCOCH_3$		(64)		(3)		(67)[d]		(96/4)
3	$C_6H_{13}CHO$; $C_7H_{15}COCH_3$		(97)		(2)		(99)		(98/2)
4	$C_8H_{17}CHO$; $C_7H_{15}COCH_3$	94		0.8		95		99/1	
5	$C_6H_{13}CHO$; t-$BuCOCH_3$		(99)		(<1)		(99)		(99/<1)
6	$C_8H_{17}CHO$; n-BuCOBu-n	99		1		99		99/1	
7	$C_6H_{13}CHO$; Cyhn[b]	96		4		100		96/4	
8	$C_6H_{13}CHO$; 2-MeCyhn[b]	98	(94)	4	(7)	102	(101)	96/4	(93/7)
9	$C_8H_{17}CHO$; 		(87)		(7)		(94)		(93/7)
10	$C_8H_{17}CHO$; 	92	(87)	4	(<1)	96	(87)	96/4	(99/1)
11	$C_8H_{17}CHO$; ℓ-Menthone		(98)		(<1)		(98)		(99/<1)
12	$C_6H_{13}CHO$; *d*-Camphor		(99)		(<1)		(99)		(99/<1)
13	$C_6H_{13}CHO$; 2-t-BuCyhn[b]		(99)		(<1)		(99)		(99/<1)

[a]Determined by GLC. [b]Cyhn: Cyclohexanone. [c]Numbers in parentheses are those with complex B. Reductions were carried out at room temperature. [d]Reaction time, 6 h.

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References

1) G. C. Andrews, Tetrahedron Lett., 21, 697 (1980) and refs. therein.
2) G. W. Gribble and D. C. Ferguson, J. Chem. Soc., Chem. Comm., 1975, 535; N. Umino, T. Iwakura, and N. Itoh, Tetrahedron Lett., 17, 763, 2875 (1976).
3) C. A. Brown, J. Am. Chem. Soc., 95, 4100 (1973).
4) H. C. Brown, "Organic Syntheses via Boranes", John Wiley and Sons, New York, 1975, p. 260.
5) M. Midland and A. Tramontano, J. Org. Chem., 43, 1470 (1978); M. J. Chapdelaine, G. H. Posner, and A. W. Runquist, ibid., 42, 1202 (1977); H. C. Brown and S. U. Kulkarni, ibid., 42, 4169 (1977).

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