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INFLUENCE OF CYCLODEXTRINS ON THE SODIUM BOROHYDRIDE REDUCTION OF CYCLOHEXENONES

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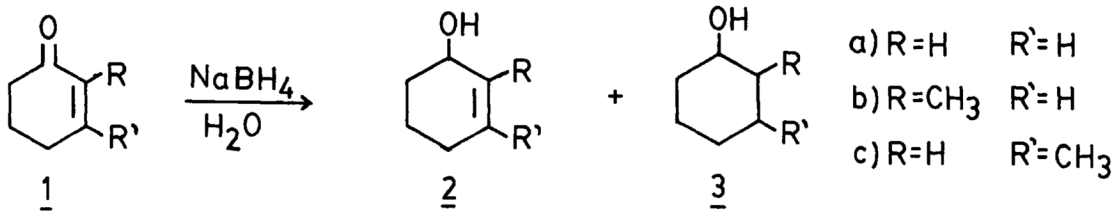
The sodium borohydride reduction of cyclohexenones in aqueous medium is changed in the presence of cyclodextrins. β-cyclodextrin favours the 1,4-reduction over the 1,2-reduction whereas α-cyclodextrin favours the 1,2-reduction.

Cyclodextrins form inclusion complexes with a wide variety of substrates.[1] Cyclodextrins and derivatives affect the rates of many kinds of chemical reactions and are used as enzyme models in biomimetic chemistry.[2] More recently, studies on the cyclodextrin reactions have been focused on their selectivity.[3] A recent report[4] prompts us to disclose our progress pertainting the sodium borohydride reduction of cyclohexenones in the presence of cyclodextrins. The following procedure is illustrative of the reaction: enone (2 mmol) was stirred in 100 mL of distilled water in the presence of cyclodextrin (2 mmol) for 2 h before the reduction. The pH of distilled water was set up at 7 by addition of sodium hydroxyde prior to use as solvent. Sodium borohydride (4 mmol) in water was added dropwise and the reaction let to stand 24 h before analysis. The aqueous phase was thoroughly extracted with ether and the product mixtures were analysed by vapor phase chromatography (flame ionization detector, carbowax 10%, relative response ratio method). The results are summarized in Table 1. Reduction of enone 1 by sodium borohydride in water gives a mixture of 1,2-reduction product 2 (major) and 1,4-reduction product 3 (minor). The presence of α-cyclodextrin favours the 1,2-reduction in every cases whereas β-cyclodextrin favours the 1,4-reduction. Replacement of cyclodextrins by the same molar equivalent of glucose or α-methyl glucoside has no influence on the reactions. Cyclodextrins have no effect on the diastereomeric composition of saturated alcohols 3b and

3c. For instance, 3c is a mixture of 84% *cis* and 16% *trans* 3-methylcyclohexanol. The extension of the study is now in progress. We are now investigating the nature of enone-cyclodextrin inclusion complexes by NMR.



1 2 3

Table 1. Reduction of enones with sodium borohydride in water

Enone	Host	Relative yields/%[a]		1,2/1,4 Reduction ratio
		2	3	
1a	none	54	46	1.2
	α-CD	66	34	1.9
	β-CD	32	68	0.5
1b	none	78	22	3.5
	α-CD	90	10	9.0
	β-CD	65	35	1.9
1c	none	74	26	2.8
	α-CD	94	6	15.7
	β-CD	68	32	2.1

a) Averages for triplicate runs. The conversion of enones is superior to 95%.

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