CHEMISTRY LETTERS, pp. 1489-1490, 1985.

SODIUM BOROHYDRIDE REDUCTION OF CYCLOHEXENONES IN THE PRESENCE OF AMYLOSE

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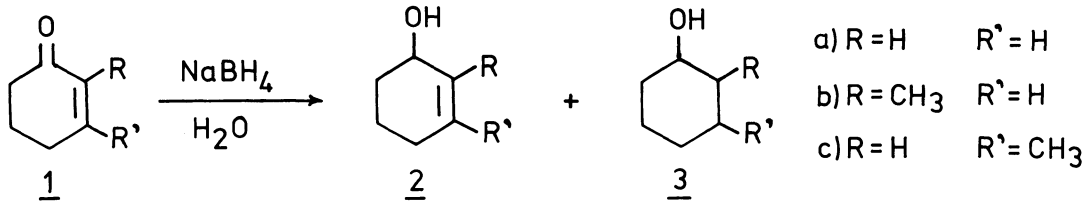
Amylose can alter the regioselectivity of the sodium borohydride reduction of cyclohexenones. Addition of amylose favours the simple carbonyl reduction over the conjugate reduction.

The modification and control of reactivity through the formation of host-guest complexes has been the subject of numerous investigations in recent years.[1-4] Hosts or receptor molecules can be natural or synthetic compounds such as cyclodextrins, crown ethers, cryptands, cyclophanes, zeolites, etc. Amylose, which is linear poly (1 → 4)-α-D-glucose, can adopt an helical conformation and can form complexes with a range of either hydrophilic or hydrophobic molecules.[5,6] Considerable latitude is allowed in the type of compound that forms a helical complex. Amylose will accommodate complexing agent of quite different molecular size by forming helices having six or seven residues per turn. Therefore we can hypothesise that amylose can influence the reactivity of molecules included in the helix. Rate accelerations with enzyme like kinetics have already been achieved in the hydrolysis of esters in the presence of amylose and derivatives.[7] More recently we reported the influence of amylose on the regioselectivity of a photo-Fries rearrangement.[8] We now report our novel finding that amylose alters the course of the sodium borohydride reduction of cyclohexenones. The typical reaction procedure is as follows: cyclohexenone (0.5 mmol) was stirred in 1500 mL of distilled water in the presence of amylose (2.0 g) for 2 h before the reduction. Sodium borohydride was added and the solution stirred at room temperature until disappearance of the starting material (ca. 1 d). The reaction mixture was then thoroughly extracted with diethyl ether and the organic layer subjected to vpc analysis (flame ionization detector, carbowax 10%, relative response ratio method). The results are summarized in Table 1. Reduction of enones 1 a-c gives a mixture of simple carbonyl reduction products (cyclohexenols 2 a-c) and conjugate reduction products (cyclohexanols 3 a-c).[9] Cyclohexenols are the major products. Cyclohexanones which are intermediates in the formation of cyclohexanols are not detected. The presence of amylose favours the simple carbonyl reduction (1,2-reduction) in every case and renders reduction of 1b and 1c specific. Such selectivity has been noted with several other reducing systems.[10,11,12] Amylose has no effect on the diastereomeric composition of saturated alcohols 3b and 3c. These effects can be attributed to the formation of organized assemblies between enones and amylose. Replacement of amylose by

the same weight of glucose or α-methyl glucoside has no influence on the reaction. We are presently studying the influence of amylose on the selectivity of other organic reactions.



1 2 3

Table 1. Sodium borohydride reductions of enones in the presence of amylose

Enone	Host	Relative yields/%[a]		1,2/1,4 Reduction ratio
		2	3	
1a	none	53	47	1.1
	amylose[b]	85	15	5.7
1b	none	78	22	3.5
	amylose	100	0	specific (1,2 reduction)
1c	none	74	26	2.8
	amylose	100	0	specific (1,2 reduction)

a) Averages for triplicate runs. Only compounds 2 et 3 are detected in vpc. Isolated yields are superior to 95%.

b) Amylose was purchased from Sigma Chem. Co. and was free of amylopectin (Type III, from potato). The viscosity-average molecular weight was found to be 4.35×10^5 g from viscosity measurements in dimethyl sulfoxide.

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(Received July 5, 1985)