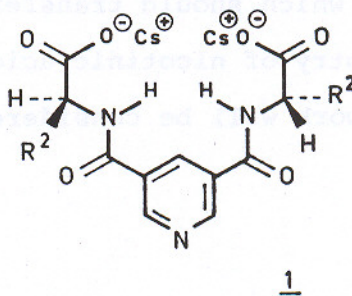
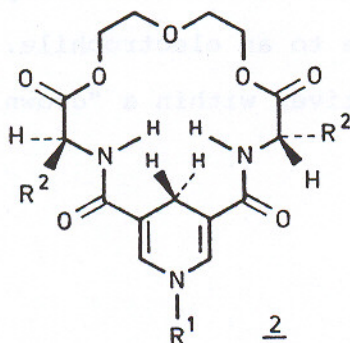


## ASYMMETRIC REDUCTIONS WITH CHIRAL 1,4-DIHYDROPYRIDINE CROWN ETHERS

Richard M. Kellogg, J.G. de Vries, and C.B. Troostwijk

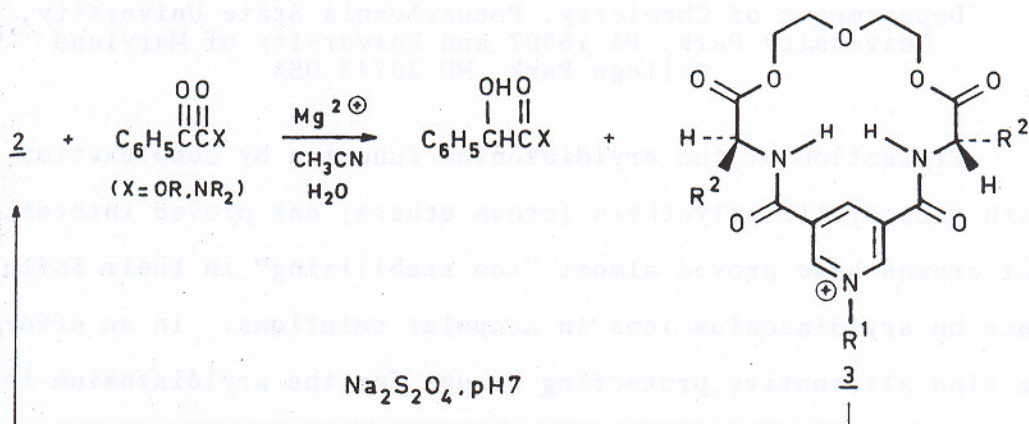
Department of Chemistry, University of Groningen, Nijenborgh, 9747 AG Groningen, The Netherlands

The synthesis of a series of chiral "crown-ether" 1,4-dihydropyridines (2) has been accomplished employing, as key to the ring-closure, the smooth reaction of the cesium carboxylates (1) with the required polyethyleneglycol dibromide. We have found that cesium salts often can be used to advantage in the syntheses of various macrocyclic compounds.



The compounds 2 ( $R^2 = \text{CH}_3$ ,  $(\text{CH}_3)_2\text{CH}$ ,  $\text{C}_6\text{H}_5\text{CH}_2$ ;  $R^1 = \text{CH}_3$ ,  $\text{C}_6\text{H}_5\text{CH}_2$ ) in the presence of  $\text{Mg}^{2+}$  ions as catalyst are capable of reducing various phenylglyoxalate derivatives. The degree of asymmetric reduction can be as high as 85-90%. From analysis of steric interactions using molecular models it is possible to predict the configuration of the major enantiomer formed

of the alcohol. Reduction of the pyridinium salts 3 back to 2 with  $\text{Na}_2\text{S}_2\text{O}_4$  completes the catalytic cycle.



Various aspects of these and other reactions will be discussed.