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THE APPLICATIONS OF DIFUNCTIONAL ORGANOSILICON COMPOUNDS TO ORGANIC SYNTHESIS; 1,3-ASYMMETRIC INDUCTION IN THE REDUCTION OF α-SUBSTITUTED β-HYDROXYKETONES

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ABSTRACT

Two α-methyl-β-hydroxyketones were reduced to anti-1,3-diols stereoselectively by a method involving presumed intramolecular transfer of hydrogen from a silicon atom to the carbonyl carbon.

INTRODUCTION

In recent years the stereoselective preparation of 1,3-diols has attracted particular attention due to the presence of such functionality in many complex natural products. Many attempts have been made for the preparation of 1,3-diols by addition reactions to the carbonyl group of β-hydroxyketones [1-8]. However, only one of these reactions a syn-selective reduction due to Narasaka and Pai [9] proceeds with useful 1,3-asymmetric induction.

While exploring the synthetic applications of "difunctional organosilicon compounds" we have reported in a recent communication [10] that β-hydroxyketones can be reduced with a remarkable level of 1,3-asymmetric induction. The reducing agent, an organosilane, initially attached to the hydroxy group of the β-hydroxyketone is induced to react with the carbonyl group by a Lewis acid catalyst to give preferentially the trans-siladioxanes. After desilylation [11] the anti-1,3-diols were obtained with diastereoisomeric excesses of 95% or better.

After this achievement, it seemed reasonable to see the effect on asymmetric induction after putting an alkyl substituent at the α-position of a β-hydroxyketone. For this purpose the reductions of two diastereomeric α-substituted β-hydroxyketones were examined.

MATERIALS AND METHODS

Proton nuclear magnetic resonance (1H-n.m.r) were recorded on a Jeol JNM-PMX-60 or a Bruker WP80 instrument at 60 or 80 MHz,