[illegible] los grupos

ISSN: 1570-193X

Enantioselective Addition of Organozinc to Aldehydes and Ketones Catalyzed by Immobilized Chiral Ligands

R. Somanathan*, L.Z. Flores-López, R. Montalvo-González, D. Chávez, M. Parra-Hake and G. Aguirre

Centro de Graduados e Investigación, Instituto Tecnológico de Tijuana, Apartado Postal 1166, Tijuana, B. C. 22000 México

Abstract: Catalytic enantioselective addition of organozinc reagents to carbonyl groups is a valuable method for the synthesis of optically active alcohols. Such asymmetric organozinc additions allow the synthesis of chiral alcohols ubiquitous in the structures of natural and manmade compounds. Recent interest in green chemistry has led to active research in the immobilization of catalysts, and their application to asymmetric reactions. Besides simplifying compound separation and recycling, immobilized catalysts offer easier handling of toxic reagents, and convenient operation in continuous flow reactors. Thus, industrial applications of even expensive and complex chiral catalysts can be achieved in an economical and environmentally benign way.

Keywords: Dialkylzinc addition, benzaldehyde, chiral secondary alcohol, immobilized catalyst.

INTRODUCTION

Enantioselective addition of organometallic reagents to aldehydes and ketones yields optically active alcohols. The relevant literature focuses mainly on the addition to aldehydes, in order to obtain chiral secondary alcohols. This reaction is one of the most important and fundamental asymmetric reactions. The optically active secondary alcohols are components of many naturally occurring and biologically active compounds, as well as materials such as liquid crystals. They are also important as synthetic intermediates of functionalities such as halide, amine, ester, ether, and others.

Two major methods for the enantioselective synthesis of optically active secondary alcohols are the enantioselective reduction of ketones and the enantioselective alkylation of aldehydes (i.e. addition of organometallic reagents to aldehydes). Enantioselective carbonyl reduction has been extensively studied and reviewed [1]. Enantioselective addition of alkyl groups to aldehydes and ketones as organomagnesium and organolithium reagents has been largely unsuccessful due to the highly reactive nature of the reagents. The breakthrough for the controlled enantioselective addition to the carbonyl group came from organozinc reagents, discovered by Oguni's group [2]. Following this, a plethora of ligands involved in the catalytic dialkylzinc addition to aldehydes under homogeneous conditions has been reported [3] (Fig. **1**).

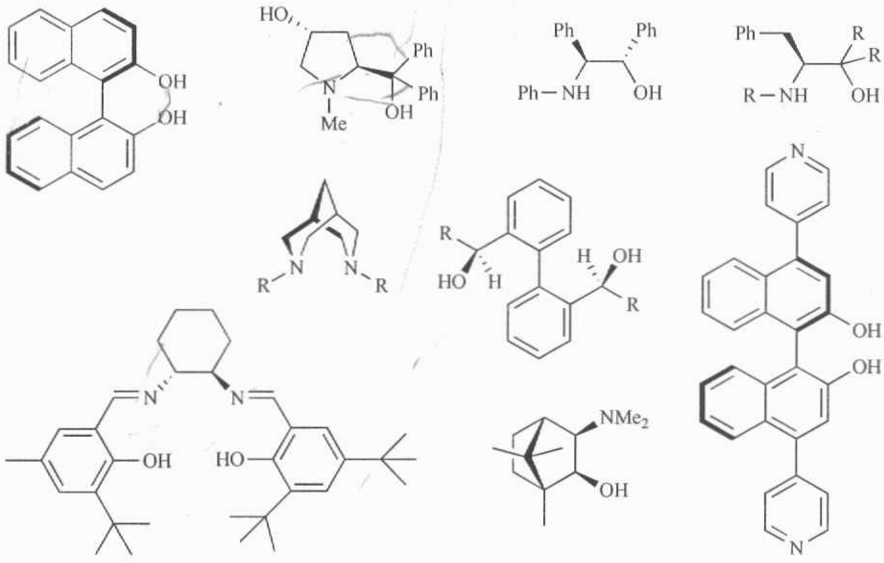

Fig. (1). Ligands used to catalyze the dialkylzinc addition to aldehyde under homogeneous conditions.

Subsequently, many of these ligands were immobilized on polymer, silica gel and dendrimers, and were applied as catalysts in the diethyl zinc addition to aromatic aldehydes in heterogeneous conditions. Immobilized catalysts have been of great interest because they offer advantages such as simplification of product work-up, straightforward separation and isolation, and re-use of the catalyst. However, their use in organic synthesis has been rather limited because in many cases immobilized catalysts are less active than the original catalysts. More importantly, recent interest in environmentally benign chemical processes, reducing waste and high-throughput organic synthesis has triggered renewed interest in the chemistry of immobilization of homogeneous catalysts.

The earlier work in the area of immobilization of catalysts for alkyl addition has been summarized in three review articles by Soai and Niwa [3a] Pu and Yu [3b], and Clapham *et al.* [4]. The objective of this review is to describe the immobilization of catalysts

---

*Address correspondence to this author at the Centro de Graduados e Investigación, Instituto Tecnológico de Tijuana. Apartado Postal 1166, Tijuana, B. C. 22000 México; Tel: +52 664 6233772; Fax: +52 664 6234043;
E-mail: somanathan@sundown.sdsu.edu

ISSN: 1570-193X/10 $55.00+.00