Chiral Polyols as Catalysts of Asymmetric C-C Bond Formation Reactions


1 - Institute of Russian Academy of Sciences, A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov 28, 119991 Moscow, Russia
2 - Yerevan State University, Department of Pharmaceutical Chemistry, A. Manoogian st. 1, 0025 Yerevan, Armenia
Gondzza@mail.ru

The creation of a chain of intramolecular hydrogen bonded hydroxyl groups could be expected to facilitate the proton transfer, accompanying the C-C bond formation. According to this hypothesis we have synthesized the series of polyols shown in Figure 1 to investigate their catalytic activity in corresponding reactions.

We have chosen Li, Na and K salts of (S)- or (R)-3,3'-bis[bis-(phenyl)hydroxymethyl]-2,2'-dihydroxy-dinaphthalene-1,1' (3) as catalysts of a model reaction of asymmetric Michael addition of malonic ester and other nucleophiles to cyclohex-2-enone.

Among other alcohols and phenols it was only BIMBOL that was an efficient catalyst of the reaction producing Michael adducts with 90% ee.

Other reactions tested with BIMBOL as a catalyst include PTC alkylations of amino acid precursors as shown in Fig. 2 and enantioselective epoxide ring opening with anilines (Fig. 3).

The asymmetric alkylation was conducted in CH$_2$Cl$_2$ in the presence of KOH and furnished different amino acids in high yield and reasonably high ee (up to 88%).

The ring opening of styrene oxide with anilines was almost not catalyzed by BIMBOL at room temperature. However, mono-lithium salt of BIMBOL showed significant catalytic activity. The reaction was stereoselective furnishing only one isomer. Kinetic resolution was observed and the asymmetric induction of the product reached 41% with 36% conversion.

The induction and catalytic activity of the system was greatly increased when Ti(OiPr)$_4$ was added to BIMBOL in a ratio 1:1. The forming catalyst was highly active even at a ratio of substrate/catalyst 1000/1. The ee of the final product varied, depending on the conditions, but reached 90% in some cases. We are going also to test polyols 5-7 hopefully to get better results.