NEW APPROACHES TO THE SYNTHESIS OF CARBOHYDRATES

Teruaki MUKAIYAMA

Department of Chemsitry, Faculty of Science The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

Carbohydrates are one of the most common organic compounds in nature, and have been a challenging target for synthetic organic chemists. However, various monosaccharides are generally synthesized starting from the easily available monosaccharides such as glucose, galactose, etc.. In these years, much interest has been focused on the synthesis of such compounds starting from the simple organic molecules, with the development of various highly stereoselective carbon-carbon bond forming reactions of acyclic system. Recently, several new and useful methods such as low valent tin promoted carbon-carbon bond forming reactions, stereoselective preparation of trans-vinyloxiranes starting from 2-allyloxybenzimidazole derivative and Zinc(II) mediated stereoselective addition of 2-furyllithium to polyoxygenated aldehyde were exploited. And convenient synthesis of a variety of monosaccharides such as 2-deoxy-p-ribose and p-erythronolactone were achieved using 2,3-O-isopropylidene-p-glyceraldehyde as 3-carbon building block.

A new and potentially useful 4-carbon building block for the L-sugars, 4-0-benzy1-2,3-0-isopropylidene-L-threose was prepared starting from L-tartaric acid and biologically important L-sugars such as 2-deoxy-L-galactose, 3-amino-2,3-dideoxy-xylo-hexose, L-diginose, and L-tagatose were successfully synthesized.

In addition to the stereoselective synthesis of various monosaccharides, stereoselective O-glycosidic bond forming reaction is an important problem in the synthetic field of carbohydrate chemistry. Based on the consideration of exploring more convenient method in glycosylation reaction, several new glycosylation reactions, which proceed under mild reaction conditions with high stereoselectivity, were exploited; namely, i) the glycosyl fluoride method, ii) the glycoside synthesis by the stereoselective internal cyclizations, and iii) by the direct introduction of alkoxy group on ketose.