

THE SUMMARY OF Ph. D. DISSERTATION

Major Chemistry	Student Identification Number 80062259	SURNAME, Firstname NAGAI, Hideyuki
Title The Development of Environmentally Benign Glycosidations Using Solid Acids		
Abstract <p>Carbohydrates are naturally abundant and recyclable feedstocks. On the other hand, a number of glycoconjugates and oligosaccharides are found in many bioactive or functional molecules. In this context, one of the most important transformation reactions of carbohydrates is a chemical glycosidation, which is very useful for preparing both natural and unnatural glycosides. Therefore, a highly effective, simple and environmentally benign glycosidation method is now urgently needed both in the laboratory and industry. In this thesis, the development of several novel and environmentally benign glycosidations using solid acids as activators are described.</p> <p>1) Environmentally benign glycosidations using a heteropoly acid.</p> <p>In this study, novel and convenient dehydrative glycosidations of 1-hydroxy glycosyl donors using a heteropoly acid as an activator have been developed. Thus, several <i>O</i>-benzylated 1-hydroxy sugars were effectively cross-coupled with a variety of alcohols by using the heteropoly acid, H₄SiW₁₂O₄₀, to give the corresponding <i>O</i>-glycosides in high yields with good α-stereoselectivities. Furthermore, the development of new methods for oligosaccharide synthesis is of growing importance. For this purpose, a novel promoter, heteropoly acid, mediated chemo- and stereoselective sulfoxide glycosidation reactions were developed. It was found that the glycosidations of several <i>O</i>-benzylated sulfoxide sugars and a variety of alcohols using the heteropoly acid, H₃PW₁₂O₄₀, in the presence of molecular sieves 5A in MeCN gave the corresponding α-glycosides in high yields. On the other hand, the corresponding sulfide and sulfone sugars were not activated by the heteropoly acid. Based on these results, the chemoselective glycosidations using the heteropoly acid were realized.</p> <p>2) Environmentally benign glycosidations using sulfated zirconia and Nafion-H.</p> <p>The stereocontrolled construction of α- and β-glycopyranosides is of considerable importance in synthetic organic chemistry. α- and β-Mannopyranosides frequently appear in glycoproteins and many antibiotics. Deoxy sugars also frequently appear in the glycosidic components of the bioactive substances. The development of direct and stereoselective α- and β-glycosidations of mannopyranoses and 2-deoxy sugars in an environmentally compatible manner is of particular interest. In this study, it was found that the glycosidations of mannopyranosyl and 2-deoxyglucopyranosyl sulfoxides with a variety of alcohols using Nafion-H in MeCN gave the corresponding α-glycosides in high yields. On the other hand, the glycosidations using SO₄/ZrO₂ in Et₂O afforded the corresponding β-glycosides in high yields.</p> <p>3) Environmentally benign glycosidations using montmorillonite K-10.</p> <p>In this study, the novel and environmentally benign glycosidations of glycopyranosyl phosphite and alcohols using a heterogeneous and reusable solid acid, montmorillonite K-10, for the highly stereoselective synthesis of β-glycopyranosides with a non-participating group were developed. Thus, it was found that the glycosidations of glucopyranosyl, 2-deoxyglucopyranosyl, 2,6-dideoxyglucopyranosyl and 4,6-<i>O</i>-benzylidene-protected mannopyranosyl phosphites and alcohols using montmorillonite K-10 gave the corresponding β-glycopyranosides in high yields. Finally, it was found that montmorillonite K-10 could be reused for several times and showed similar yields and stereoselectivities.</p>		

