Superbases for Organic Synthesis

The definition of “superbases” adopted by the editor and contributors to this book describes compounds whose basicities are comparable to or greater than the bidentate proton chelator “proton sponge” (1,8-bis(dimethylamino)naphthalene; DMAN). In addition to having unusually high lone-pair Lewis basicity, organic superbases are also generally characterized by good kinetic activity in proton exchange processes and by the ability of their protonated forms to delocalize their positive charge via conjugation over two or more bonds, thus stabilizing the conjugate acid. These bases include nitrogen-containing compounds such as amidines and guanidines, and phosphorus-containing molecules such as phosphazenes, guanadinophosphazenes, and proazaphosphatranes. Superbase chemistry has been attracting increasing interest over the past two decades, from both theoretically and synthetically oriented investigators. Evidence for this assertion arises from the fact that 57 % of the papers in the reference sections of the eleven chapters were published in the year 2000 or after.

This book contains a well-organized and thorough overview of superbase properties and their broad synthetic applications in organic chemistry. The first two chapters cover general aspects and properties of the aforementioned superbases, the next four chapters emphasize their catalytic and stoichiometric applications in organic synthesis, the next two chapters describe applications of the related organocatalysts DMAN and derivatives of urea, the penultimate chapter reports the occurrence of amidine and guanidine moieties in natural products and pharmaceuticals, and the last chapter offers some thought-provoking ideas regarding acid–base systems for asymmetric synthesis and for molecular recognition of substrates based on the formation of multiple intermolecular hydrogen bonds.

Because of their weak nucleophilicity, strong basicity, and good regioselectivity, nonionic bases are increasingly replacing ionic bases (which in many cases reduce the product yield owing to competing nucleophilic reactions) in stoichiometric and catalytic transformations. The nonmetallic character of superbases also lends itself well to meeting the increasing need for environmentally friendly organic catalysts and base reagents.

It is apparent that there is still room for much more research on the synthesis of new examples of superbases for use in expanding the scope of organic synthesis methodologies. Therefore, there is a need for the additional development of new superbases which can function homogeneously as catalysts or stoichiometric reagents, and can be used to make polymer-bound superbase analogues for heterogeneous catalysis. Future polymer-bound systems should be designed to be not only efficient, but also easily recyclable for rapid production of chemical libraries, for the economical synthesis of industrial products, and for applications to total syntheses of large molecules of biological or of broader industrial interest. Such new and efficient superbases should also include chiral versions capable of introducing high *ee* values into reaction products, and some that can activate a wider variety of nonmetallic and metallic atoms for important transformations.

As might be expected, the quality of English varies somewhat among the chapters, but seldom to the point where the reader has significant difficulty understanding the text. A considerable number of spelling errors could have been corrected, either in the copy-editing process or by using spell-checking computer program. Nevertheless, this book contains a wealth of valuable information for organic chemists, and it stimulates ideas for the synthesis of new superbases for both old and new applications.

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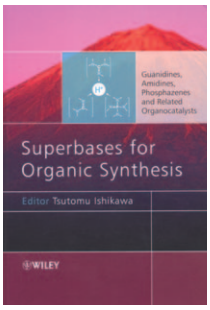

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