CHEMICAL REVIEWS

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Introduction: Heterocycles

Heterocycles form by far the largest of the classical divisions of organic chemistry and are of immense importance biologically, industrially, and indeed to the functioning of any developed human society. The majority of pharmaceuticals and biologically active agrochemicals are heterocyclic, as are countless additives and modifiers used in industries as varied as cosmetics, reprography, information storage, and plastics. Nevertheless, it is still, in the 21st century, possible to graduate from an American university with a Ph.D. in organic chemistry with but a desultory knowledge of heterocyclic chemistry (and even in extreme cases to be proud of it!). For many recruits to positions in the pharmaceutical industry, a fast introduction to heterocyclic chemistry is a must.

The breadth and diversity of the subject are reflected in the composition of the 20 individual reviews of the present issue. About half deal with a variety of topics on the synthesis of heterocyclic ring systems, and the others range widely in their focus and scope.

The increasing importance of transition-metal-mediated heterocyclic synthesis is attested by five reviews that cover such techniques. Yamamoto and Nakamura present a wide-ranging overview of work published since 2000 on transition-metal-catalyzed C−C and C−Y bond formation leading to heterocyclic rings. Important heteroring-closing metatheses are covered in two reviews: one by Martin and Deiters on the synthesis of O- and N-containing rings and the other by Hanson et al. on P- and S-containing analogues. Barluenga and co-workers describe applications of Fischer carbene complexes in heterocyclic synthesis, while Larock and Zeni summarize the utility of palladium π-olefin and π-alkyne complexes.

Further reviews deal with chiral heterocycle synthesis by way of iminium ion intermediates (Royer, Bonin, and Micouin) and the significance of 1-azaallylic anions in heterocyclic chemistry (De Kimpe, Mangelinckx, and Giubellina). Padwa and Bur recount the many applications of the Pummerer reaction in the formation of complex heterocyclic skeletons, and Stanovnik and Svete cover the diverse utility of dimethylaminopropenoates. The significance of vinylpyrroles as building blocks is treated by Trofimov, Sobenina, Demenev, and Mikhaleva. Formation of heterocycles involving heteroatom-substituted carbene intermediates is described by Cheng and Meth-Cohn. The utility of fluorous techniques in heterocyclic synthesis is dealt with by Zhang.

Dondoni and Marra discuss thiazole-mediated synthetic methodology. Two more reviews are concerned with the synthesis and transformations of specific classes of hetercycles: Tartakovsky and Churakov cover 1,2,3,4-tetrazines, while Rees, Konstantinova, and Rakitin deal with pentathiepins.

Applications of nucleophilic substitutions of hydrogen to synthesis of heterocycles and their substitutions are described by Mąkosza and Wojciechowski, while the complementary processes of the preparation and subsequent reactions of metallated heterocycles are the subject of the review by Yus, Nájera, and Chinchilla.

Gokel, Leevy, and Weber review applications of crown ethers as ion sensors and molecular scaffolds. The photo-, thermo-, solvato-, and electrochromic properties of spiroheterocycles are discussed by Minkin, and, to close the issue, Balaban, Oniciu, and the guest editor and writer of this introduction discuss the function of aromaticity as a cornerstone for understanding heterocyclic chemistry.

These articles amply illustrate the ongoing vitality of heterocyclic chemistry—a classical subject of immense practical and theoretical importance. The authors particularly hope that they will capture the interest of graduate students and postdoctorals at the beginning of their career and pass on to them some of our enthusiasm for the field.

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