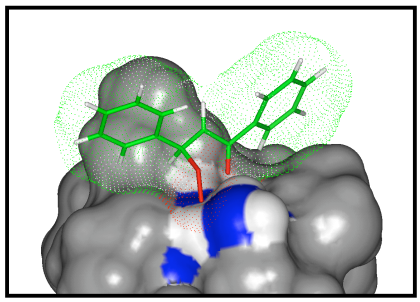

Organocatalysis by Hydrogen Bonding Networks
Mechanisms, Applications, and Relations to Enzymatic Transformations

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In metal-free enzymes, catalysis can be effected by the formation of covalent intermediates (such as enamines in class I aldolases), and by hydrogen bonding networks. In the latter case, the lowering of activation barriers results (*inter alia*) from the stabilization of developing charges (e.g. by the "oxy anion hole" in serine hydrolases), the facilitation of proton translocations, or the polarization of nucleophilic/electrophilic reaction partners.

Numerous examples exist how enzymatic "covalent organocatalysis"[1] can be mimicked by low-molecular weight organocatalysts. Prominent examples are proline-catalyzed aldol and Michael-reactions (*via* enamines), iminium ion catalysis in cycloadditions, acylpyridinium ions in acyl transfer reactions etc.. On the other hand, the design of "non-covalent" organocatalysts, acting solely by hydrogen bonding, is a new and emerging branch of (biomimetic) organocatalysis.[1]

The lecture will present four examples of non-enzymatic (but in some cases enzyme-like!) catalysis effected by hydrogen bonding networks: (i) epoxidation of olefins and Baeyer-Villiger oxidation of ketones with H_2O_2 in fluorinated alcohol solvents,[2] (ii) peptide-catalyzed asymmetric epoxidation of enones by H_2O_2,[3] (iii) dynamic kinetic resolution of azlactones, affording enantiomerically pure α-amino acids,[4] (iv) kinetic resolution of oxazinones, affording enantiomerically pure β-amino acids.[5] All four types of transformations are of preparative value, and their scope and mechanisms are discussed.

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