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New Systems for Organocatalytic Asymmetric Epoxidation

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The development of methods for the introduction of asymmetry into organic molecules remains a topic of great importance. Catalytic systems are particularly desirable, and the combination of a catalytic asymmetric process with an environmentally friendly reaction system and an inexpensive oxidant offers an especially attractive goal. Non-racemic chiral epoxides are important intermediates for enantioselective carbon-carbon bond formation. We are developing organocatalytic systems in which asymmetric oxidants are formed by reaction of iminium salts with simple oxidants under mild conditions. We currently formulate the reactive intermediates as oxaziridinium ions, from which the iminium salt mediators are regenerated following oxygen transfer to alkene substrates. We can accomplish epoxidation of simple alkenes with up to ca 99% ee. Catalyst loading may be as low as 0.1 mol%. The epoxidation reactions may be carried out under aqueous or non-aqueous conditions. The iminium salt mediators can be easily prepared without chromatography in many cases, and the procedures used are simple to carry out, and require no preparation of unstable reagents. The lecture will discuss recent developments including new generations of catalyst, the first examples of kinetic resolution, the use of non-aqueous as well as the usual aqueous conditions, and alternative oxidants in place of Oxone, including hydrogen peroxide, bleach, and even electrochemical conditions by oxidant generation at boron-doped diamond electrodes.

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