Intermolecular Hydrogen Atom Transfer Reactions to π-Systems

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Water activation, which allows this earth-abundant resource to be transferred into value added compounds, is a key topic in the field of small molecule activation. We demonstrate a unique water activation strategy enabled by a photocatalytic phosphine-mediated radical process under mild conditions, generating a metal-free PR_3-H_2O radical cation intermediate, where both hydrogen atoms are used in the following chemical transformation through sequential heterolytic (H+) and homolytic (H•) cleavage of the two O-H bonds.[1]

In the second part of the lecture, pyridine C-H functionalization through a dearomatization /rearomatization sequence will be discussed. The dearomatized oxazino pyridines can be easily prepared on a large scale, and *meta*-functionalization becomes achievable through light-initiated radical alkylation and ionic transformations.[2] The same intermediates also allow the highly regioselective *Minisci para*-alkylation[3,4], Cu-catalyzed *meta*-arylation,[5] and switchable *para/meta*-difluoromethylation.[6] Furthermore, it will be shown that the concept is also applicable to pyridine skeletal editing.[7]

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