Access to *ortho*-Hydroxyphenyl Ketimines via Imine Anion-Mediated Smiles Rearrangement and its Application

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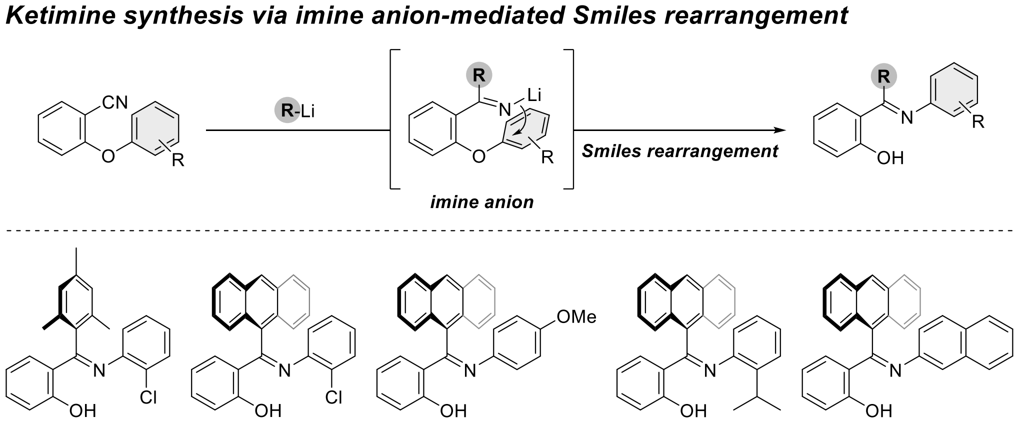
The imine structure is one of the most important structural motifs, which is found in numerous useful organic molecules such as ligands, biologically active molecules, and so on. Recently, we developed a novel synthetic method to the target structure via imine-anion mediated Smiles rearrangement.[1] The reaction has two characteristics: (1) easy modification of substituents on imino-carbon atom, and (2) access to *ortho*-hydroxyphenyl ketimines, whose effective synthetic approach is limited. This synthetic strategy can lead to various ketimines with bulky mesityl group, or even 9-anthryl one on imino-carbon atom. Products are also notable because these are quite tough to form by conventional condensation reaction between ketones and amines. Another intriguing feature is that reacting the bulky nucleophiles such as anthryl-, and 1-naphthyl-lithium enables a rearrangement of aryl rings such as electron-rich aryl groups and sterically hindered one, unsuited groups for S_NAr-type reactions.[2] Obtained ketimines are good synthetic platform, and they could be transformed into a nitrogen-containing polycyclic aromatic compounds by Lewis acid-catalyzed photo-induced electrocyclic reaction.


Ketimine synthesis via imine anion-mediated Smiles rearrangement

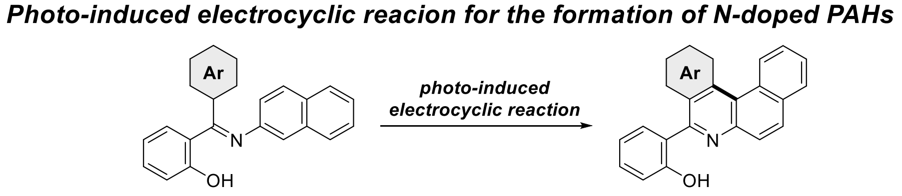


Photo-induced electrocyclic reacion for the formation of N-doped PAHs

1) Jinno, S.; Senoo, T.; Mori, K. *Org. Lett.* **2022**, *24*, 4140.
2) Jinno, S.; Kawasaki-Takasuka, T.; Mori, K. *Synlett* **2024**, *35*, 1565.