Exploring the reactivity of phosphiranium salts with simple amine nucleophiles

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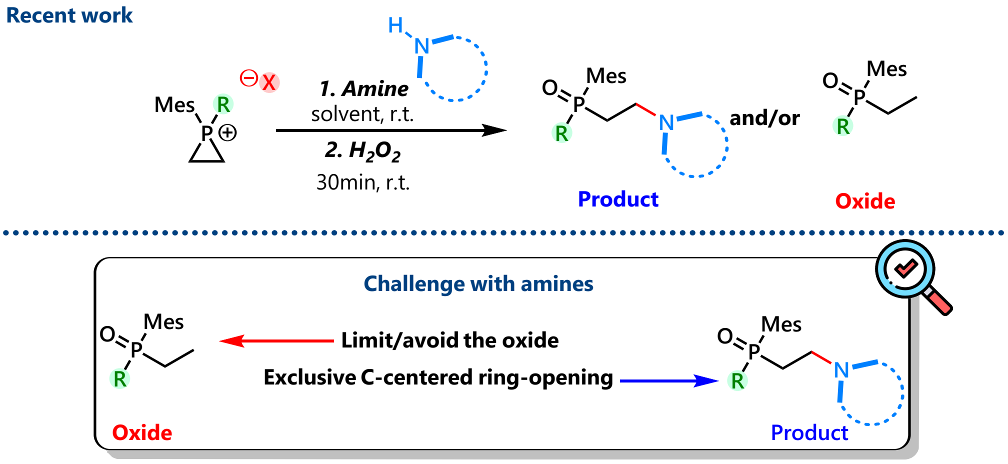
For about a decade, our laboratory has been interested in the chemistry of phosphiranium salts, an area of phosphorus chemistry that has long been neglected by the scientific community.[1] Our objective is to understand, develop and expand their chemistry, by demonstrating that their ring-opening by different classes of nucleophiles constitutes a direct and complementary approach to the synthesis of β-functionalized tertiary phosphines.[2]

Significant advances have been made since the beginning of our work including the synthesis of stable phosphiranium salts and, more importantly, the development of the first examples of C-centered ring-opening, using aniline derivatives as nucleophilic partners.[2a] More recently, we have demonstrated that by properly modulating sterics and electronics around phosphorus, the reaction can be extended to other classes of nucleophiles, such as sulfur and oxygen nucleophiles.[3]

In our early studies, the use of simple amines as nucleophiles systematically resulted in the formation of open phosphine oxide. Herein, we present our recent efforts to overcome this limitation, which revolve around understanding the formation of this oxidized by-product and evaluating the parameters governing the C-centered ring-opening of phosphiranium salts. We seek to understand the influence of both the phosphiranium counterion and the amine basicity, which may play a key role in influencing the stability and reactivity of the reaction intermediates and thus modulating the reaction outcome.



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