

Faculty of Pharmaceutical Sciences

Silane- and peroxide-free hydrogen atom transfer hydrogenation using ascorbic acid and cobalt-photoredox dual catalysis

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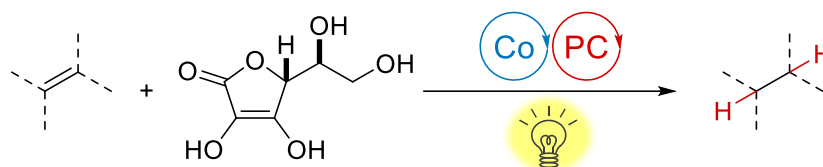
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Hydrogen atom transfer (HAT) hydrogenation of alkenes developed by Shenvi^{1a} and Herzon^{1b} provides a complementary method for conventional noble metal-catalyzed hydrogenation and is increasingly appreciated in the synthesis of complex molecules. However, reported catalytic HAT hydrogenation generally requires stoichiometric silane and peroxide to achieve a wide substrate scope. This limitation has posed challenges regarding sustainability and safety concerns.²

In 2020, we have developed a silane- and peroxide-free HAT hydrogenation of alkenes using cobalt-photoredox dual catalysis and ascorbic acid (vitamin C) as a sole stoichiometric reductant.³ The reaction retained favorable features of HAT hydrogenation and demonstrated superior performance for hydrogenation of an unprotected sugar derivative compared to established protocols. Several new reactions based on this regime are under investigation in our group.

However, due to transient nature of the catalytically active species of the HAT hydrogenation, mechanistic studies by experimental means could not strongly support the feasibility of the proposed hydrogen atom transfer step. Fortunately, we had a chance to start collaboration with Prof. Maeda in MANABIYA system at ICRéDD at that very moment. Using quantum chemical calculations, we have successfully proved that the reaction should proceed via hydrogen atom transfer from H-Co^{III} to an alkene, and this exergonic radical reaction is expected to be a rapid process.



HAT hydrogenation using vitamin C
Theoretical study @MANABIYA, ICRéDD

Reference

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