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Oxygen mediated highly efficient cobalt(II) porphyrin-catalyzed reduction of functional chromones: experimental and computational studies†

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The highly efficient oxygen mediated reduction of functional chromones with sodium borohydride ($NaBH_4$) catalyzed by cobalt(II) porphyrins afforded biologically active chroman-4-ols as the reduction products in 80–98% yields. Oxygen assists in the formation of hydridocobalt(III) porphyrin as a key intermediate, which releases hydride rapidly to reduce the chromones. Additionally, the correlation between quantum calculation results of the catalysts' conversions, yields, times and logarithms of the rate constants for the oxygen assisted reduction reaction was studied. The mechanism of the reaction was also justified by establishing a quantitative relationship between the rate constant, the α-HOMO orbital of the catalytic complex and the stabilization energy of the complex with oxygen.

Introduction

Chromones are a significant member of the flavonoid family that contribute to pigmentation in fruits, vegetables and flowers, as well as to flavors in foodstuff. Chromones, an important class of heterocyclic compound containing two chromophoric units, *i.e.* C═C and C═O, are the essential component of various natural products and medicinal agents.[1] Chromones actively participate in several plant cycles, including growth regulation, indole acetic acid oxidation and dormancy inhibition, and also exhibit cytokinin-type behavior and stimulate oxygen uptake in plant tissue.[2] Chromone analogs are abundant in nature and exhibit a variety of biological activities, *viz.* anti-bacterial,[3] anti-oxidant,[4] immunostimulation,[5] anti-ulcer,[6] anti-inflammatory,[7,13] anti-cancer,[8] anti-HIV,[9] biocidal,[10] wound healing,[11] anti-fungal,[12] immune-stimulatory[13] and anti-Alzheimers.[14]

The reduced analogs of chromones possessing hydroxyl groups are known to exhibit various biological activities with outstanding pharmacological profiles.[15] In general, when a chromone (**1**) is subjected to reduction, various bioactive compounds are obtained such as chroman-4-ones, chroman-4-ols, chromenes, chromans and chromenols. Recently, the transition-metal-catalyzed asymmetric hydrogenation of chromones was also shown to give chiral reduced products.[16] As such, a number of reducing agents, *e.g.* DIBAL-H,[17] complex hydrides,[18] lithium aluminium hydride,[19] $NaBH_4$/Lewis acid,[20] $NaBH_4$/excimer laser[21] and nickel boride,[22] have been employed to achieve the reduction of chromones.[23] However, these methods suffer from several drawbacks such as the requirement of harsh reaction conditions, observed slower reaction rates, the formation of a mixture of products, low product yields, catalyst consumption and the need for tedious work-up procedures.

Several catalytic systems based on metalloporphyrins (MTPPs) and metallophthalocyanines (MPc) have been developed for various oxidative and reductive chemical transformations.[24] Their excellent electrocatalytic properties, the stability of porphyrins[25] and their ability to coordinate to a large number of metal ions[26] have established them as promising catalysts. The exceptional catalytic properties of MTPP are due to the diversity of the central metal ions as well as the substituent groups on the macrocycle. Additionally, the easy recovery and reusability of MTPP catalysts positions them as an attractive alternative to existing catalytic methods for efficient reduction reactions. As a continuation of our work highlighting and elaborating the role of MTPPs as reduction-promoting catalysts, herein we report the efficient and rapid reduction of substituted chromones (**1a–1e**), using $NaBH_4$ in the presence of a series of MTPP catalysts (**3a–3f**) under an oxygen atmosphere at room temperature. The oxygen-mediated reduction of the functional chromones with sodium borohydride ($NaBH_4$) catalyzed by

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