

Study of Photoactivatable Processes

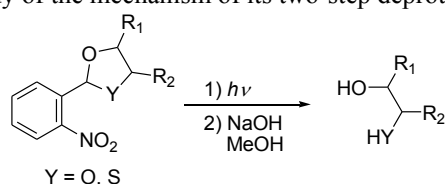
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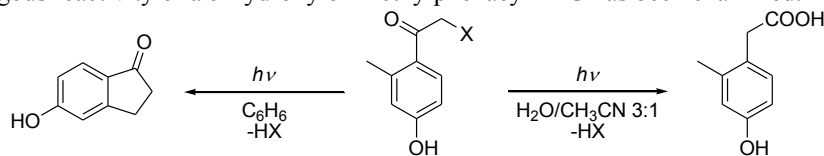
Photoactivatable processes have been of interest not only for synthetic applications but also for many promising applications in biologically related areas.¹

Photoremovable protecting groups (PPG) have been intensively studied in last few decades because they are an excellent tool for protection and easy deprotection of various functionalities.² *o*-Nitrobenzyl (*o*NB),³ *p*-hydroxyphenacyl (*p*HP)⁴ and *o*-methylphenacyl (*o*MP)⁵ chromophores are among the most widely used PPGs.⁶ To determine the scope and limitations of their utilization, we carried out a series of projects on their mechanistic and synthetic photochemical behavior.

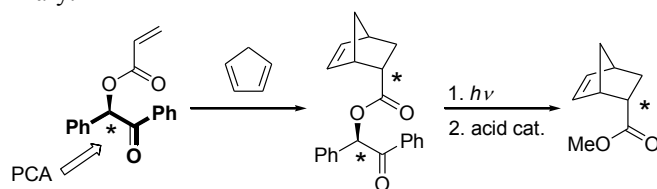
*o*NB has been shown as a promising and useful PPG for both aliphatic and aromatic diols, as well as mercaptoalcohols along with a study of the mechanism of its two-step deprotection.⁷



A clean bifurcation between a Type II photochemistry⁸ and photo-Favorskii rearrangement⁹ has been discovered in a chromophore combining *p*HP and *o*MP functionalities depending on water content in media.¹⁰ In addition an analogous reactivity of a *o*-hydroxy-*o*'-methylphenacyl PPG has been examined.



The desyl chromophore¹¹ is analogous to that of phenacyl, but contains an asymmetric carbon. We employed this chromophore as a “photoremovable chiral auxiliary” to introduce a new reagentless method for cleaving-off the chiral auxiliary.¹²



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