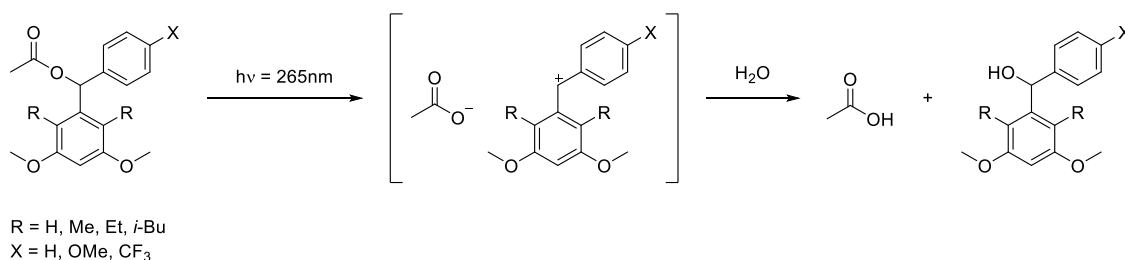


Mechanistic Studies on Photochemical Reactions: Can the Hammond Postulate be Applied to the *meta*-Effect ?

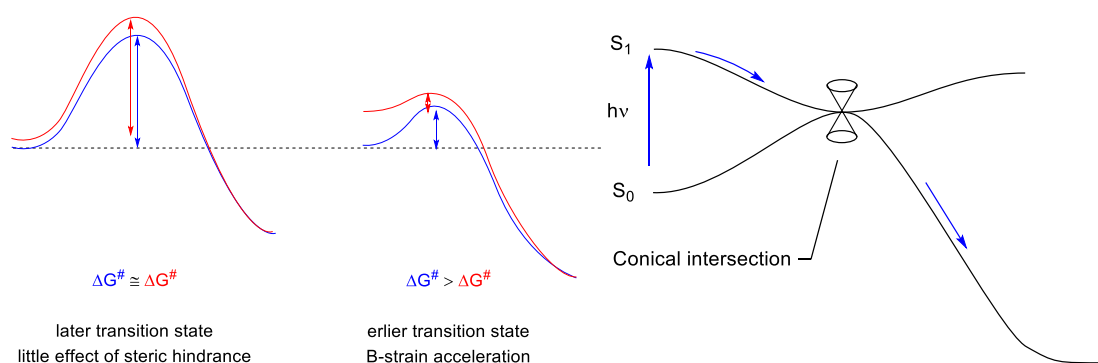
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Previous work in our group suggests that the Hammond postulate can be applied to Norrish – Yang type II reactions.¹ This project aims to expand this claim to other photochemical reaction, in this case, to *meta*-effect induced photo-solvolysis of benzylic esters. This effect, as described by Zimmerman and Sandel,² is a stabilization, in the excited state, of a benzylic cation with electron donating substituents on the *meta* positions. This cation being formed by the heterolysis of a benzylic ester. To probe for the Hammond postulate in this reaction, a series of photo-substrates, bearing alkyl groups with increasing steric hindrance on the *ortho* positions and different functional groups on a second para-substituted aryl group, is being synthesized, and is being subjected to UV-irradiation (**Scheme 1**). The quantum yield of these reactions is being measured. A high steric hindrance should facilitate the photo-solvolysis through B-strain release, and the substituents on the secondary aryl group have a stabilizing (EDG) or destabilizing (EWG) effect on the carbocation, allowing the tuning of the reaction profile. One can expect a larger effect of the steric hindrance on an early transition state than for a late one, should the Hammond postulate be applicable (**Scheme 2**). The spin state of the reaction is also being probed to determine whether the reaction goes through a more classical transition state or through a conical intersection.



Scheme 1. Photo-chemical reactions being performed



[1] C. G. Bochet, F. M. Harvey, **2021**, *Chemical Science*, 12(2), 599 – 605.

[2] H. E. Zimmermam, V. R. Sandel, **1963**, *J. Am. Chem. Soc.*, 85(7), 915 – 922.