

Further Investigations on Excited State Potential Energy Surfaces:

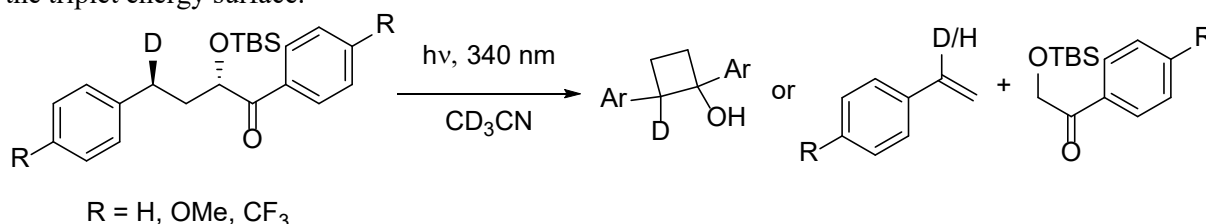
Can the Hammond Postulate be Applied to Photochemical Reactions?

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The Hammond postulate is a principle of the ground-state chemistry used to locate and estimate the structure of transition states along a reaction coordinate. It is based on the concept of a potential energy surface, which itself comes from the Born-Oppenheimer approximation.

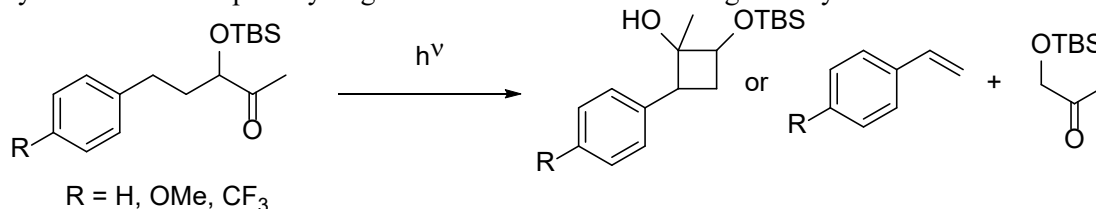
The Born-Oppenheimer approximation can fall through at Excited State Transition States (ESTS) and Conical Intersections (CI) in photochemistry. The concept of a single potential energy surface determining the structure is not valid at these points. As a consequence, the Hammond postulate has not been extended to the excited state until now.

In previous work on Norrish-Yang Type II photoreaction of γ -deuterated substrates with a deuterium atom *syn* or *anti* to a bulky OTBS group, our group observed that the Hammond postulate can be extended to the excited state for this family of reactions. However, we could not prove the applicability of the Hammond postulate to CI because we would need a reaction independent from the triplet energy surface.



Scheme 1: Norrish-Yang type II reaction previously investigated.

We imagined the following experiment (*Scheme 2*) as a start for further investigations on the applicability of the Hammond postulate for the CI in photochemistry. As for the previous work, the molecules can undergo a Norrish-Yang Type II photoreaction. The ratio between the product of the cyclisation and the photolysis gives us information about the geometry of the molecule at the CI.



Scheme 2: Norrish-Yang type II reaction investigated in this work.

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