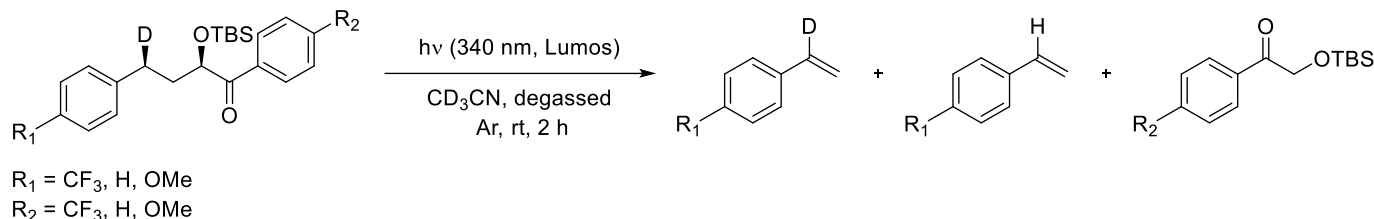


Further Investigations on Excited State Potential Energy Surfaces: Can the Hammond Postulate be Applied to Photochemical Reactions?

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Our group has been studying photochemical reactions for a long time. With the results obtained, we became interested in whether the Hammond Postulate could be extended to the excited state. To study this applicability, we designed a series of γ -deuterated arylketone photosubstrates, with a deuterium atom *syn* to a sterically hindered OTBS group. These photosubstrates were designed to undergo a Norrish-Yang type II photoreaction on the triplet Potential Energy Surface (PES) as depicted in **Scheme 1**.¹ Indeed, the conjugation of the aryl moiety with the carbonyl group lowers the $n\text{-}\pi^*$ singlet energy state, bringing it close to the triplet energy states. This leads to an almost effortless intersystem crossing from the S1 to the T1 PES.



Scheme 1 Photolysis of the γ -deuterated arylketone photosubstrates to form the fragmented photoproducts

Our hypothesis is that the ratio of the formed H:D styrene photoproduct will give us information about the geometry of the excited state transition state (ESTS). By altering the substituents on *para* position of the aromatic rings, the benzylic radicals will either be stabilized or destabilized, which will move the position of the ESTS along the photochemical reaction coordinate. This will influence the incorporation of the hydrogen atom in the α -position of the styrene moiety. Moreover, these photosubstrates will also be photolyzed, once in presence of triplet sensitizer (acetophenone), once with an excess of triplet quencher (piperylene) to probe the spin state of the reaction.

We have synthesized and photolyzed the arylketone photosubstrates and several conclusions could be drawn.² The modification of the aryl group close to the deuterium atom has a significant impact. The greater the electron density, the more the percentage of H-styrene incorporation tends towards 50%. Meaning that the ESTS turns more free-moving with growing electron density, and there is less preference for either H or D abstraction. Furthermore, the Norrish type II fragmentation reaction takes place only on the T1 PES. This is demonstrated by the significant, if not total, reduction in quantum yield when piperylene is present in the reaction medium. We have also performed the same experiments with the *anti* diastereoisomers to get a clear and complete picture of the project.

[1] C. G. Bochet, F. M. Harvey, *Chem. Sci.*, **2021**, 12(2), 599-605.

[2] F. M. Harvey, C. G. Bochet, *J. Org. Chem.*, **2020**, 85(11), 7611-7619.