Investigation of substituent effects on the photodecarboxylation of phenylacetic acid in aqueous solution

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Unsubstituted phenylacetic acid has been reported to undergo an inefficient photodecarboxylation ($\Phi < 0.01$) in the excited state to produce carbon dioxide and a benzyl radical through a homolytic cleavage. When phenylacetic acid is substituted with electron withdrawing groups (NO_2, COR), the photodecarboxylation occurs more efficiently and via a heteorolytic mechanism to give CO_2 and a benzylic carbanion. The benzylic carbanions produced are of interest because of their potential use as carbon-centered nucleophiles in synthesis. Additionally, a new class of photoremovable protecting groups (PPGs) has been developed that involve initial photodecarboxylation of a substituted phenylacetic acid to generate a carbanion intermediate that subsequently releases the leaving group. These PPGs boast several advantages including clean and efficient photochemistry, rapid release kinetics, and good aqueous solubility.

We have been interested in the chemistry of the intermediate carbanions since it is this chemistry that dictates both the release rates and 'cleanliness' of the PPGs. Depending on the intermediate carbanion involved, rates can range from the sub-nanosecond to several seconds range. In addition, we have been interested in finding new carbanion progenitors from which new PPGs can be designed. To this end, we have begun an exploration of phenylacetic acids bearing electron withdrawing activating groups beyond those already known. So far we have found very efficient ($\Phi > 0.5$) carbanion formation from phenylacetic acids containing CF_3, CN, and coumarinyl groups.

The present study focuses primarily on the investigation of the photochemistry of a number of additional phenylacetic acids: 4-sulfonylphenylacetic acid and 3-formylphenylacetic acid in neutral aqueous solution. 4-sulfonylphenylacetic acid was prepared by sulfonation of phenylacetic acid, and 3-formylphenylacetic acid was made by reduction of 3-cyanophenylacetic acid using Raney Nickel. The photochemistry of these compounds was explored using UV-Vis, NMR and GC-MS techniques and both undergo efficient photodecarboxylation. Our results indicate that the ionic pathways to produce the toluene derivatives were generally preferred. Characterization of reactive intermediates using LFP was attempted and compared with available data for related systems.