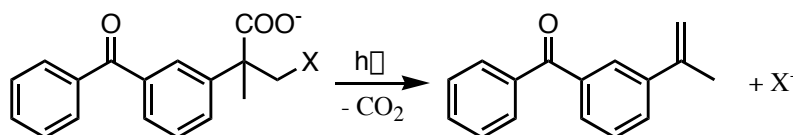


Toward an improved photocage: photodecarboxylation of xanthone-acetic acids.

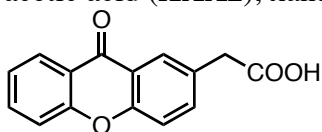
E. Gagnon, M. Lukeman, J.C. Scaiano, Department of Chemistry, University of Ottawa, Ottawa, On.

Ketoprofen, a commercial non-steroidal anti-inflammatory drug (NSAID) contains a benzoyl group meta to the phenyl propionic acid. This particular functional group arrangement shows great photoreactivity: upon irradiation in neutral aqueous media, carbon dioxide is released and a carbanion is generated. This highly reactive intermediate is rapidly ($k \approx 10^7 \text{ s}^{-1}$) protonated by water. Indeed, this reactivity has been shown to be general for other compounds with similar functional group arrangements. Recent work in the Scaiano lab has shown that if a leaving group is strategically positioned on a carbon adjacent to the photogenerated carbanion, it can be eliminated by an elimination mechanism:

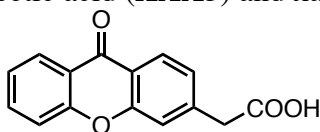


A drawback associated with using benzophenone-based molecules to achieve photorelease is their weak absorption in the UV-A region. It was the purpose of this project to find compounds with similar reactivity but better UV-A absorption characteristics. This would facilitate *in vivo* application since light can penetrate deeper at longer wavelengths. Our choice of the xanthone moiety as the chromophore was motivated considering many factors: they possess suitable absorbance characteristics, their synthesis was feasible in a realistic timeframe, and some derivatives are known to show biological activity against certain kinds of tumor.

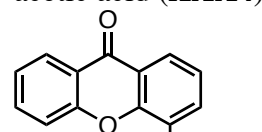
This presentation will discuss the synthesis of three isomeric derivatives: xanthone-2-acetic acid (**XAA2**), xanthone-3-acetic acid (**XAA3**) and xanthone-4-acetic acid (**XAA4**):



XAA2



XAA3



XAA4

We found that XAA2 and XAA4 efficiently photodecarboxylate in aqueous media with high quantum yield ($\Phi = 0.6-0.7$) whereas XAA3 is photochemically inert. The mechanism of their reactivity has been examined by product studies, fluorescence and laser flash photolysis and a mechanism describing the behavior of the three isomers that is consistent with all available data is presented.