

Exploring the photochemistry of lithiated enolates

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Photochemistry has enjoyed a prominent spike in publications in the past decade, mainly as a result of the growing accessibility of low-cost, more energy-efficient LED lamps. Our group has previously capitalised on these energy-efficient LEDs, employing the thermally unstable polycyclic enolate in the enantioselective synthesis of cycloheptatrienes through photochemical transformations. Now, we want to expand this chromoselective transformation, utilising various enolate chromophores to facilitate LED-initiated photochemical reactivity. This should lead to a wider understanding of which atomic, steric and electronic factors are required for photochemical transformations derived from those previously reported by the group.

This photochemistry has recently been expanded into acyclic enolate amides, where nitrogen to carbon shift of a benzyl has been shown to occur under photochemical irradiation to give three migration products from reactivity across the trienolate.

This migratory process may also be used in the ring-contraction of a five-membered lactam, where a cyclopropyl ring is formed from simple deprotonation and irradiation of a conjugated system. With this new photochemistry in hand, we are aiming to facilitate the ring-contraction of even larger ring sizes, while further exploring the photochemical reactivity of different, non-cyclic enolates of similar conjugation.

We hope that the unusual chemistry presented could eventually be used to enable facile synthesis of products from conjugated enolates and organolithiums, in particular for the synthesis of novel molecular scaffolds which may otherwise require transition metal-mediated catalysis for their formation.

Biography

James Mortimer is a second-year PhD student in the group of Prof. Jonathan Clayden at the University of Bristol, UK. His research has a focus on the visible-light photochemistry of conjugated enolates, which our group has shown to undergo an interesting photochemical migration across an extended chromophore. He obtained his first-class MChem degree from the University of York with a year working at AstraZeneca and is currently a STEM ambassador, with an interest in engaging young students in the study of light and photochemistry through interactive means.

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