Abstract

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Photochemistry is a core methodology within modern day organic chemistry. It often enables alternative or complimentary chemistry to traditional reactivity but under milder and greener conditions and therefore is highly desirable.

The carbonyl moiety is ubiquitous within organic chemistry and is a constituent of many fundamental functional groups such as esters, aldehydes and amides. In classical chemistry, α-functionalisation of carbonyl compounds is easily achieved by displacing heteroatoms, for example, the conversion of acyl chlorides to carboxylic acids, however, α-functionalisation of alkyl groups is typically restricted to enolate-derived reactions. Photochemical methods have enabled a wide range of new reactivity within organic chemistry and are also highly relevant in the α-functionalisation of carbonyl compounds. In this context, direct irradiation of diazo compounds, primarily phenyl diazoacetates, within the last decade have been found as a convenient source of singlet carbenes, which can then undergo reactivity such as cycloadditions, X-H insertions and ylide generation.

The main objective of my work was to explore new reactivity of photochemically generated carbenes and radicals towards the construction of C-C and C-X bonds at the α-position to the carbonyl moiety.

Four publications are included as part of the doctoral thesis. The first paper is a book chapter that encapsulates all of the known reactions that utilise photochemically generated carbenes, primarily from diazo compounds but also from silyl ketones that undergo Brook rearrangement to form α-silyloxy carbenes.

The second publication discusses a photochemical cyclopropanation of diazo compounds in a micellar medium, which enables the usage of carbenes in an aqueous environment. We could also generate diazo compounds in-situ from hydrazones with the addition of a base, which yielded the cyclopropane typically in diminished yields but much higher diastereoselectivity.

The third publication describes the first instance of 4-diazoisoquinoline-1,3(2*H*,4*H*)-diones being employed in a photochemical context, which facilitate O-H, S-H and C-H insertion reactions. In addition, I reported the first synthesis of a new group of diazo compounds, namely 4-diazo-2*H*-benzo[e][1,2]thiazin-3(4*H*)-one 1,1-dioxides, and explored their reactivity under violet light irradiation.

The final paper, in collaboration with Dr. Geraldine Masson and Dr. Luc Neuville, reports a photochemical HAT reaction with chiral *N*-sulfinyl imines to synthesise highly diastereoselective amines. Removal of the sulfinyl group brandishes the unprotected amine in 99% ee.

In summary, I have described new bond forming reactions via the generation of reactive intermediates, namely carbenes and radicals, at the α-position to the carbonyl moiety. The majority of my work utilised diazo compounds, which are convenient sources of carbenes and undergo atom efficient reactions without the need for a photocatalyst.