

## My life with light

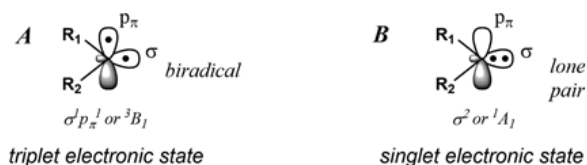
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I sincerely thank Dr. Ranmal Gunatilake, Hon. Editor, Institute of Chemistry Ceylon for the opportunity to address the Chemistry in Sri Lanka readers through the medium of this guest editorial. It is a real honor and pleasure for me. Herein, I would like to share with you the unprecedented results of my scientific research, life with light.

The ability to access the divergent reactivity of organic molecules by thermal or photochemical control was exquisitely described by Woodward and Hoffmann in a series of papers dating back to 1965. From this work, the so-called “Woodward–Hoffmann rules” established a distinction between the stereospecificity observed under thermal and photochemical control based on the topology of orbital interactions. In parallel to these findings, advances in quantum mechanics and molecular orbital theory helped to delineate the dichotomy between the structure and reactivity of the triplet and singlet ground-state carbenes. While the origin of triplet carbenes date back to the early 1800s when Dumas attempted to dehydrate methanol, the existence of singlet carbenes was first elucidated in the late 1950s by Breslow and Wanzlick (Figure 1).

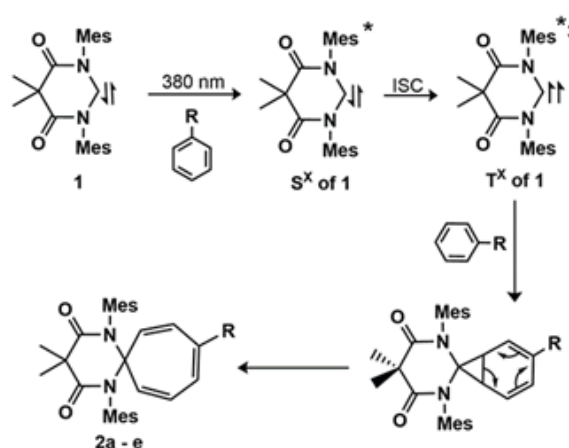


**Figure 1:** Electronic spin states of triplet (A) and singlet (B) carbenes.

Despite numerous modifications to the structure of singlet and triplet carbenes, there has been a minimal

success in preparing isolable triplet analogs, or singlet carbenes that display triplet reactivity (Figure 2).

The discovery of thermal and photochemical control by Woodward and Hoffmann revolutionized how we understand chemical reactivity. Similarly, we were able to show the first example of a carbene that exhibits differing thermal and photochemical reactivity. When a singlet ground-state N,N'-diamidocarbene (DAC) **1** was photolyzed at 380 nm, excitation to a triplet state was observed. The triplet-state electronic structure was characteristic of the expected biradical  $\sigma^1\pi^1$  spin configuration according to a combination of spectroscopic and computational methods. Surprisingly, the triplet state of **1** was found to engage a series of arenes in thermally reversible Büchner ring expansion reactions, marking the first examples where both cyclopropanation and ring expansion of arenes were rendered reversible.<sup>4</sup> Not only are these photochemical reactions different from the known thermal chemistry of **1**, but the reversibility enabled us to perform the first examples of photochemically induced arene exchange/expansion reactions at a single carbon center.



**Figure 2:** Proposed mechanism for the formation of **2a-e**

We have revised the long-standing precept that stable, isolable carbenes exist as a singlet ground state whereas transient carbenes are typically regarded as triplet ground-state carbenes, showing that it is no longer

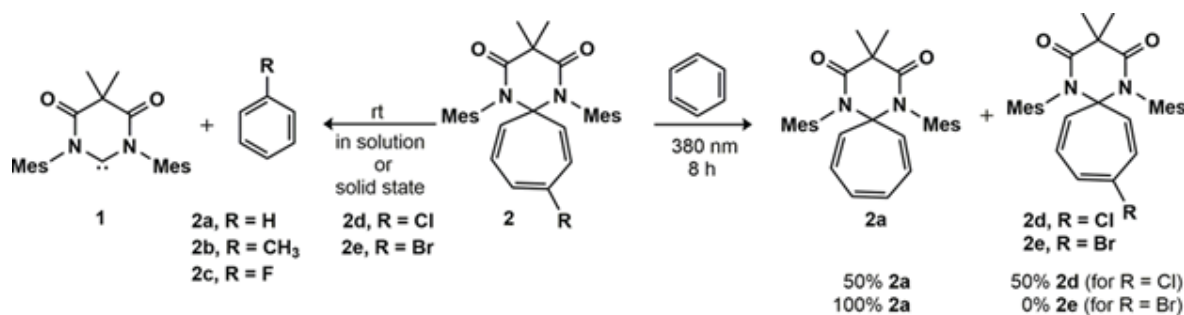


Figure 3: Reversibility of Büchner ring expansion reactions

valid. We reported that both spin states (and attendant reactivity) are accessible for the diamidocarbene **1**. While **1** is isolated as a highly stable singlet electronic ground-state, carbene photolysis at 380 nm allows for the rapid conversion through intersystem crossing to an excited triplet state. The triplet excited state of **1** has been fully characterized through a combination of low-temperature spectroscopic measurements and computational analyses. These studies indicate that the excited state of **1** can be characterized as the expected spin-unpaired biradical structure, typical of triplet carbenes. The triplet excited state of **1** was also found to engage a series of aromatic compounds in the known Büchner ring expansion reaction to cleanly afford a single cycloheptatriene isomer in all cases (**2a–2e**) (Figure 3). Remarkably, the photochemical reaction of **1** with benzene or toluene provided drastically different products than the known thermal products (which forms the from C–H activation processes) reported by Bielawski. In this regard, we equate the two distinct reactivity profiles of **1** as photochemical and thermal control like what Woodward and Hoffmann described for pericyclic electrocyclic reactions.

Beyond the novelty of accessing the triplet excited state of DAC **1**, the subsequent Büchner ring expansion reactions were found to exhibit unprecedented reversibility, even in the solid state for some derivatives. This unique feature provided the first examples where both cyclopropanation and ring expansion reactions were rendered reversible, enabling the ability to interconvert **2d** or **2e** into **2a** through atom-economic, high-fidelity photochemical reactions. The surprising discoveries presented herein are likely to initiate new fundamental studies and expand the applications of stable carbenes. Similar to other reversible ring-forming reactions, such as the Diels–Alder reaction, reversible Büchner ring expansion processes may also

find applications ranging from structurally dynamic materials to novel methodologies in organic synthesis as the cycloheptatriene motif is commonly found in biologically active molecules.

College of Chemical Sciences is home, a place very close to my heart. Whenever I think of CCS, it reminds me of three things: vibrant schedule, great friends and amazing teachers. Speaking of amazing teachers, Late Emeritus Prof. J N O Fernando, Prof. S P Deraniyagala, Mr. Mevan Pieris, Dr. Sisira Weligamage, Prof. S Sotheeswaran, Prof. S A Deraniyagala, Prof. H D Gunawardhana, Prof. M D P De Costa and Mr. M R M Haniffa are few of many teachers who have made a distinct impression in my mind. I'm forever grateful to them for their guidance, help, support and best wishes.

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