Pablo Wessig

Preparative Organic Photochemistry

Our research group is working on several areas of *Preparative Organic Photochemistry*. The photochemical preparation of organic compounds differs from other methods in that the energy is supplied by irradiation instead of heating. By this way a reaction course can be achieved, which often differs substantially from that of thermal reactions. Furthermore, owing to the high energies supplied to a molecule by photochemical excitation, highly strained and reactive products can be obtained.

Currently we are working mainly in three research areas:

- The *Norrish-Yang* reaction
- The *Spin-Center Shift* in photochemically generated biradicals
- The *Photo-Dehydro-Diels-Alder* reaction.

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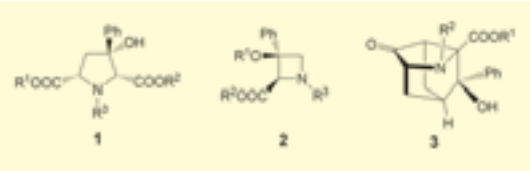

Fig. 1
Unnnatural amino acids that were prepared in our group

The *Norrish-Yang* reaction comprises the photochemical excitation of ketones, followed by an intramolecular hydrogen migration and the formation of biradicals. These highly reactive intermediates, the lifetimes of them are only few nanoseconds, can form a new carbon-carbon-bond and thus providing cyclic products. We have applied this reaction on the synthesis of unnatural amino acids, which are interesting building blocks for peptide research. Fig. 1 shows three unnatural amino acids (1-3) that were prepared in our group. [1-3]

The *Spin-Center Shift* is an approach, developed in our group, which considerably widens the scope of the *Norrish-Yang* reaction. It is based on the idea to alter the position of one of the radical centers of the intermediate short-lived biradicals by means of a very fast process and, consequently, alter the size of the rings in the obtained cyclization products. We have chosen the elimination of acids in hydroxysubstituted radicals A, bearing a leaving group at the adjacent carbon atom. By this method we prepared cyclopropanes 4, oxazinones 5 and indanones 6 (Fig. 2). [4-6]

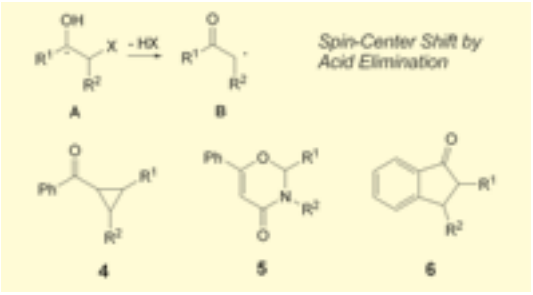

Fig. 2
Spin-Center Shift by Acid Elimination

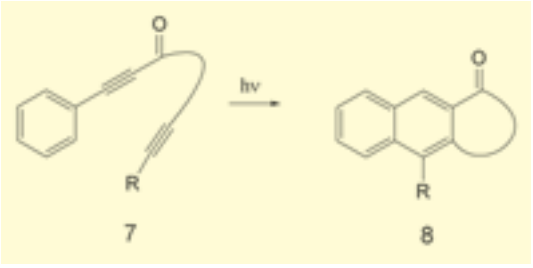

Fig. 3
Photo-Dehydro-Diels-Alder reaction

The *Photo-Dehydro-Diels-Alder* reaction is our third research area. Recently, we found that 1-acyl-2-arylacetylenes, bearing a second acetylene moiety in the same molecule (7), undergo on irradiation a cycloaddition to naphthalenes 8. Currently, we are investigating the synthetic scope of this interesting reaction (Fig. 3).

Präparative Organische Photochemie
Unsere Gruppe beschäftigt sich mit präparativer organischer Photochemie. Photochemische Methoden zur Synthese organischer Moleküle besitzen verglichen mit thermischen Methoden eine Reihe von Besonderheiten, wodurch oftmals ein deutlich anderer Reaktionsverlauf erreicht wird. Darüber hinaus sind durch die großen Energiebeträge, die bei der Bestrahlung zugeführt werden, hoch gespannte und reaktive Moleküle zugänglich. Gegenwärtig arbeiten wir hauptsächlich auf den Gebieten *Norrish-Yang*-Reaktion, *Spinzentrenverschiebung* und *Photo-Dehydro-Diels-Alder-Reaktion.*

References

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