

# PHOTOCYCLOADDITION OF CONJUGATED ENYNES AND ITS APPLICATION IN NATURAL PRODUCTS SYNTHESIS

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## Abstract

Aromatic 2-pyridones and 2-pyrones are known to undergo a facile [4+4] photocycloaddition with themselves and other conjugated molecules. The unifying objective of this work is to explore the potential of conjugated enynes as a photocycloaddition partner with a variety of unsaturated systems and establish it as a path for the synthesis of valuable natural products and molecular scaffolds. With a 1, 3-enyne as a reactant, the immediate photocycloadduct, a highly strained cyclic allene, was stabilized and functionalized to give advanced intermediates in natural product synthesis. Participation of substituted benzenes in higher order photocycloaddition with 2-pyridones was also discovered.

Intramolecular enyne-pyridone [4+4] photocycloaddition led to the formation of cyclic, strained allenic products that undergo rapid dimerization through various modes leading to complex mixtures. Such allene-allene dimerization was suppressed by introducing steric shielding. With reactive tethered functional group present, the intermediate allene can undergo a secondary cycloaddition with either the proximal or distal double bond, depending on the tether length. In the absence of such functional groups, the allene can isomerize to a 1,3-diene. Oxidation of the allene led to a cyclopropanone, a bicyclo-[5.1.0]-octane, which was transformed into pseudoguaiane-like 7-5 ring systems.

Participation of enynes in the photocycloaddition of other unsaturated systems was also investigated. Anthracene, naphthalene derivatives and 2-pyrones were all found to undergo quantitative photocycloaddition with an enyne. During this investigation, a low temperature Cope rearrangement was also discovered. In addition, meta-substituted benzenes were reluctant partners in [4+4] photocycloaddition with enynes but underwent efficient [4+4] photocycloaddition with 2-pyridones.

The synthetic utility of enyne photocycloaddition was applied in the synthesis of the cyclooctanoid containing natural product, (+)-dactylo. The intramolecular enyne – 2-pyrone [4+4] photocycloaddition-isomerization gave a lactone bridged-cyclooctanoid product which serves as an advanced intermediate for sesquiterpene synthesis.