

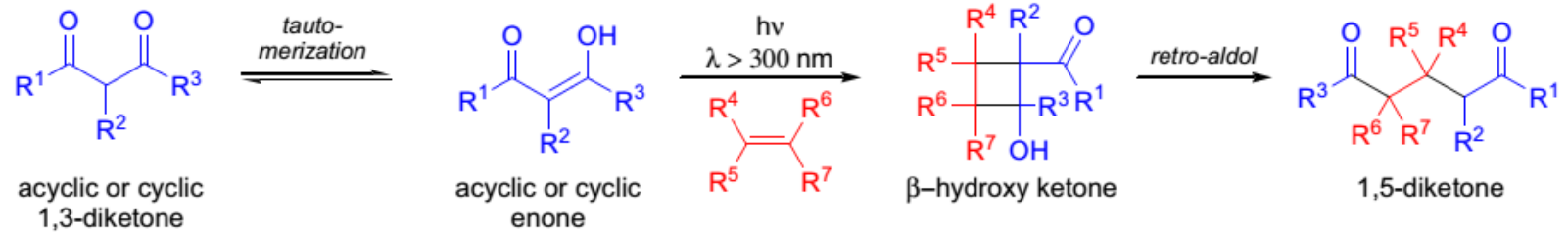
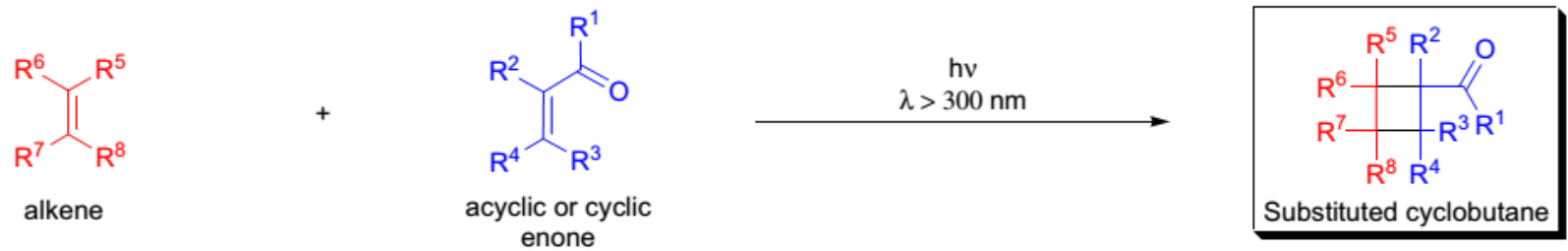
DE MAYO CYCLOADDITION (ENONE-ALKENE
[2+2] PHOTOCYCLOADDITION)

Introduction



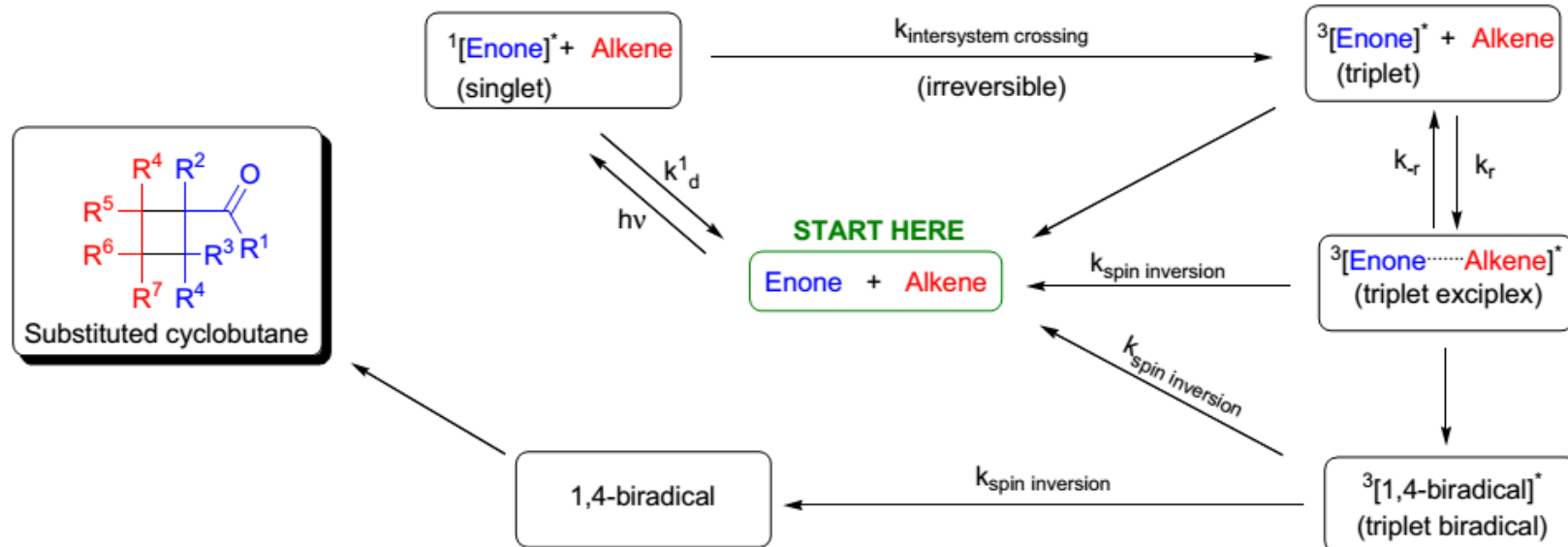
Dr. Paul de Mayo August 8, 1924-July 26, 1994

The photochemical [2+2] cycloaddition of enones (α,β -unsaturated carbonyl compounds with alkenes) is known as the de Mayo cycloaddition.



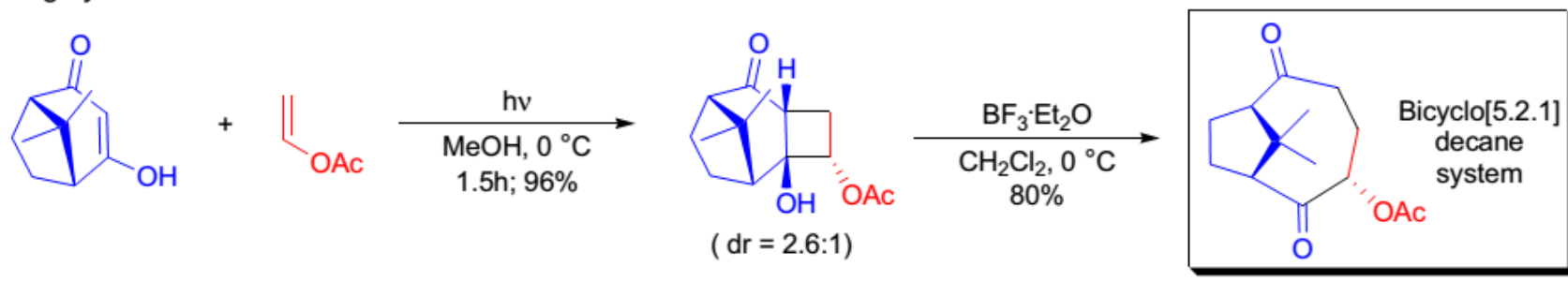
Mechanism

The mechanism of the *enone-alkene* [2+2] photocycloaddition presumably follows the scheme below. Upon irradiation: 1) a triplet exciplex is irreversibly formed from the triplet enone and ground state alkene; 2) the triplet exciplex collapses to one or more 1,4-biradicals.; 3) the biradicals either cyclize to the cyclobutane or revert to starting materials; and 4) the biradical reversion decreases the overall efficiency of the process.



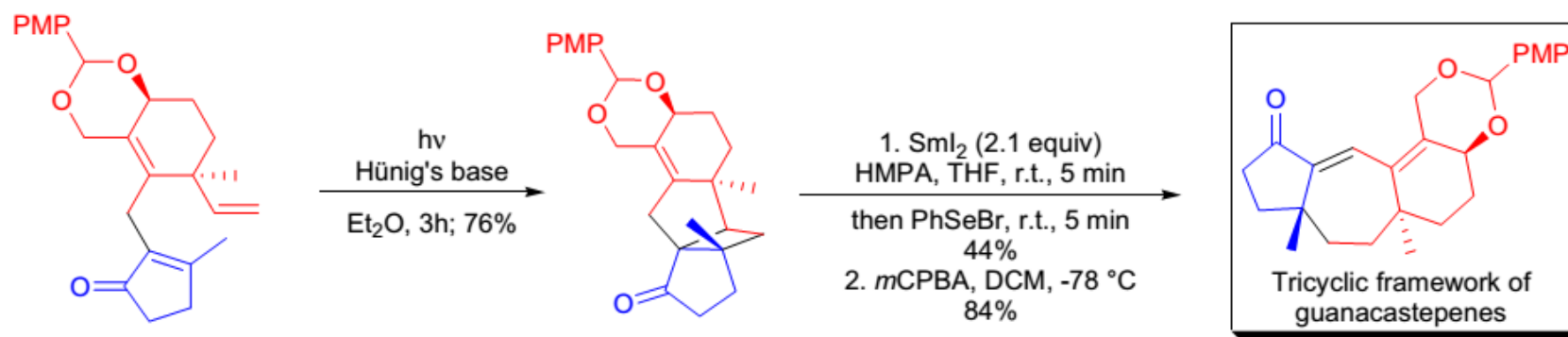
Synthetic Applications

During the early 1990s, the research group of M. Fetizon was developing novel methods for the synthesis of taxane diterpenes.²⁹ Their goal was to construct the AB ring skeleton of taxol. The construction of the **bicyclo[5.2.1]decane system** was realized by the *intermolecular de Mayo cycloaddition* of an enolized bicyclic 1,3-dione and vinyl acetate followed by a *Lewis acid catalyzed ring opening reaction*. The methanolic solution of the β -diketone and vinyl acetate was irradiated ($\lambda > 245$ nm) at 0 °C and a mixture of diastereomers was formed in excellent yield. The *retro-aldol reaction* was effected by treatment with BF_3 etherate in dichloromethane to afford good yields of the desired bicyclic ring system.

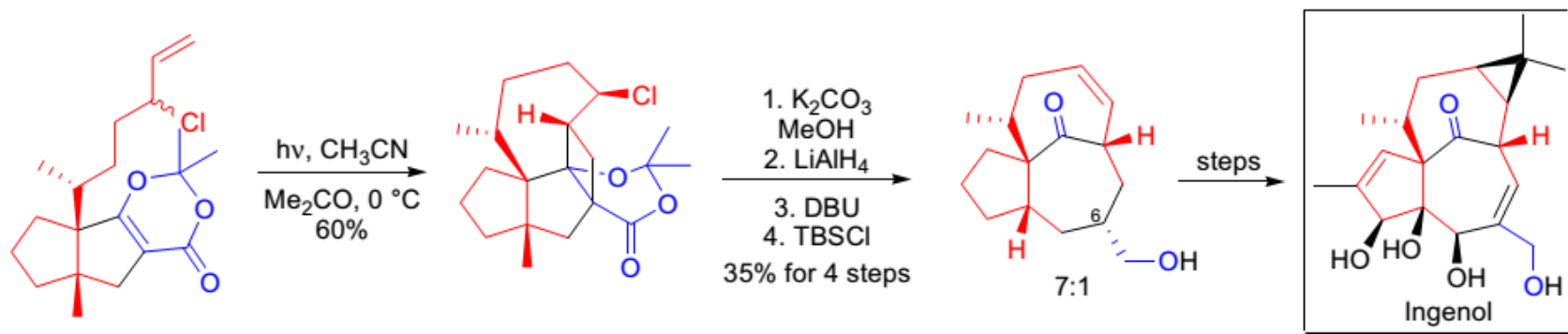


Synthetic Applications

E.J. Sorensen and co-workers have synthesized the tricyclic carbon framework of [guanacastepenes](#) by applying an *intramolecular [2+2] photocycloaddition* followed by a SmI_2 -induced fragmentation as key steps.³⁰ The enone was irradiated to effect an *intramolecular enone-olefin [2+2] cycloaddition* to afford the desired cyclobutyl ketone in 76% yield. The cyclobutane fragmentation was achieved by treatment with SmI_2 and the resulting Sm(III) enolate was trapped with a selenium electrophile. The double bond in the seven-membered ring was introduced by the oxidation of the selenium with *mCPBA*.



The first total synthesis of (\pm)-ingenol was accomplished in the laboratory of J.D. Winkler.³¹ In order to establish the highly unusual C8 / C10 *trans* ("inside-outside") intrabridgehead stereochemistry of the BC ring system of the natural product, a *dioxenone-alkene intramolecular [2+2] photocycloaddition-fragmentation* sequence was employed. The photocycloaddition of the allylic chloride with the tethered dioxenone proceeded in 60% yield. The fragmentation was induced by methanolic potassium carbonate, followed by LAH reduction of the ester, elimination of the chloride with DBU, and silylation of the primary alcohol with TBSCl. The yield was 35% over four steps and the product was a 7:1 mixture of epimers at C6.



A scenic photograph of a calm lake reflecting the sky and surrounding greenery. In the background, a tall, modern building is visible through the trees. The text "Thank you" is written in a large, stylized, purple cursive font across the center of the image. The entire scene is framed by a purple border at the top and a light brown textured border on the right and bottom.

Thank you