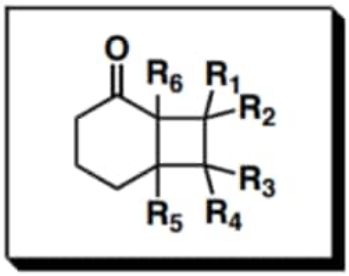
Enone Photochemistry:

Fundamentals and Applications

Significance

Why should we be interested in enone photochemistry?

1. It is theoretically interesting.
2. For its synthetic utility:
    i) Efficient cyclobutane synthesis;
    ii) Regiochemical control;
    iii) Predictable stereochemistry at the ring fusion(s);
    iv) Great method for accessing medium sized rings *via* fragmentation.



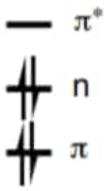
Mechanism, Part 1

What happens when an enone is irradiated with UV radiation?

If the radiation is of appropriate wavelength (i.e. frequency, energy), excitation will occur.

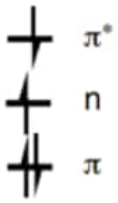
$$E = h\upsilon = (h\lambda) / c$$

ground state configuation



$^1(\pi^2n^2)$

first excited state



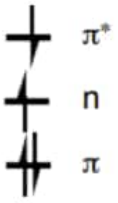
$^1(\pi^2n^1\pi^{*1})$

What next?

An enone in the first excited state (singlet) can:

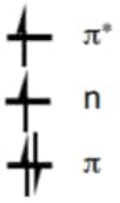
1. Return to the singlet ground state (fluorescence);
2. Undergo internal conversion to the ground state *via* "trickle down" energy loss;
3. Undergo intersystem crossing (ISC; a.k.a. spin flip) to give the lower energy triplet and proceed to the next step of product formation;
4. Skip ISC altogether and proceed to the next step.

first excited state (singlet)



$^1(\pi^2 n^1 \pi^{*1})$

first excited state (triplet)



$^3(\pi^2 n^1 \pi^{*1})$

Mechanism, Part 3

The excited enone (triplet state) can proceed to the next set of events:

1. Exciplex formation with the alkene.

The exciplex has a lifetime of 10 to 100's of ns. In this time it can:

1. Initiate carbon-carbon bond formation at *either* the α or β carbon of the enone;
2. *Revert to starting materials. All intermediates up to the 1, 4 diradical are suceptible to this process.*

If the diradical survives long enough, it may revert to a singlet state *via* ISC to give an excited singlet state which can then form the second bond and give the product.