Enone Photochemistry:
Fundamentals and Applications
Initial Discovery

Ciamician and Silber were the first to report a $2 + 2$ light-induced cycloaddition in 1908:

\[
\text{carvone} \xrightarrow{\text{Italian sunlight, one year}} \text{camphorcarvone}
\]

Buchi and Goldman confirmed the structure originally proposed for camphorcarvone in 1957.

Ciamician, G.; Silber, P. *Ber.*, **1908**, *41*, 1928.
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.

\[ E = h\nu = \frac{\hbar \nu}{c} \]

ground state configuration

first excited state

What next?

Schuster, D. I. "The Photochemistry of Enones," (p. 629-635) in:
Mechanism, Part 2

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.

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 \( \text{ } \) or \( \text{ } \) carbon of the enone;

2. Revert to starting materials. All intermediates up to the 1, 4 diradical are susceptible 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.

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Evidence for Similar Rates of Initial Bond Formation, Part 1

Evidence for Similar Rates of Initial Bond Formation, Part 2

Regioselectivity, Part 1

Regioselectivity, Part 2

Corey’s exciplex model correctly predicts regiochemical outcomes:

Regioselectivity, Part 3

Other factors that affect regiochemistry:

1. Less polar solvents favor products predicted by the Corey exciplex model;
2. Lower temperatures have the same effect;
3. In general, two to four membered tethers set regiochemistry. Examples:

Stereochemistry, Part 1

General considerations:

1. Cyclopentenones and smaller enones give *cis* fused products;
2. Cyclohexenones give significant amounts of *trans* product;
3. Strained enones or strained cyclobutane products preclude *trans* products;
4. *trans* Fused products are easily epimerized to *cis*.

Total Synthesis, Part 1

Total Synthesis, Part 3

Total Synthesis, Part 4

Total Synthesis, Part 5

Main Contributors to Enone Photochemistry's Development

P. E. Eaton: discovered that cyclopentenone and cyclopentadiene reaction under photochemical conditions; synthesized cubane to exemplify utility.

E. J. Corey: established the usual stereochemistry of 2 + 2 photochemical cycloadditions; advanced the notion of an exciplex to explain regioselectivity.

P. de Mayo: established that intermolecular 2 + 2 was feasible; invented a method for the preparation of 1, 5 dienes by photochemical means, postulated that the first triplet state is the reactive one in enones; found that intermediates could revert to starting materials.

D. I. Schuster: determined lifetimes of reactive intermediates thereby disproving Corey's exciplex mechanism; in particular, he determined that rate constants for enones triplet quenching were previously overestimated; proved that enone triplets were reactive intermediates.

A. C. Weedon: determined that regioselectivity is governed by diradical lifetimes.

H. E. Zimmerman: explained triplet electronics and reactivity using HMO theory.

G. S. Hammond and N. J. Turro: carried out experiments that suggested enone triplets were reactive intermediates.