Lecture XIII: Organic Photochemistry, continued

1. Bimolecular photophysical processes
2. Photochemical electrocyclizations
3. Photochemical cycloadditions
4. Photochemical [1,3]-shifts

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① What happens when a molecule in its excited state interacts with another molecule in a ground state?

A) Quenching – most common outcome. For excited-state ketones, both EWG and EDG alkenes are efficient quenchers. Quenching is a radiationless energy transfer from S_1 to S_0 of a different molecule.

B) Exciplex formation:

$$A \xrightarrow{h\nu} A^* \xrightarrow{B} [A\cdots B]^* \longrightarrow \text{emission}$$

$$A \xrightarrow{h\nu} A^* \xrightarrow{A} [A\cdots A]^* \quad \text{(exciplex)}$$

$$A \xrightarrow{B} A\cdots B \xrightarrow{h\nu} [A\cdots B]^* \quad \text{(excimer)}$$

absorption complex

C) Photoinduced ~~energy~~ electron transfer (PET) – excited state is both easy to oxidize and easy to reduce. It has a hole in its HOMO and 1 electron in its LUMO – It can easily transfer an $e^\ominus$ onto an acceptor, or take one from the donor.

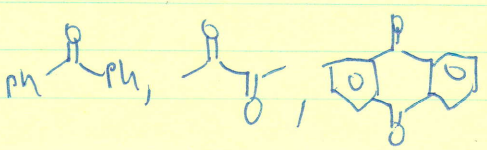
D) Energy transfer $D \longrightarrow D^* \xrightarrow[-D]{A} A^*$

This process can be: radiative ET: D emits, A absorbs. but more commonly: Collisional ET: mixing of A and D^* wavefunctions this form drop off quickly (exponentially) with distance between A and D^*

often used to create triplet states of molecules:

$$^3D^* + A \longrightarrow {}^3A^* + D$$

sensitizer ↗ ↖ spin conservation

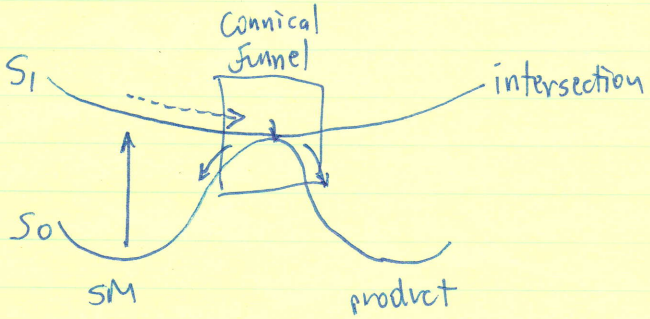


Common sensitizers

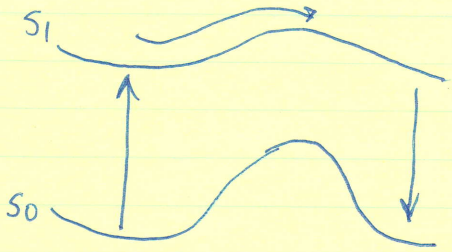
Förster energy transfer – coupling of two transitions, not necessarily wavefunctions. Can occur over large distances, but the energies must be somewhat matched, which means that the emission spectrum of D* and absorption spectrum of A must overlap to some extent. This is the basis of FRET (p. 960-961 in Anslyn & Dougherty).

(2) Photochemical reactions: inversion of Woodward-Hoffman rules

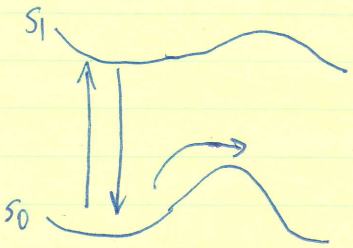
Theory:



Excitation "dumps" reactants onto the transition state



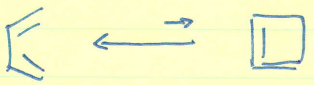
adiabatic process
only a single energy surface (S_1) is involved



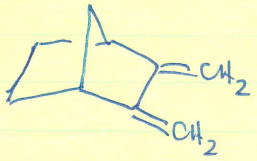
hot-atom process
thermal reaction caused by excess vibrational energy of SMs occurs from S_0

diabatic process – two energy surfaces involved

Electrocyclizations:



⟷ thermally unfavorable, since II is less stable, but



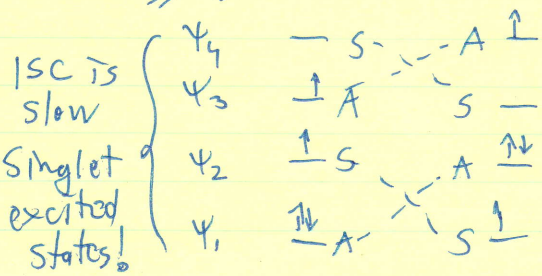
$h\nu > 200nm$ →

cyclobutenes and butadienes absorb in different regions

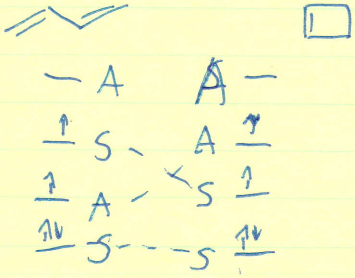
Fixed in S-cis

conrotatory

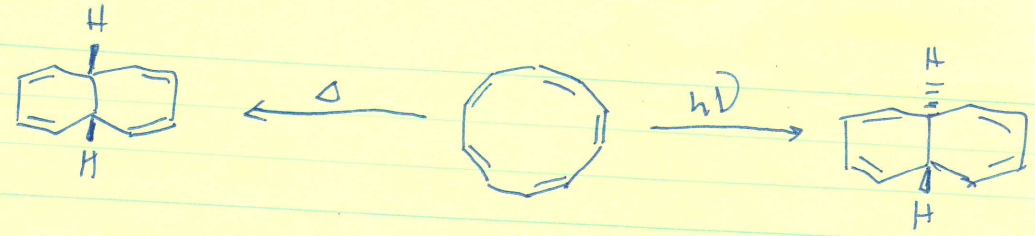
II

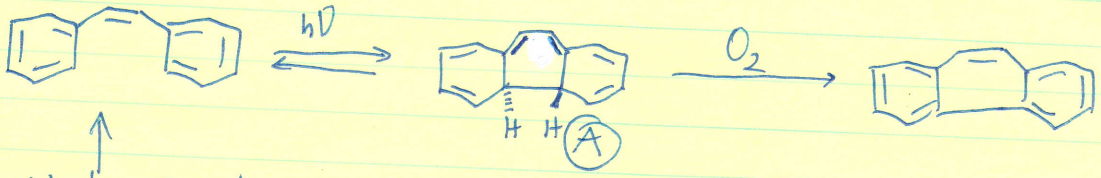


disrotatory

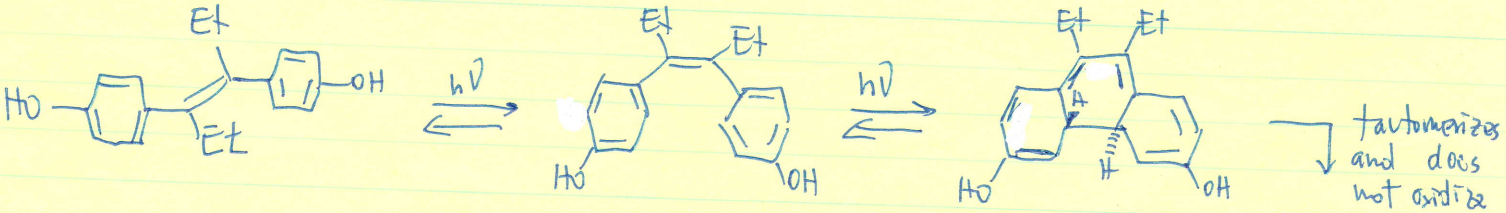


This is now favored!

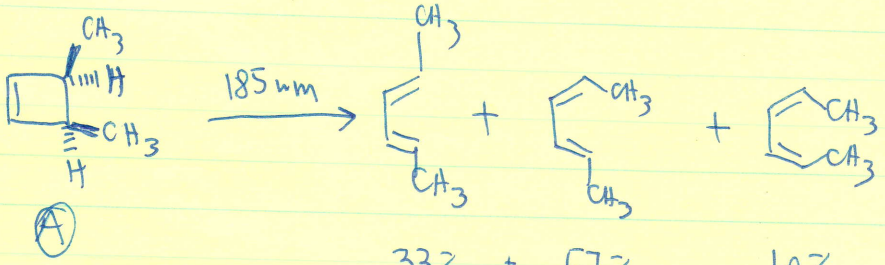




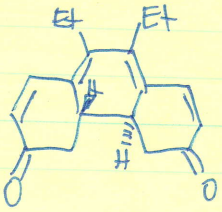
could be viewed as 6π, 10π, 14π } => ALL conrotatory. But how do you prove it? (A) is almost impossible to isolate?



But things are not always stereospecific:



33% + 57% 10%

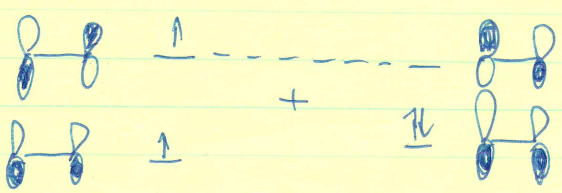


this could be for a number of reasons: (A) not reacting from an excited state, or products rearranging!

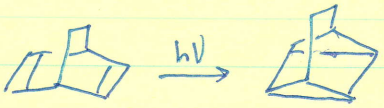
(3) Photochemical cycloadditions

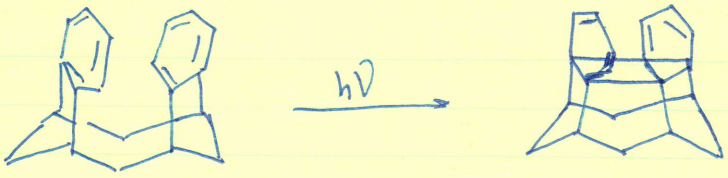
$A^* + D \longrightarrow$ ... never $A^* + D^* \longrightarrow$

2+2 allowed, 4+2 forbidden!

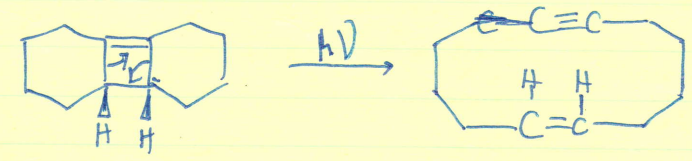


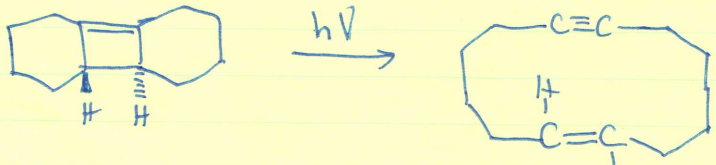
Reaction is fast, but going back to ground state is faster - a lot of irradiation is required; Low quantum yield of cyclizations → but in close proximity:



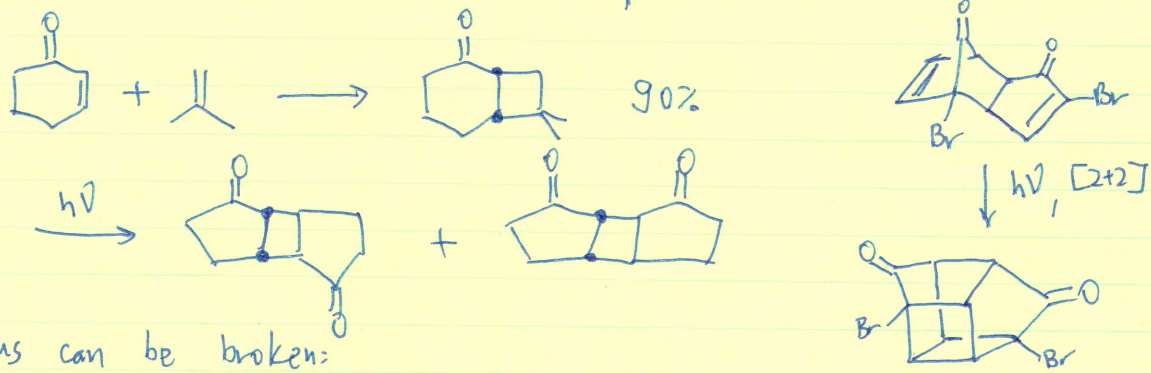


Cycloreversions proceed suprafacially:

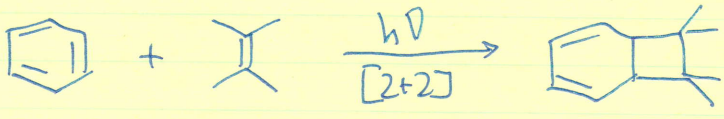


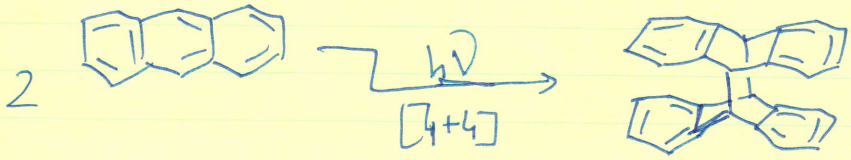


Alkene singlets are short-lived, but triplets are not. Easier cycloadditions, in the presence of sensitizers. This also helps in rxns with α/β-unsaturated ketones:



Even aromatic systems can be broken:





(4) Photochemical [1,3]-shifts

Although in principle these should work too, most examples go through triplet excited states. In these cases, orbital conservation rules are irrelevant. However, sometimes singlet states react suprafacially, as expected: