



Photochemistry of Alkenes and Alkynes

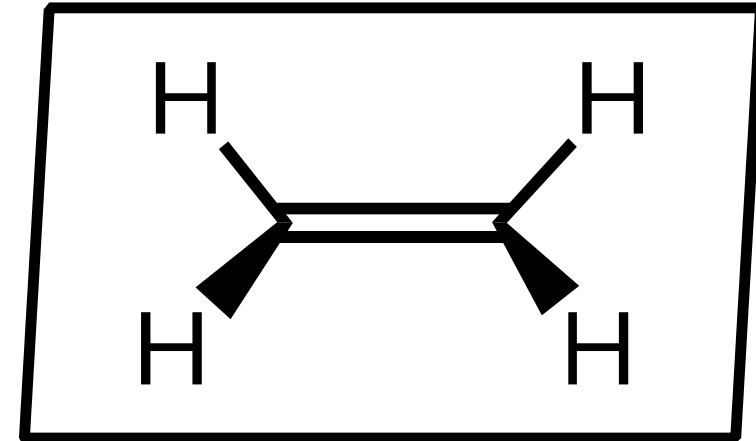
Molecular Photochemistry

CHEM 4801

Structures and General Dynamics of Alkene (π, π^*) States

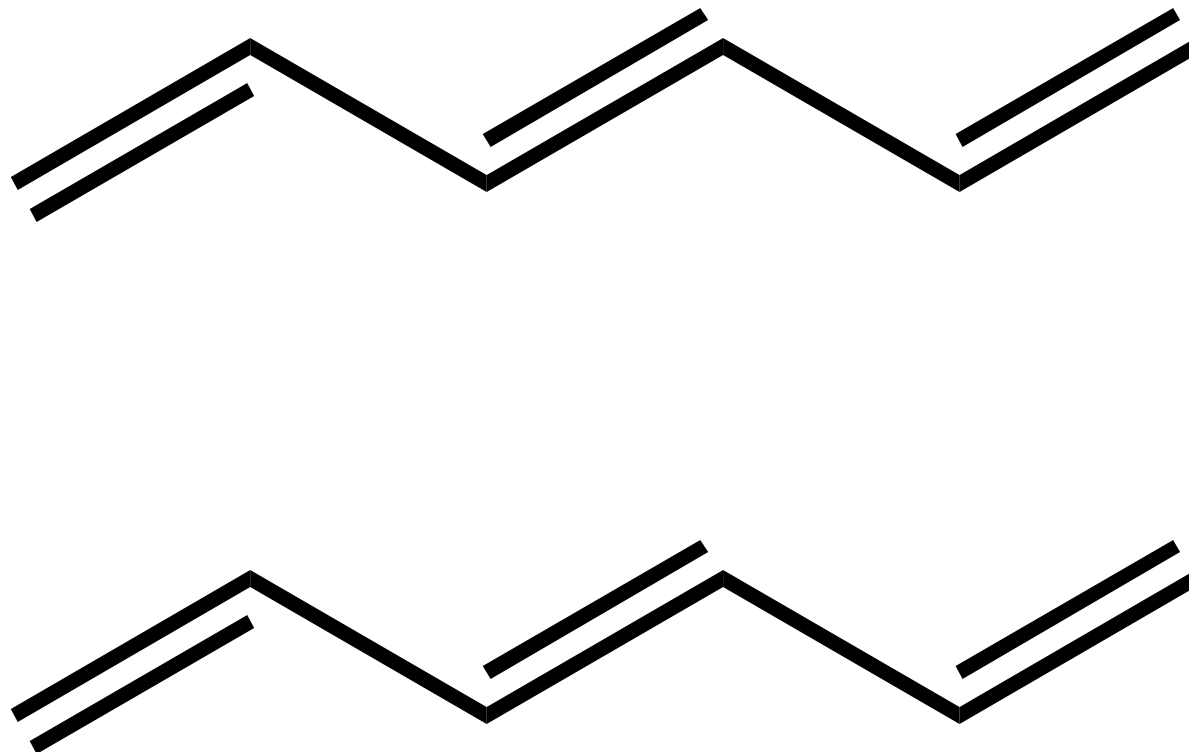
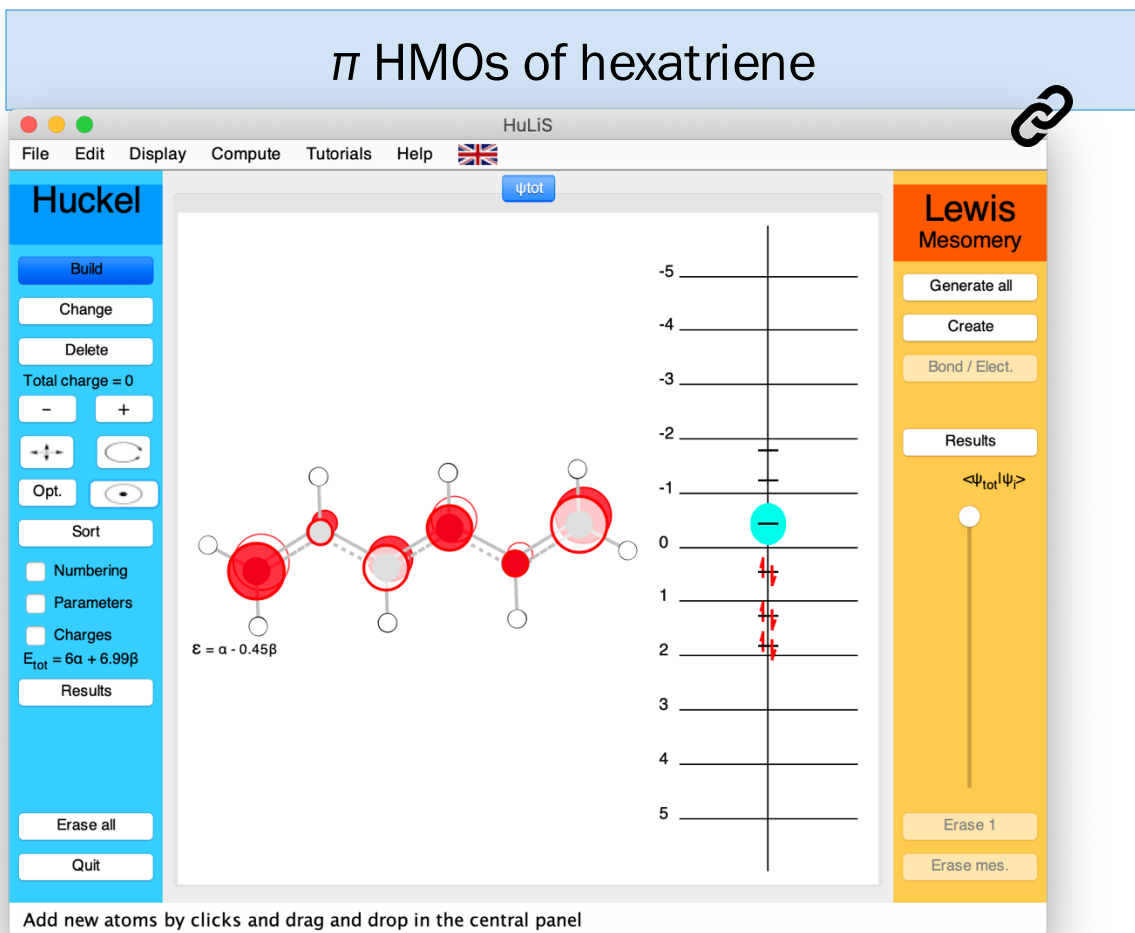
Photochemistry of Alkenes and Alkynes

π HMOs of ethylene



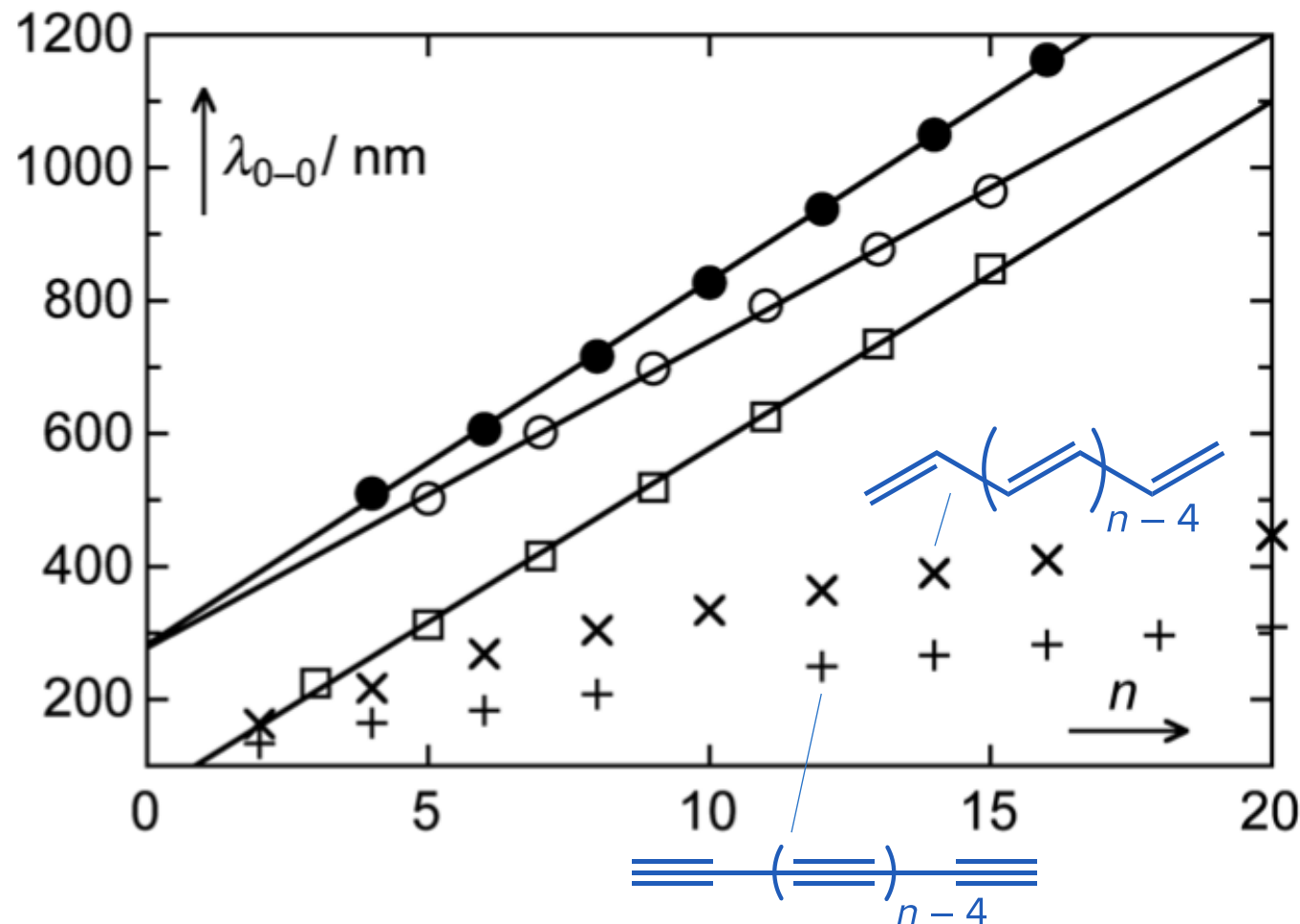
$\pi \rightarrow \pi^*$ Transitions

For extended pi systems such as polyalkenes, excitation strengthens the ground-state single bonds and weakens the ground-state double bonds.



Extended Pi Systems

Hückel theory predicts a linear increase in the wavelength associated with the HOMO → LUMO transition as the pi system lengthens. Experiment disagrees for polyenes/ynes with bond-length alternation.



$$\epsilon_j = \alpha + 2\beta \cos \left(\frac{\pi j}{n+1} \right), \quad j = 0, 1, \dots, n$$

$$\epsilon_{LUMO} - \epsilon_{HOMO} \approx -2\pi\beta/(n+1)$$

$$\lambda_{0-0} \approx -\frac{hc(n+1)}{2\pi\beta}$$

Doubly Excited S_1 ?!

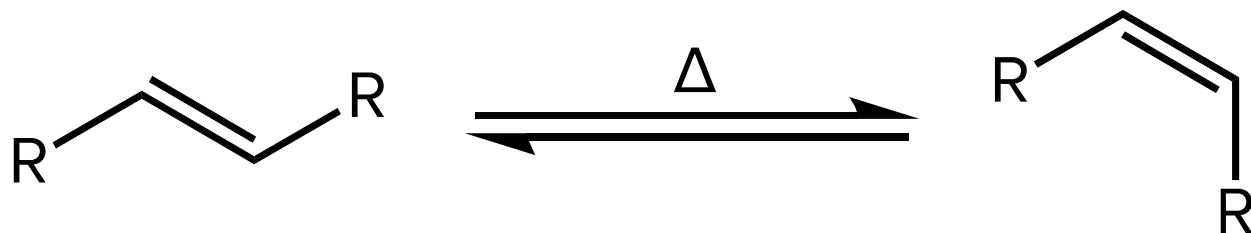
For some long linear polyenes, the first singlet excited state has π^{*2} configuration rather than π, π^* . Stabilizing exchange interaction in the π^{*2} configuration brings its energy below that of π, π^* .

E-Z Isomerization

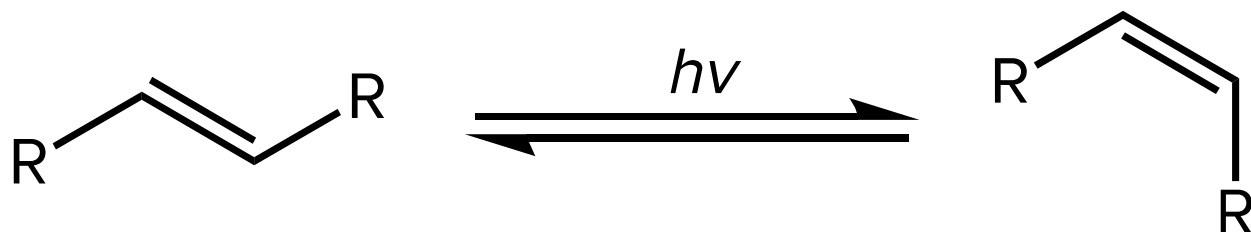
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E-Z Isomerization

Most unconstrained alkenes undergo rapid *E-Z isomerization* following excitation. Excitation results in a weakening of the C=C pi bond. The singlet or triplet state may be involved.



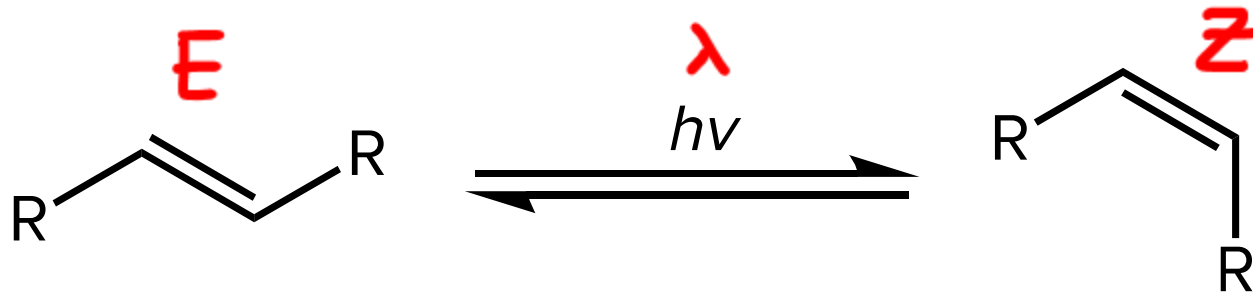
Thermal *E/Z* ratio at equilibrium is governed by the thermodynamic stabilities of the isomers.



Photochemical *E/Z* ratio at equilibrium is governed by the absorption and efficiency properties of the isomers.

Photostationary State

The **photostationary state (PSS)** refers to the steady state under constant irradiation. In this state, the rates of forward and reverse reaction are equal.



Photochemical *E/Z* ratio at equilibrium is governed by the absorption and efficiency properties of the isomers.

Forward reaction: 1. absorption by *E*; 2. $*E \rightarrow Z$ rate = $\epsilon_E(\lambda)[E]\Phi_{E \rightarrow Z}$

Reverse reaction: 1. absorption by *Z*; 2. $*Z \rightarrow E$ rate = $\epsilon_Z(\lambda)[Z]\Phi_{Z \rightarrow E}$

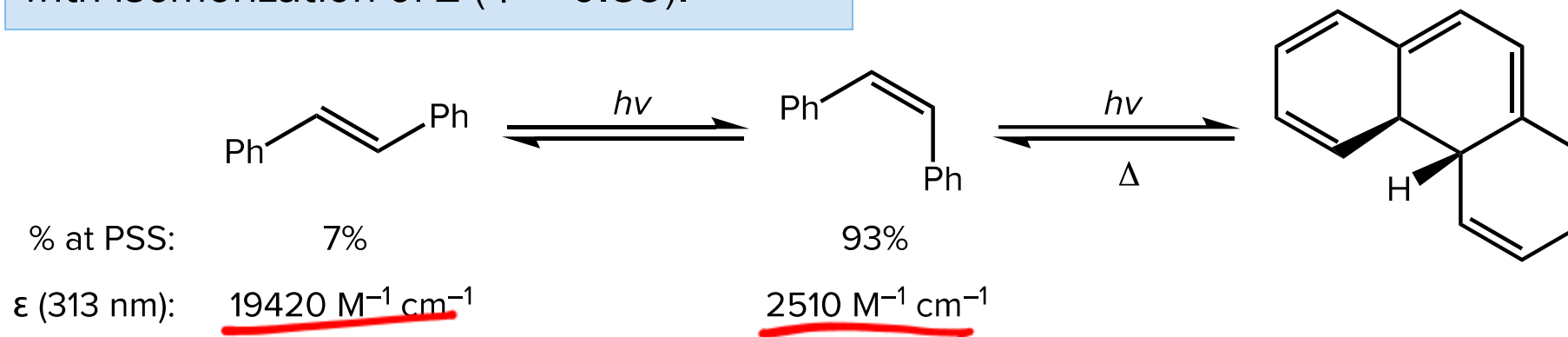
Photostationary ratio

$$K = \frac{[Z]}{[E]} = \frac{\epsilon_E(\lambda)\Phi_{E \rightarrow Z}}{\epsilon_Z(\lambda)\Phi_{Z \rightarrow E}}$$

Stilbenes as a Case Study

The isomerizations of stilbenes, including derivatives with heavy atoms, have been studied in considerable detail.

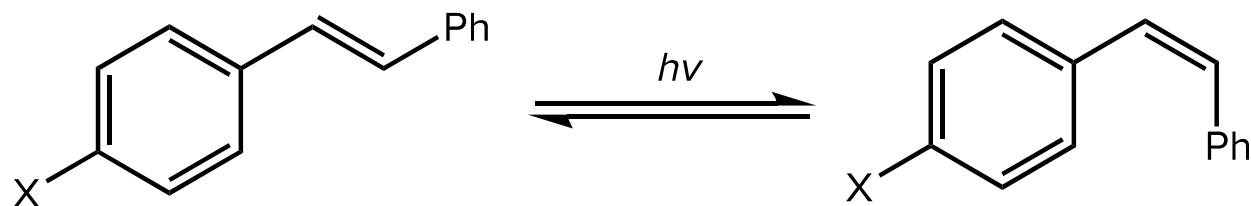
6 π electrocyclization ($\Phi = 0.10$) competes with isomerization of Z ($\Phi = 0.35$).



Stilbenes as a Case Study

The isomerizations of stilbenes, including derivatives with heavy atoms, have been studied in considerable detail.

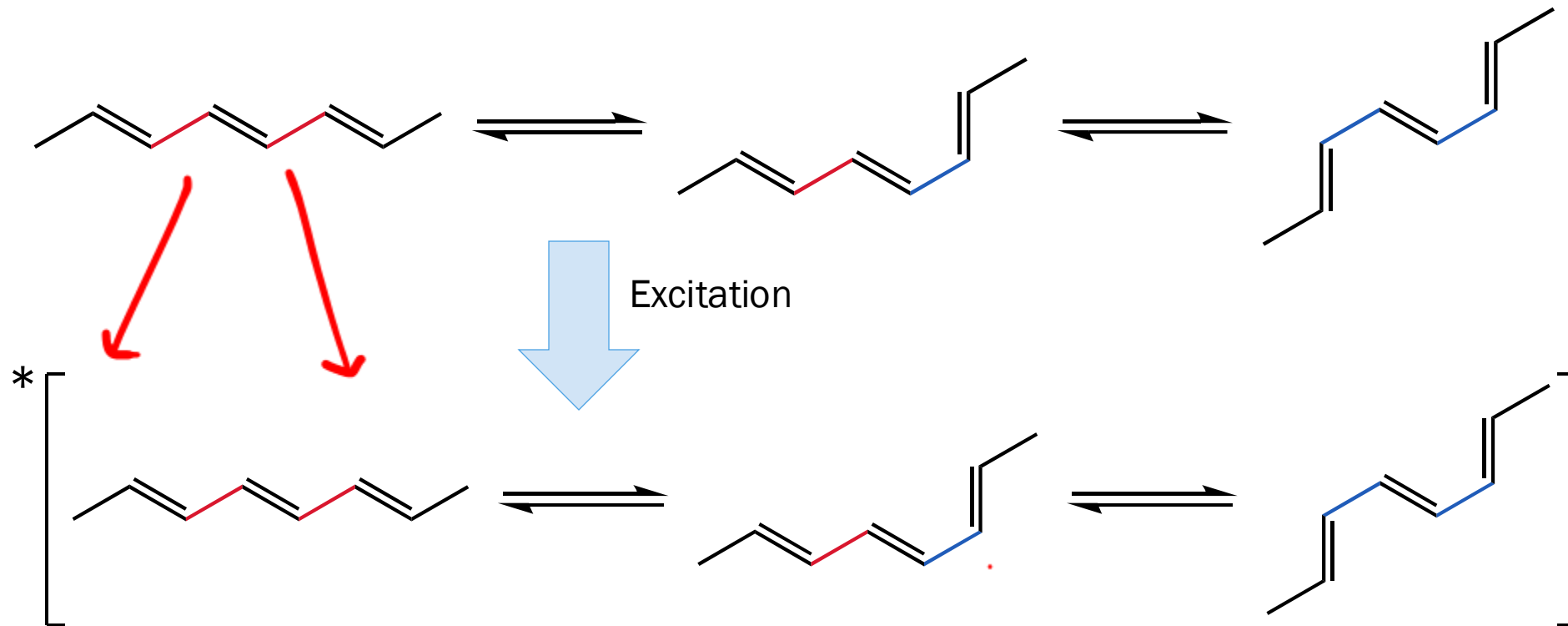
Heavy atom effect results in competing isomerization via T_1 .



X	$\Phi_{E \rightarrow Z}$	$\Phi_{Z \rightarrow E}$	Mechanism	[Z]/[E]
H	0.52	0.35	S_1	93/7
Cl	0.60	0.42	$S_1 + T_1$	91/9
Br	0.52	0.35	$S_1 + T_1$	88/12

Extended Polyenes: The NEER Principle

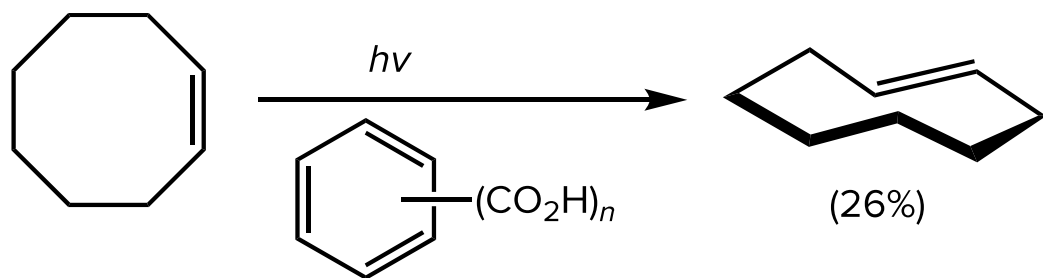
For extended polyenes, the population of *ground-state* conformers controls the composition of the product mixture (*non-equilibration of excited rotamers, NEER*).



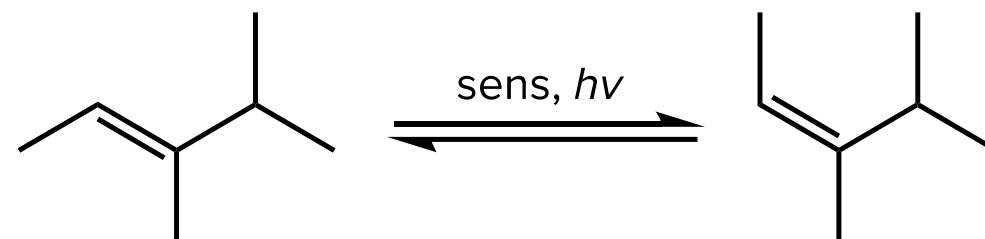
Sensitized Isomerization

Simple aliphatic alkenes do not absorb over 200 nm and thus are amenable to sensitized isomerization via their T_1 states. Because energy transfer is more efficient to the higher-energy *Z* isomer (energy gap law!), $[Z]/[E] < 1$.

Efficient generation of *trans*-cyclooctene



The *E* isomer is favored at the PSS.



Sensitizer	E_T (kcal/mol)	$[Z]/[E]$
benzene	84.4	39/61
<i>p</i> -xylene	80.5	34/66
pentamethylbenzene	79.6	—

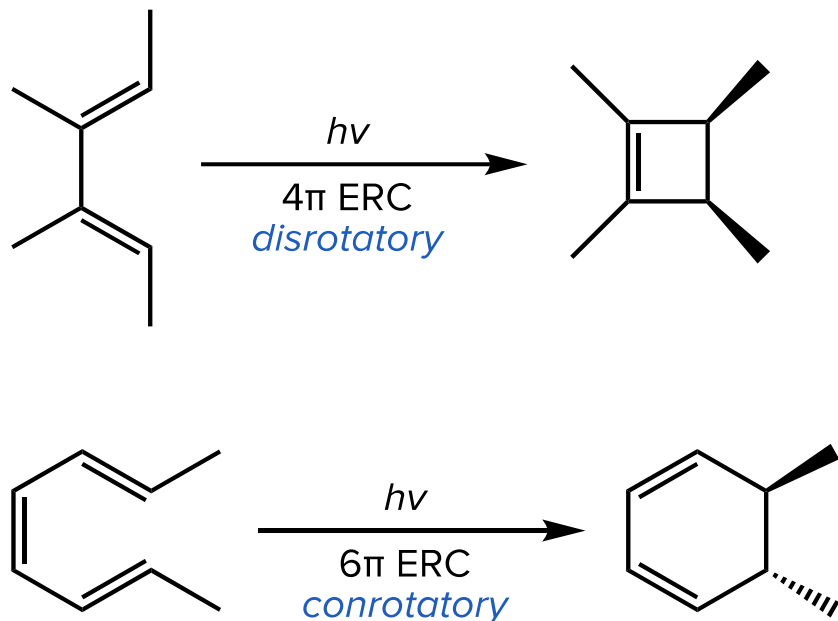
Table 6.3. Sensitized *E*-*Z* isomerization of (*E*)-3,4-dimethylpent-2-ene

Pericyclic Photorearrangements: Electrocyclic and Sigmatropic Reactions

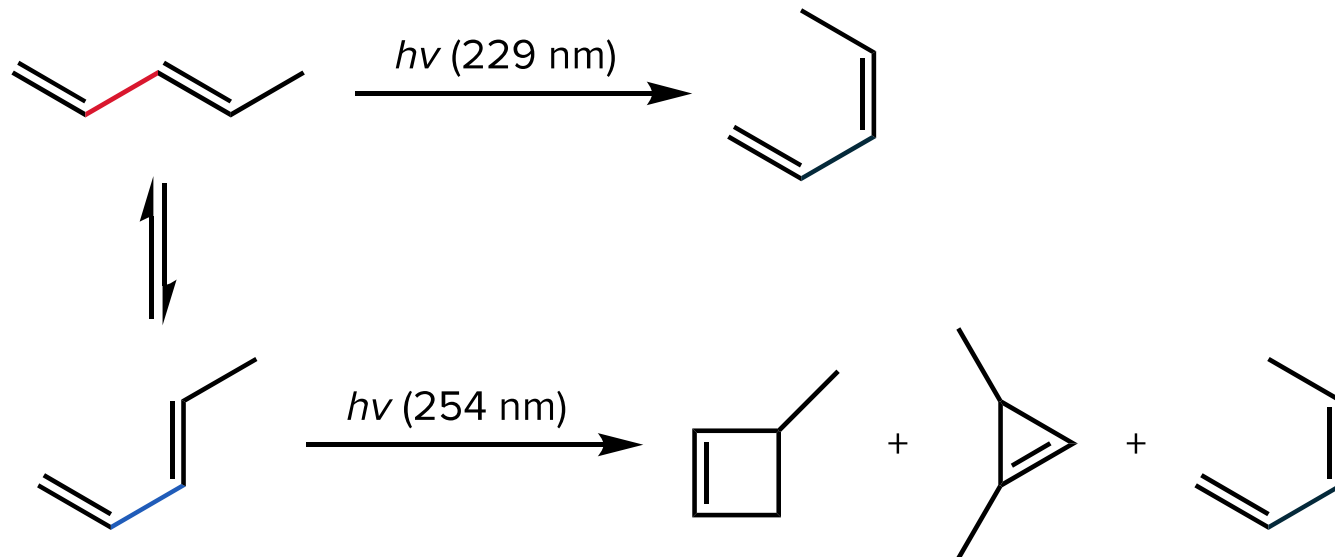
Photochemistry of Alkenes and Alkynes

Electrocyclic Reactions

Polyenes participate in electrocyclic ring opening and closing reactions via their singlet states. **Torquoselectivity** is opposite that observed in thermal reactions.



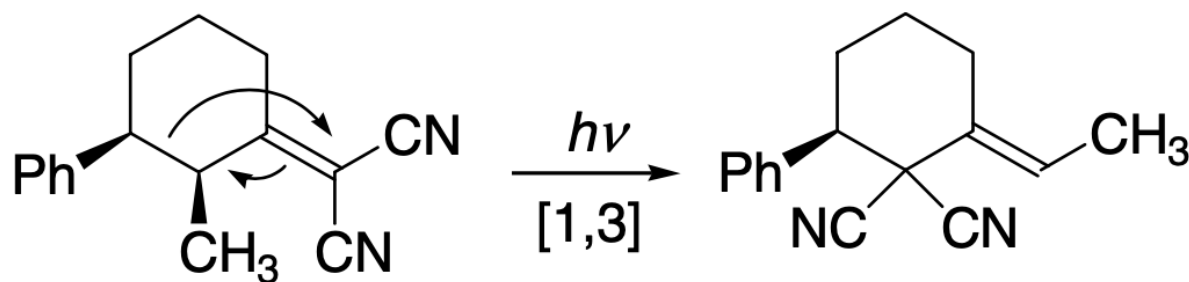
Reactivity depends on conformer populations (recall NEER) and their absorption properties, giving rise to wavelength-dependent product distributions.



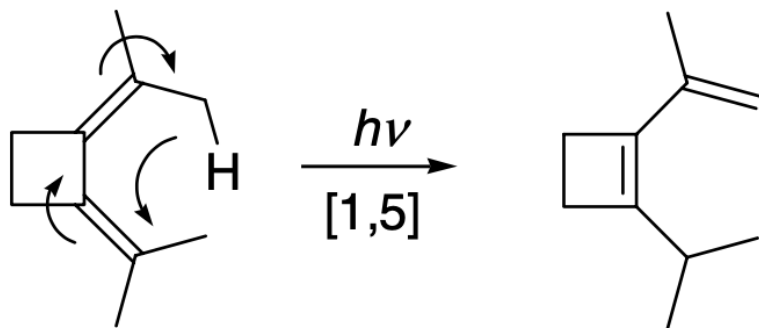
Generally, photopericyclic reactions compete with other processes such as isomerization.

Sigmatropic Rearrangements

Excited alkenes and polyenes engage in sigmatropic rearrangements with opposite facial selectivity of the corresponding thermal processes.



$4n$ electrons involved \rightarrow
supra-supra facial selectivity

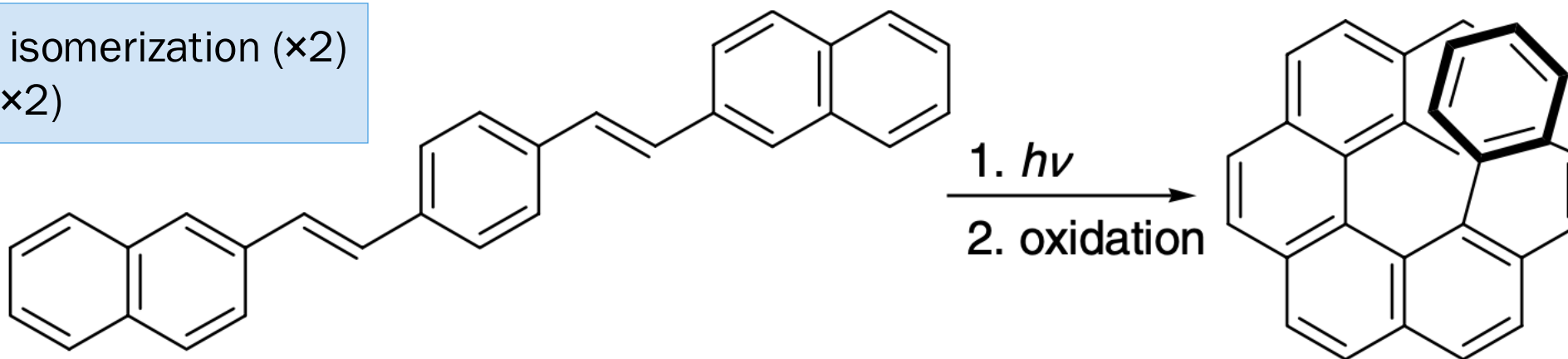


$4n + 2$ electrons involved \rightarrow
supra-antara facial selectivity

Applications of Photopericyclic Rearrangements

Light-induced electrocyclic ring closure has been applied for the synthesis of helicenes, polyaromatic compounds with a helical shape.

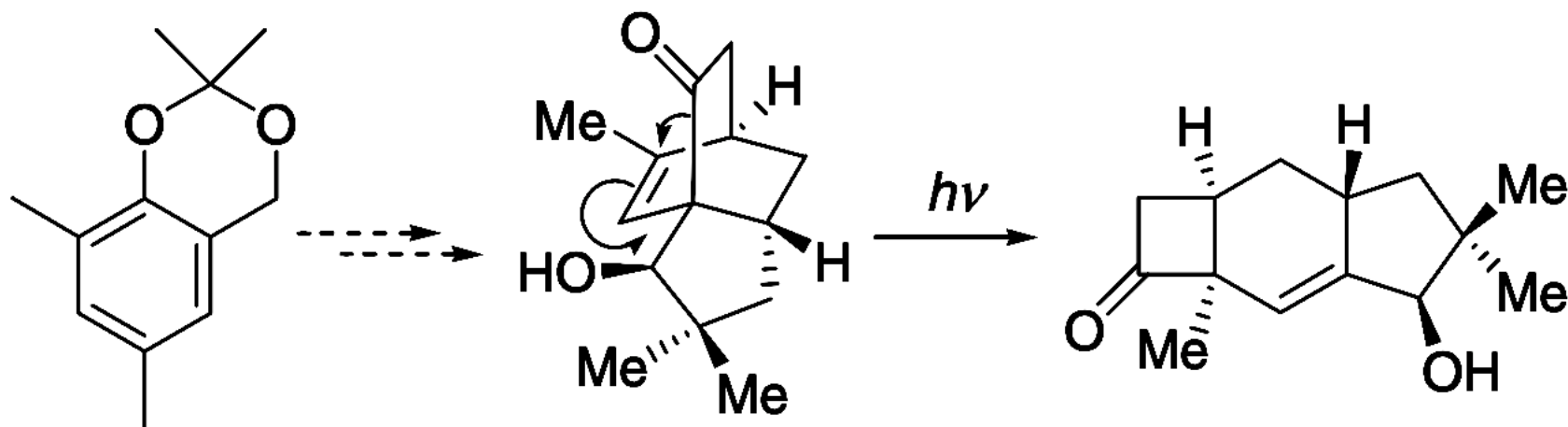
1. *cis-trans* isomerization ($\times 2$)
2. 6π ERC ($\times 2$)



Applications of Photopericyclic Rearrangements



A suprafacial [1,3]-acyl shift was applied in the synthesis of a derivative of stepurane, a fungal metabolite.

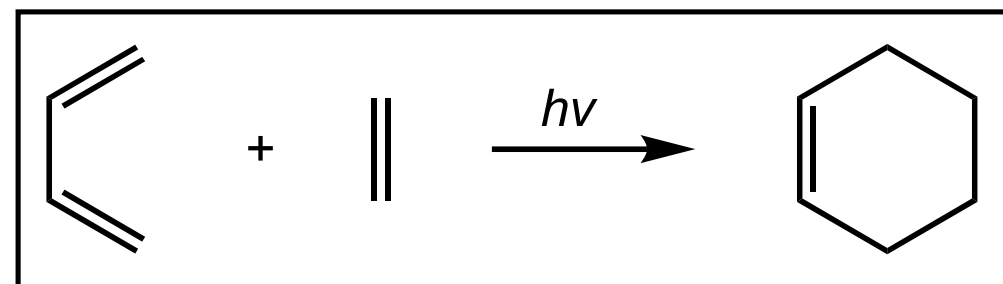
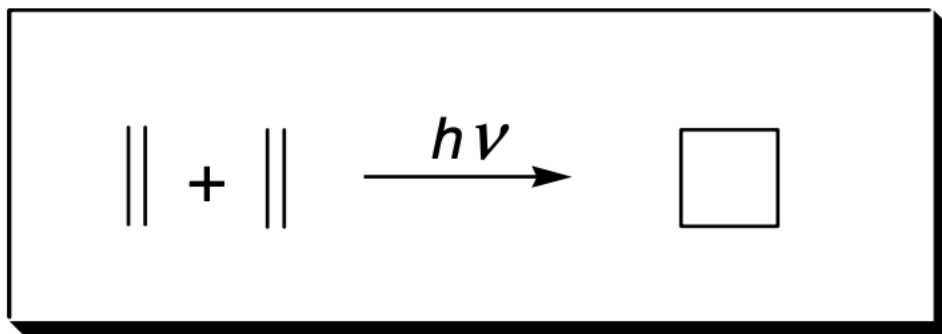


Photocycloaddition Reactions

Photochemistry of Alkenes and Alkynes

Photocycloadditions of Alkenes

Photochemical [2 + 2] and [4 + 4] cycloadditions are *supra-supra* and thus allowed; [4 + 2] cycloadditions are *supra-antara* and thus typically go via stepwise (biradical) pathways, if at all.

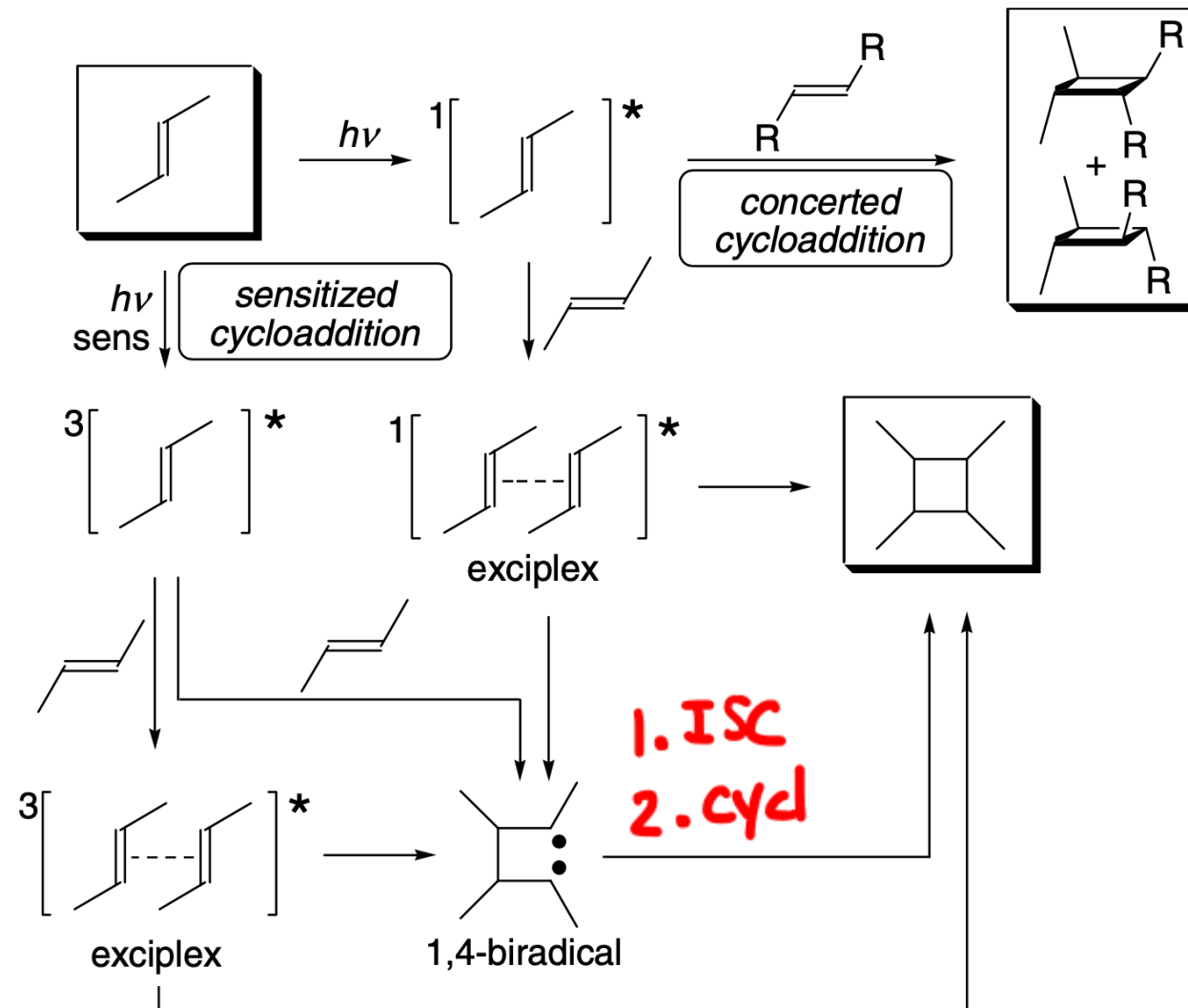


This reaction competes with *cis-trans* isomerization...and isomerization usually wins!

General Mechanistic Picture for [2 + 2]



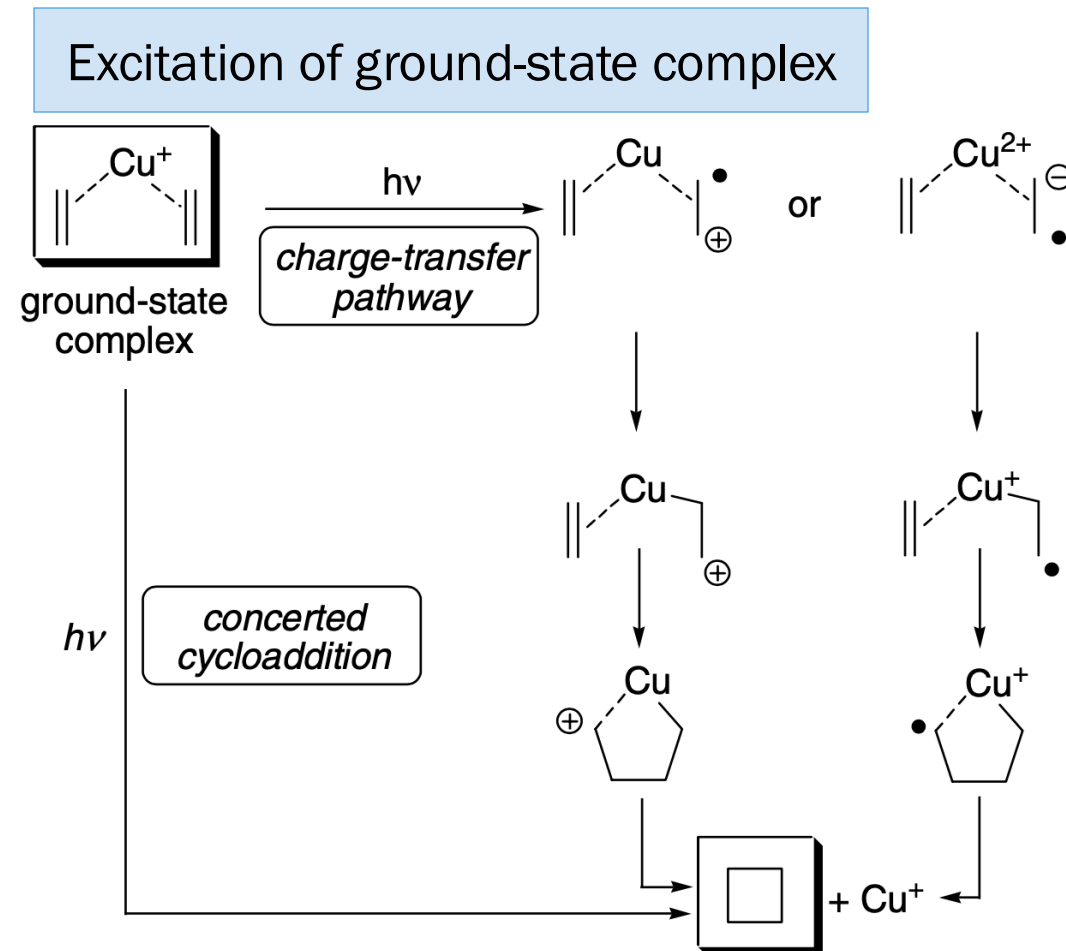
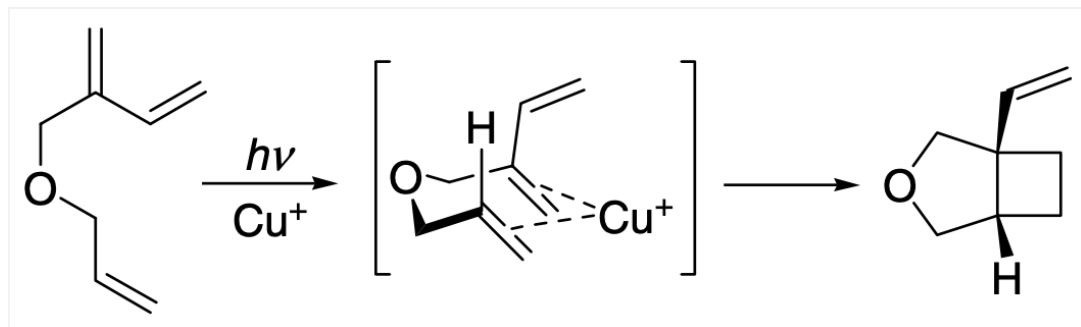
Singlet (π, π^*) states undergo concerted cycloaddition possibly via an exciplex. Triplet states react through a stepwise pathway involving a biradical intermediate and possibly an exciplex.



Copper(I)-catalyzed Photochemical [2 + 2]

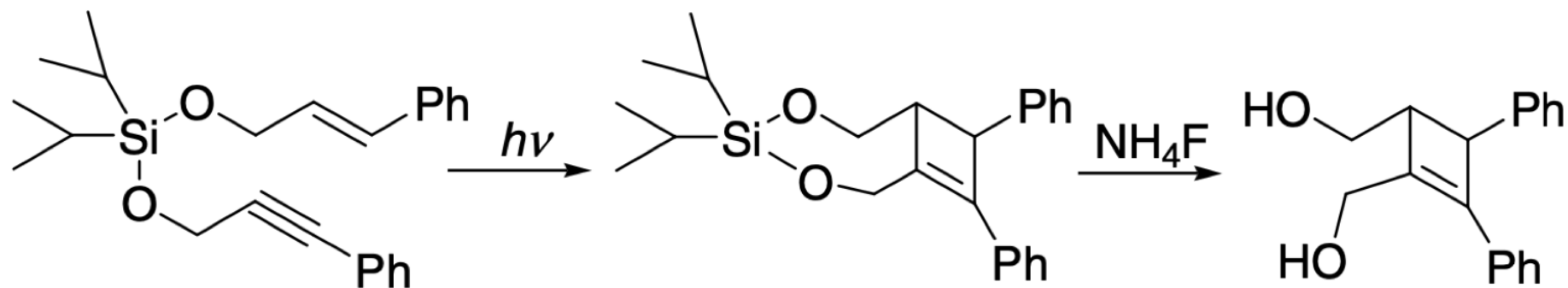
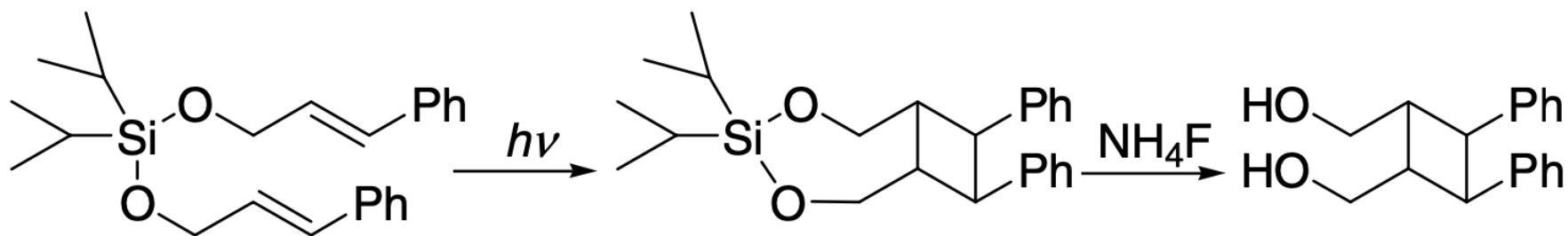


Coordination of two alkenes to copper(I) has been used as a strategy to “template” cycloaddition and eliminate alternative decay pathways of the excited alkenes.



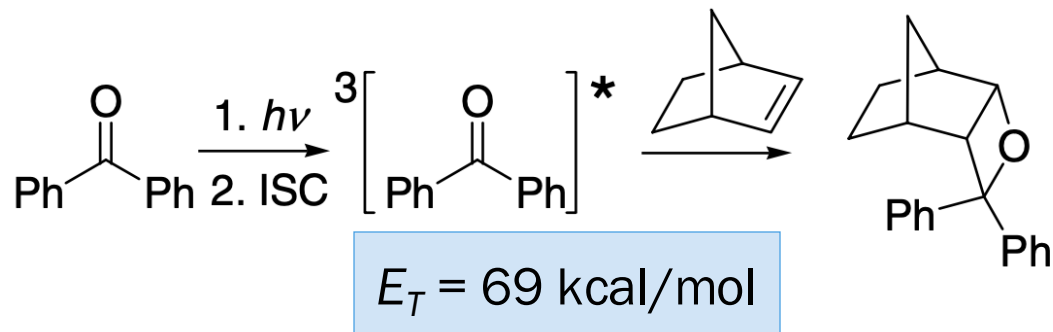
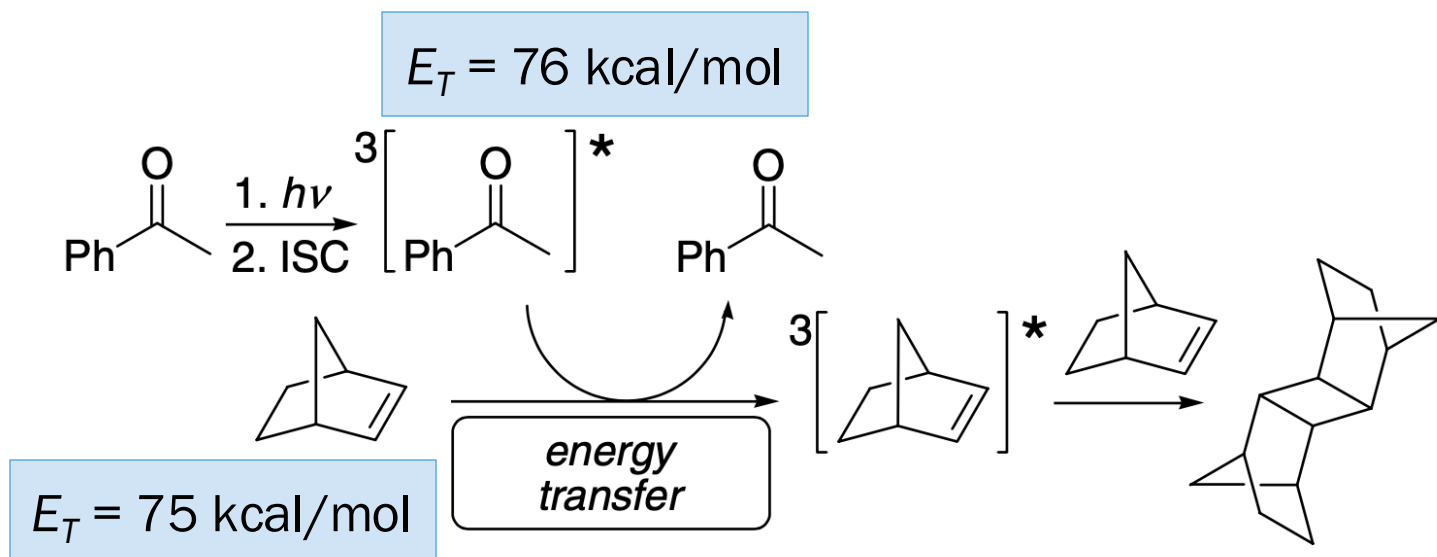
Intramolecular [2 + 2] Reactions

Intramolecular cycloadditions can be much more efficient than comparable intermolecular cases due to high local concentration of the alkenes or alkynes.



Cycloaddition via Triplet Sensitization

Cycloaddition from the triplet state can be promoted via triplet sensitization. However, reaction with the sensitizer can occur if its E_T is much lower than E_T for the alkene!

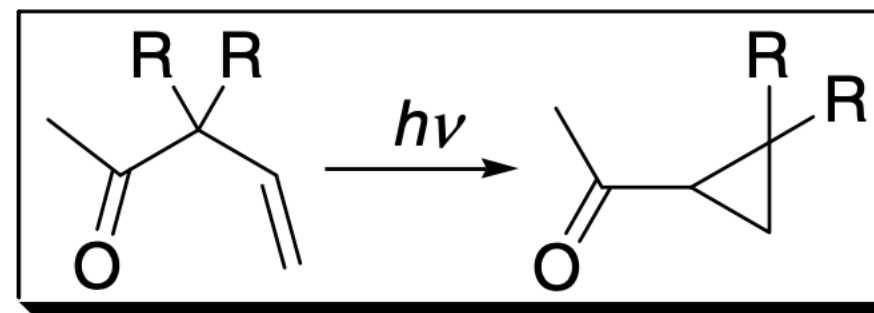
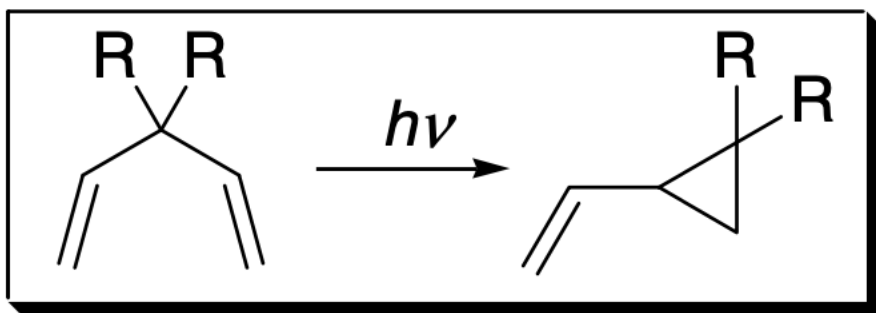


Di- π -Methane Rearrangement

Photochemistry of Alkenes and Alkynes

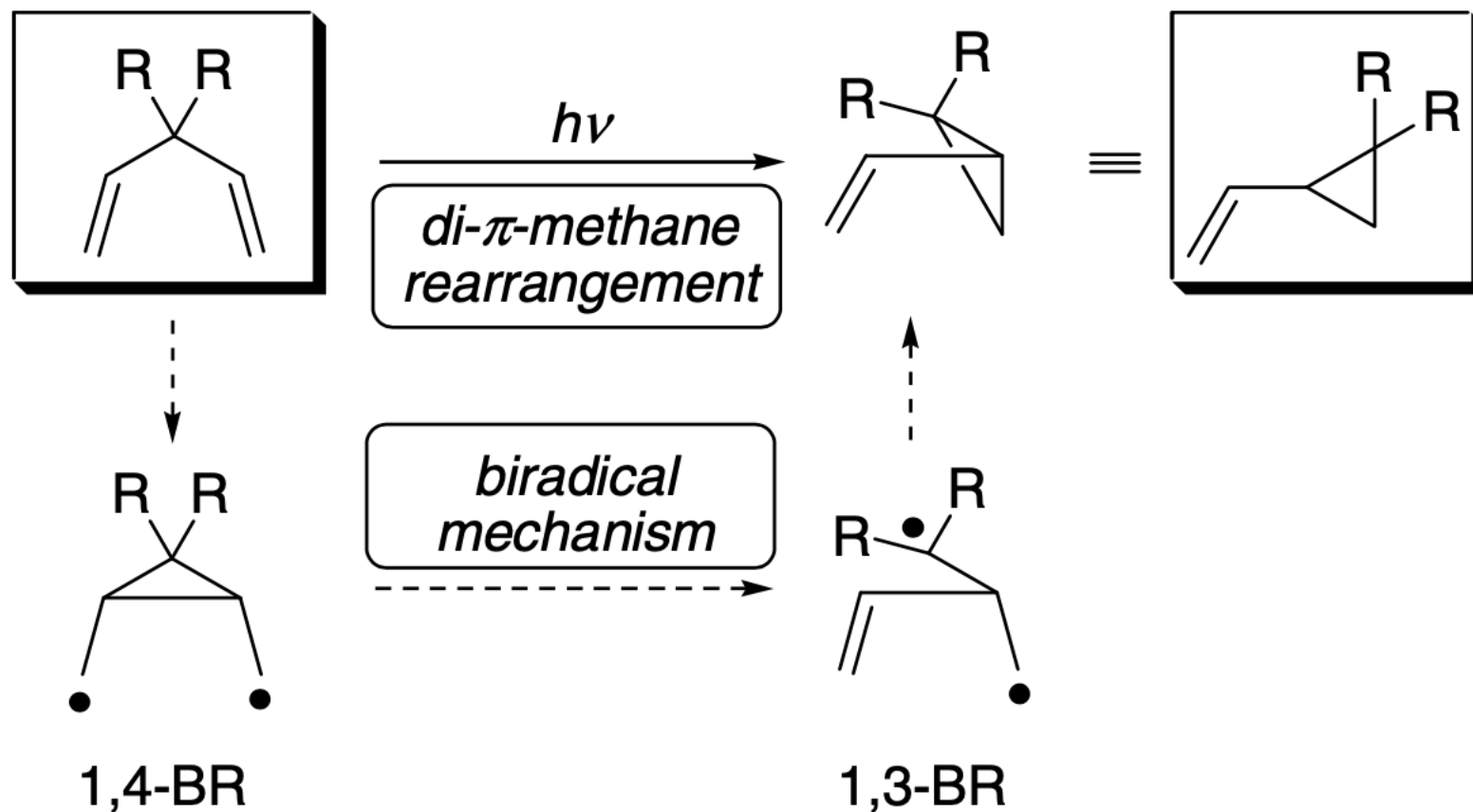
Photochemical Rearrangement of 1,4-Dienes

The photochemical rearrangement of 1,4-dienes to afford alkenyl cyclopropanes is called the *di- π -methane rearrangement*. An “oxa-” version can occur from β,γ -unsaturated carbonyl compounds.



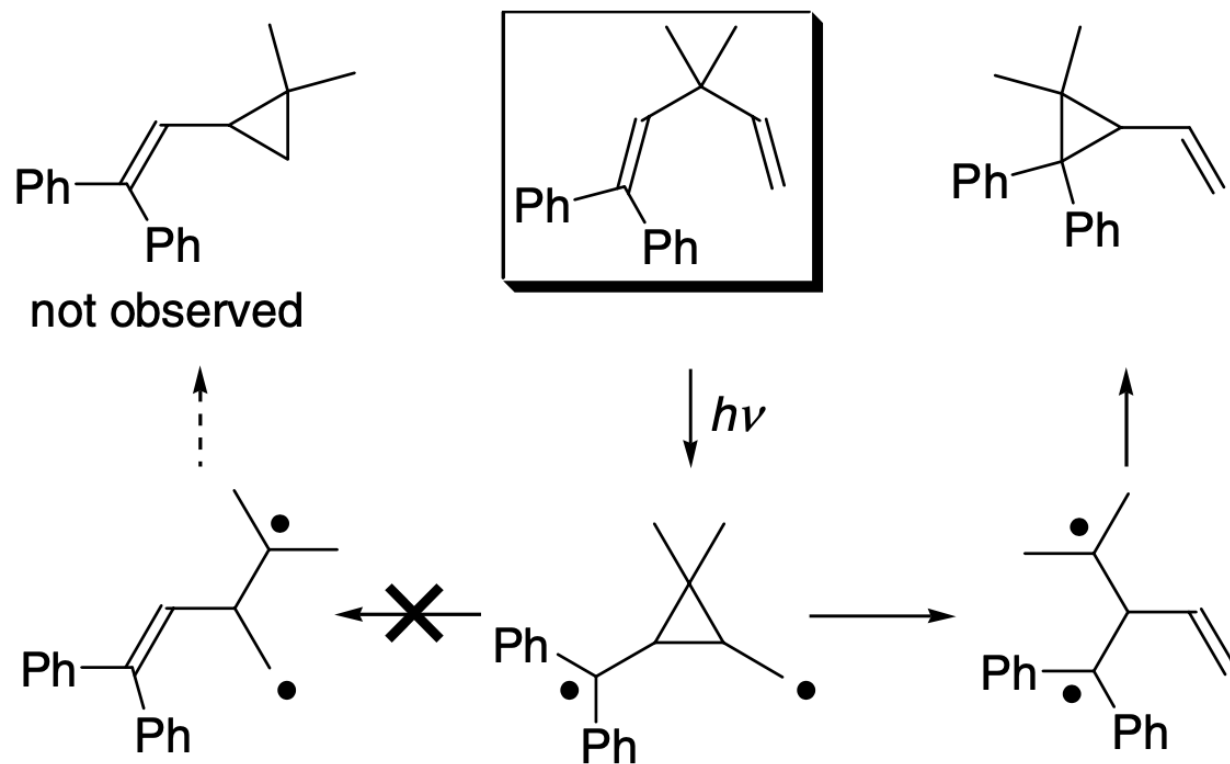
General Mechanistic Picture

The mechanism is generally thought to involve biradical intermediates from both $^1(\pi,\pi^*)$ and $^3(\pi,\pi^*)$, although a fully concerted pericyclic pathway is possible from singlet states.



Accounting for Regioselectivity

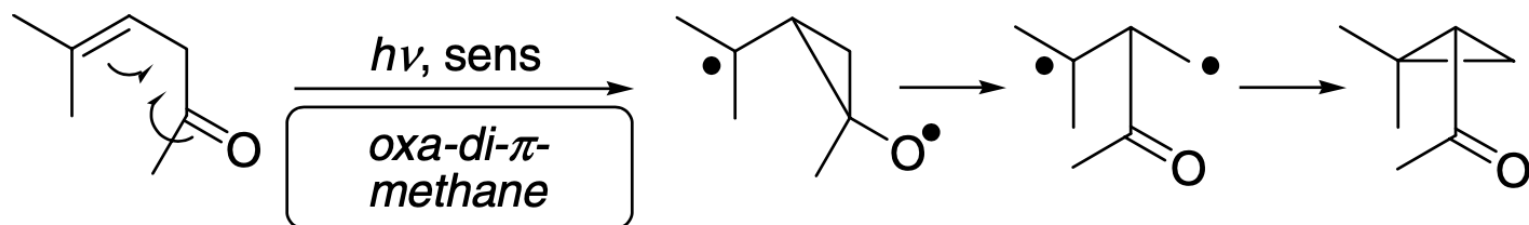
The biradical mechanism is commonly invoked to explain regioselectivity by appealing to intermediates that place radical character on the most stable positions.



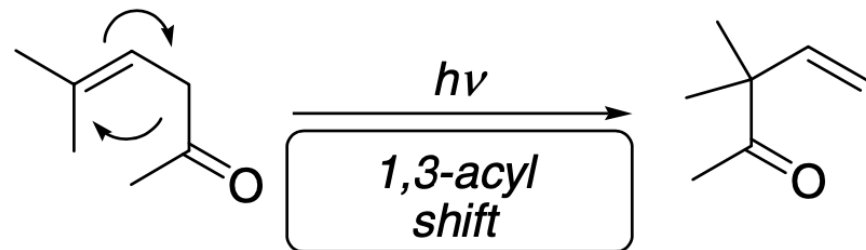
Regioselectivity is driven by radical stability

Oxa- and Aza-Di- π -methane Rearrangements

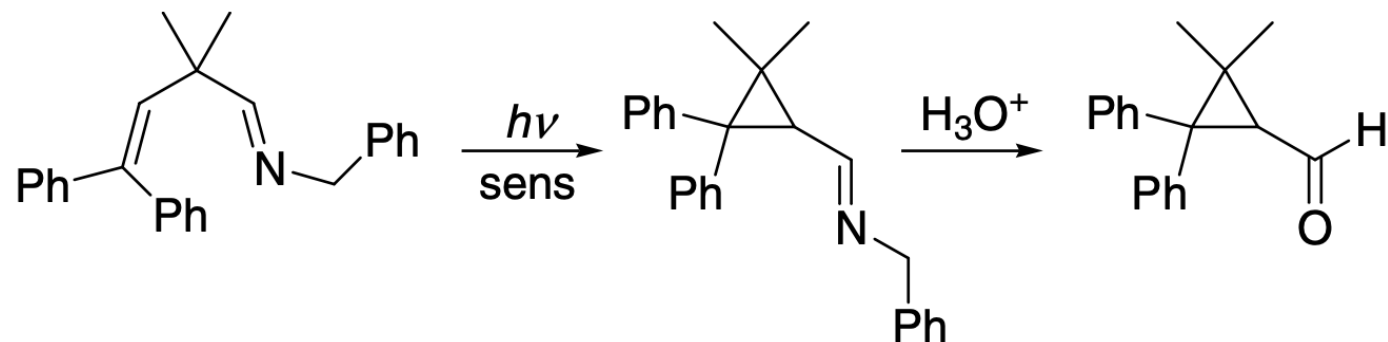
Unsaturated ketones and imines can participate in oxa- and aza-di- π -methane rearrangements. Absorption by the C=X chromophore drives this chemistry.



Oxa-di- π -methane rearrangement
via triplet sensitization



Direct excitation results in
[1,3]-sigmatropic rearrangement



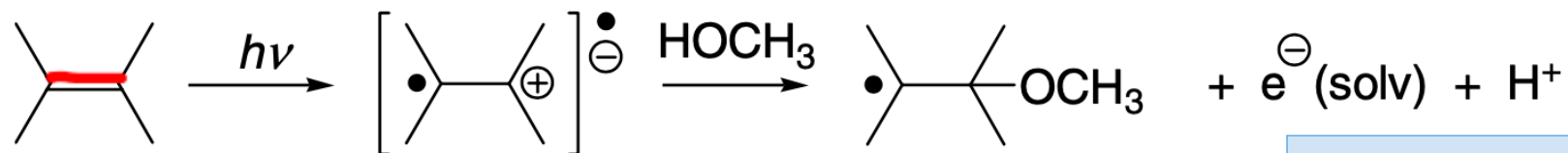
Aza-di- π -methane rearrangement
via triplet sensitization ($\Phi = 0.01$)

Photochemical Additions: Nucleophilic Addition, Proton Transfer, and Electron Transfer

Photochemistry of Alkenes and Alkynes

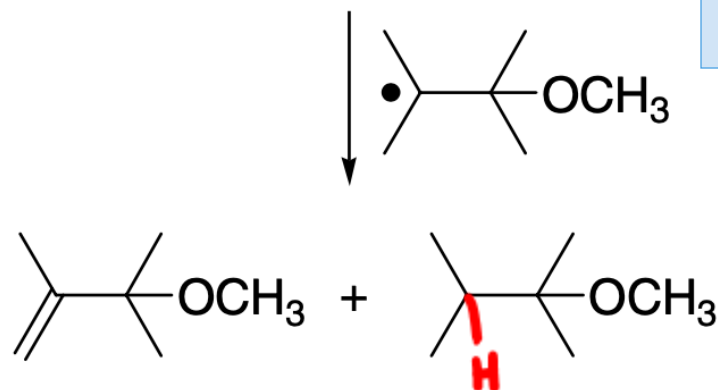
Photoadditions via Rydberg Excited States

Excitation of a π electron to a high-energy unfilled (Rydberg) atomic orbital produces a **Rydberg state** such as $(\pi, R(3s))$. These states have radical cation character and undergo nucleophilic addition reactions.



$\pi, 3s$
★

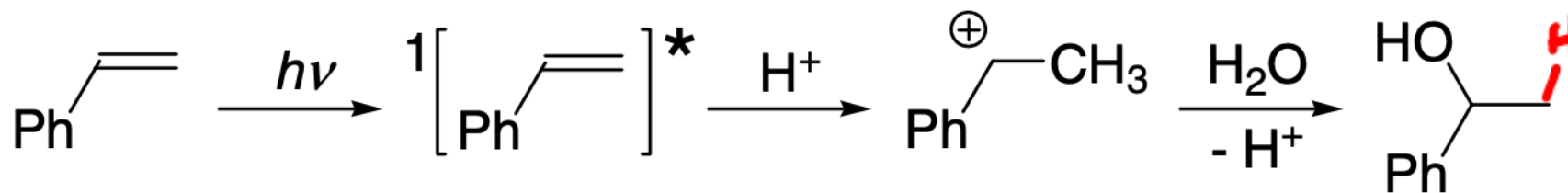
The “Rydberg electron” becomes a solvated electron.



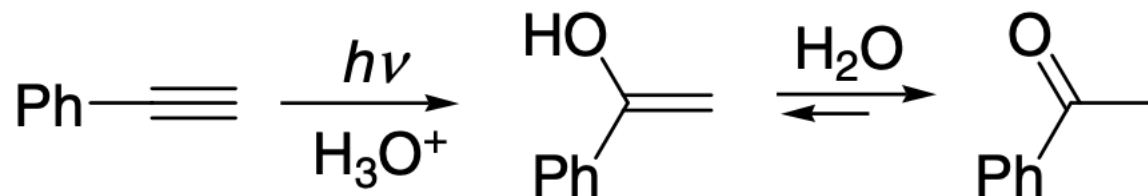
Disproportionation affords two ether products.

Markovnikov Hydration of Aryl Alkenes

Photoexcitation promotes extremely rapid acid-catalyzed hydration of alkenes and alkynes in a Markovnikov fashion.



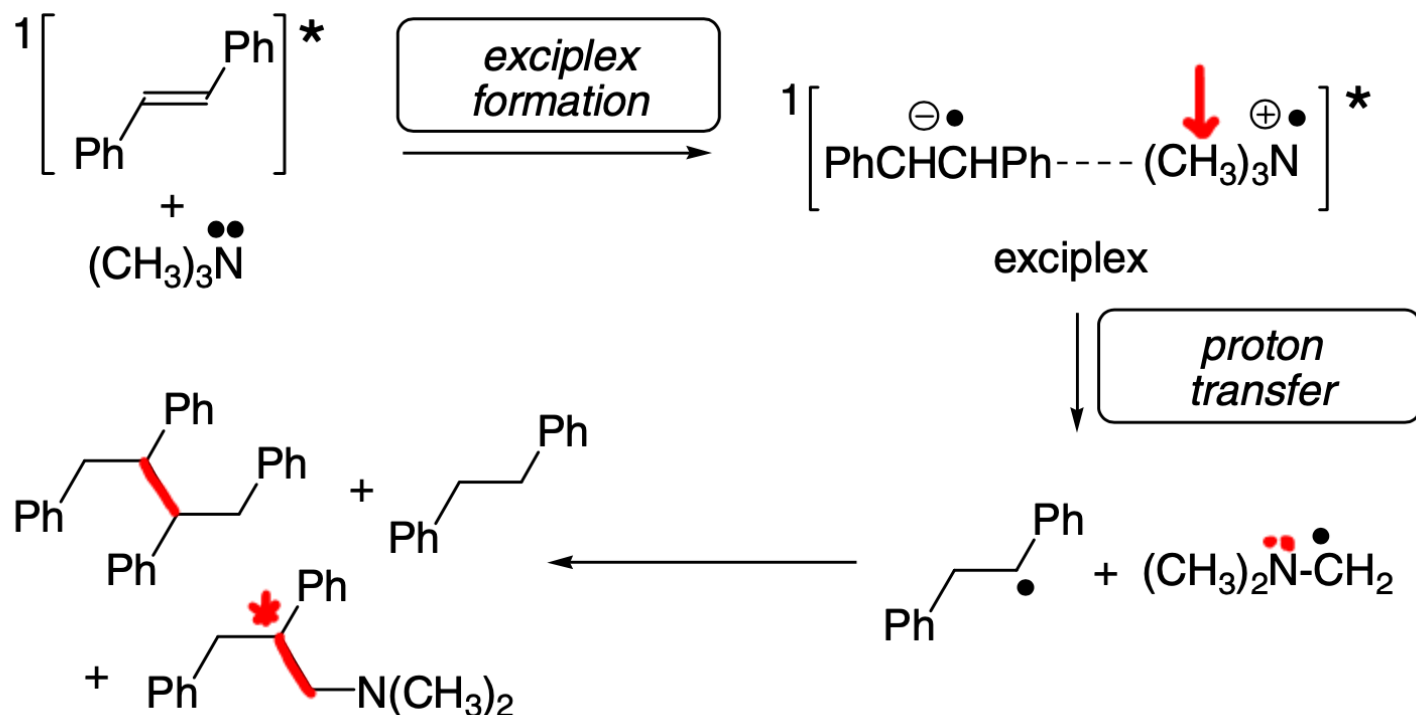
*Markovnikov
product*



Electron Transfer from Amines

Amines can donate electrons to excited alkenes to form exciplexes and/or radical ion pairs, which may undergo back electron transfer to reactants or a variety of chemical reactions.

Hydroaminoalkylation of stilbenes

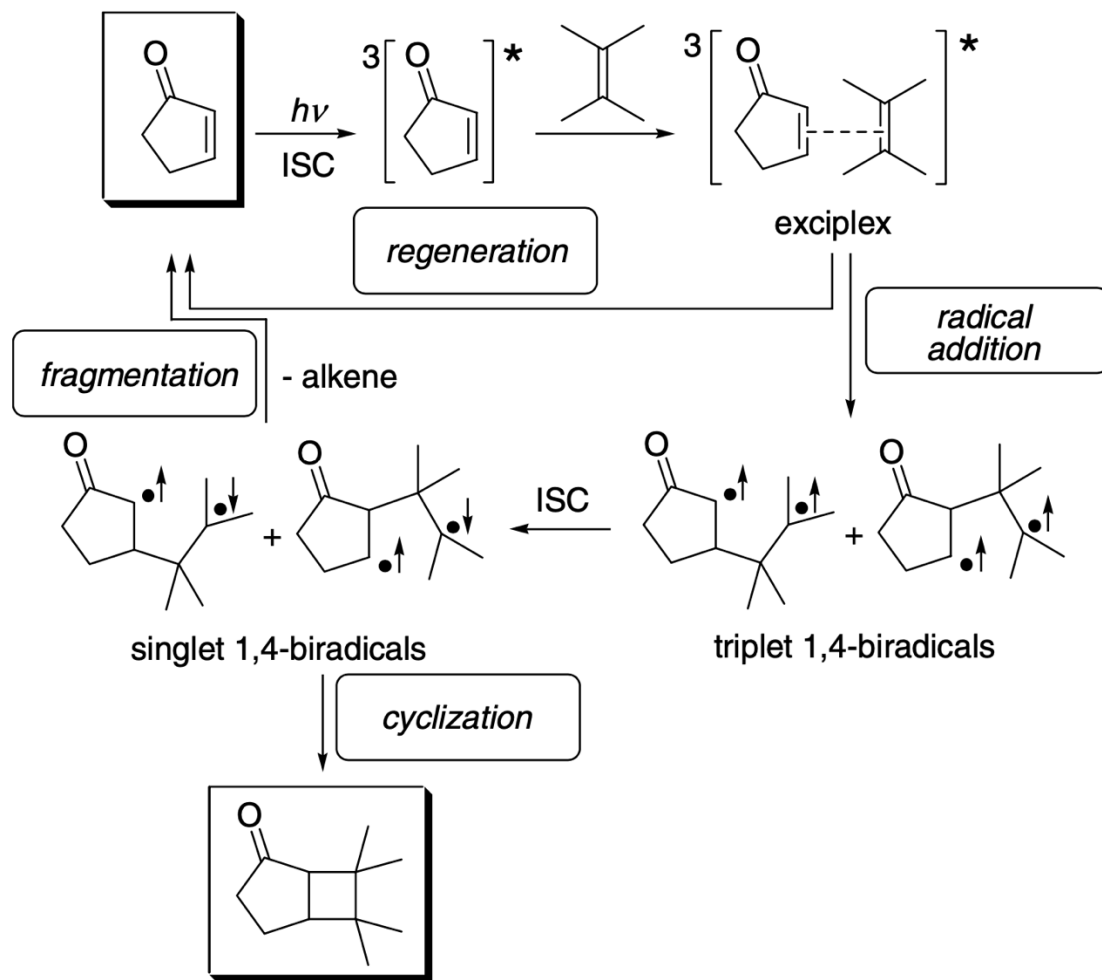


Photocycloadditions and Rearrangements of Enones

Photochemistry of Alkenes and Alkynes

[2 + 2] Photocycloadditions of Enones

Excited α,β -unsaturated ketones may react with alkenes to form acyl cyclobutanes. The triplet state of the enone is generally involved.



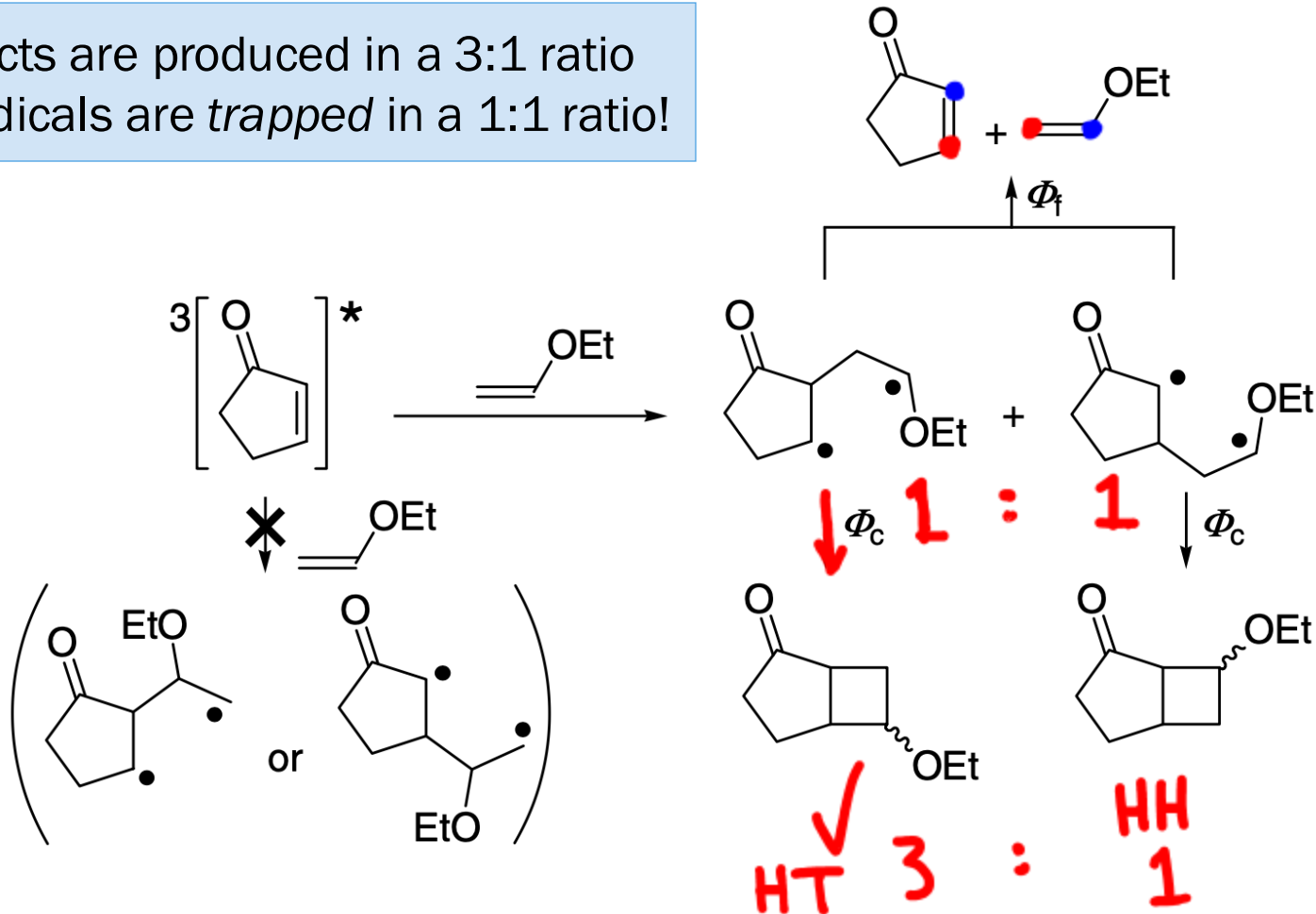
The lowest triplet state of cyclic enones is (π,π^*).

Dissociation of the exciplex and elimination of the biradical can regenerate starting materials.

Regioselectivity of [2 + 2]

Regioselectivity is dictated by the relative rates of cyclization and fragmentation for the possible 1,4-biradicals. Radical trapping experiments support this complex picture.

The HT and HH products are produced in a 3:1 ratio but the HH and HT radicals are *trapped* in a 1:1 ratio!



Sigmatropic Rearrangements

Depending on the configuration of the excited state, enones may undergo two types of sigmatropic reactions. Both concerted and stepwise mechanisms have been proposed.

