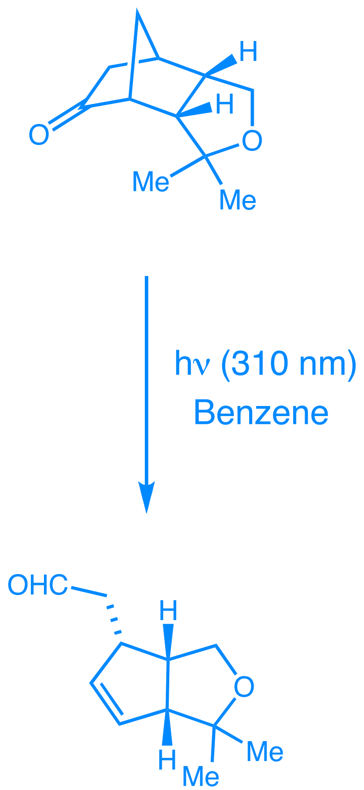
Physical Organic Photochemistry and Basic Photochemical Transformations



Group Meeting

Jan 26th 2011

Scott Simonovich

Electromagnetic Radiation

	λ (nm)	E (kcal/mol)
UV	200	143
	300	95
Vis	400	72
	500	57
	600	48
	700	41
IR	1,000	29
	5,000	6
	10,000	3
μW	10^7	3×10^{-2}
	10^9	3×10^{-4}
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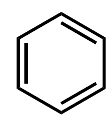
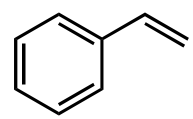
Group	λ (nm)
C=C	180
C=C–C=C	220
	260
	282
C=O	280
C=C–C=O	350

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BDE (kcal/mol)	
C—C	83
O—O	35
C—H	99
O—H	111
C—N	73
C—O	86
C=C	146
C=O	180

X-rays and gamma-rays lead to ionization

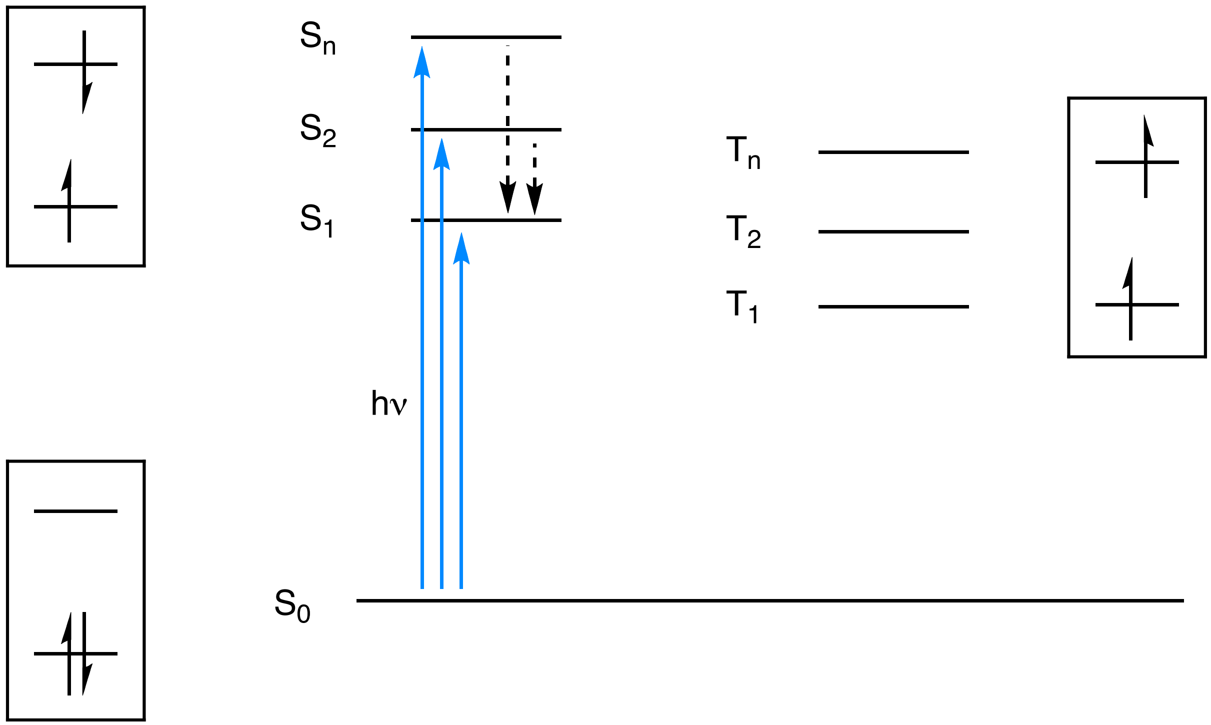
UV/Vis for electronic absorption

IR for nuclear vibrational motion (IR)

μW for electron spin precession (EPR)

Radio for nuclear spin precession (NMR)

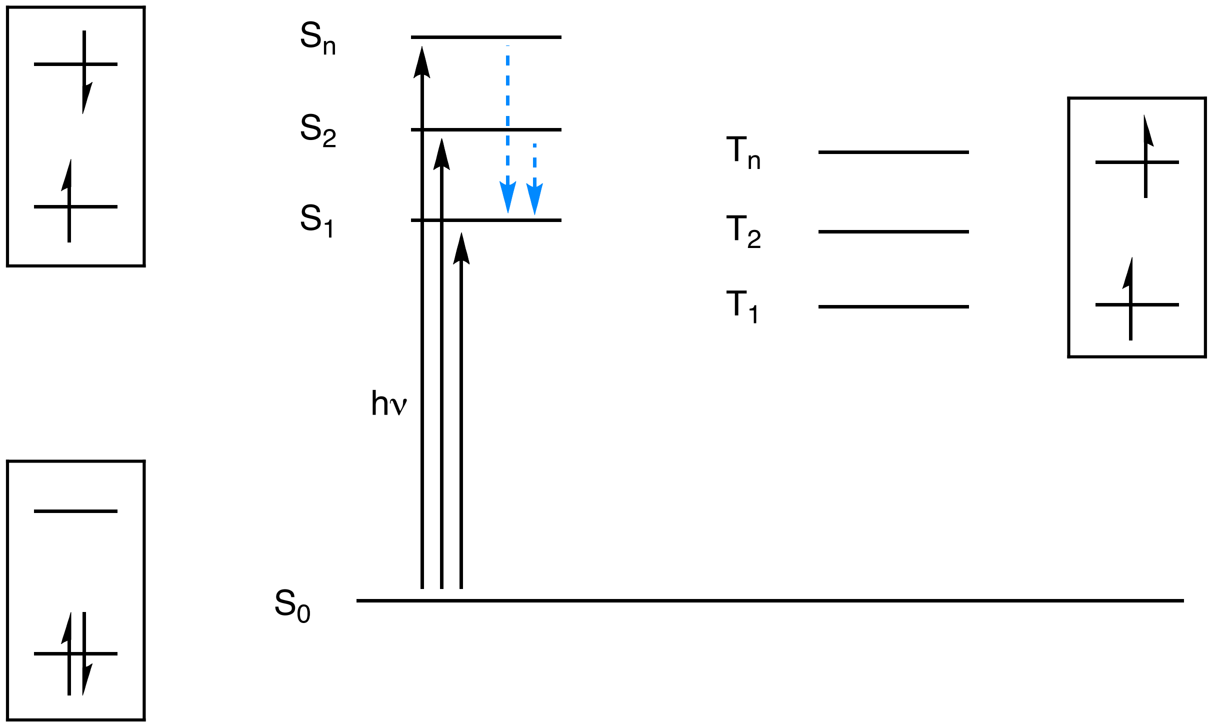
Jablonski Diagram



Stark-Einstein law - molecule will absorb light to excite a single electron and energy of light must match difference between S_0 and S*

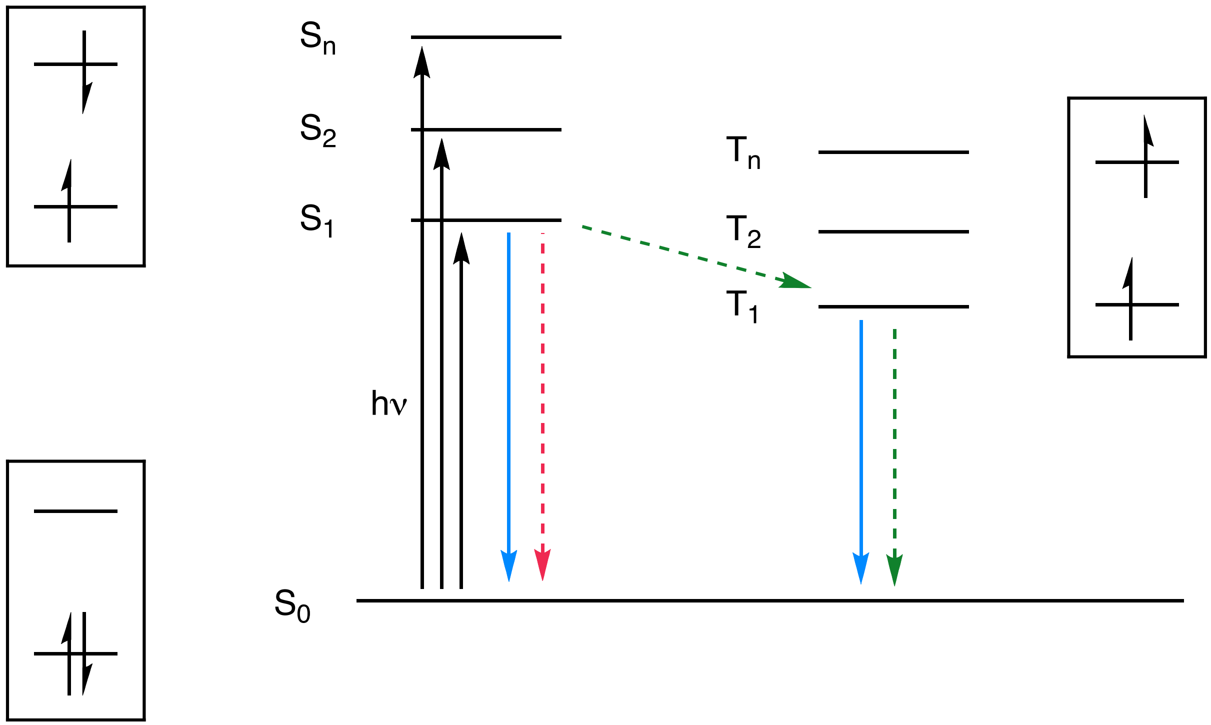
High probability transitions usually occur with conservation of spin

Jablonski Diagram



Kasha's rule - relaxation to S_1 is very rapid compared to other processes

Jablonski Diagram

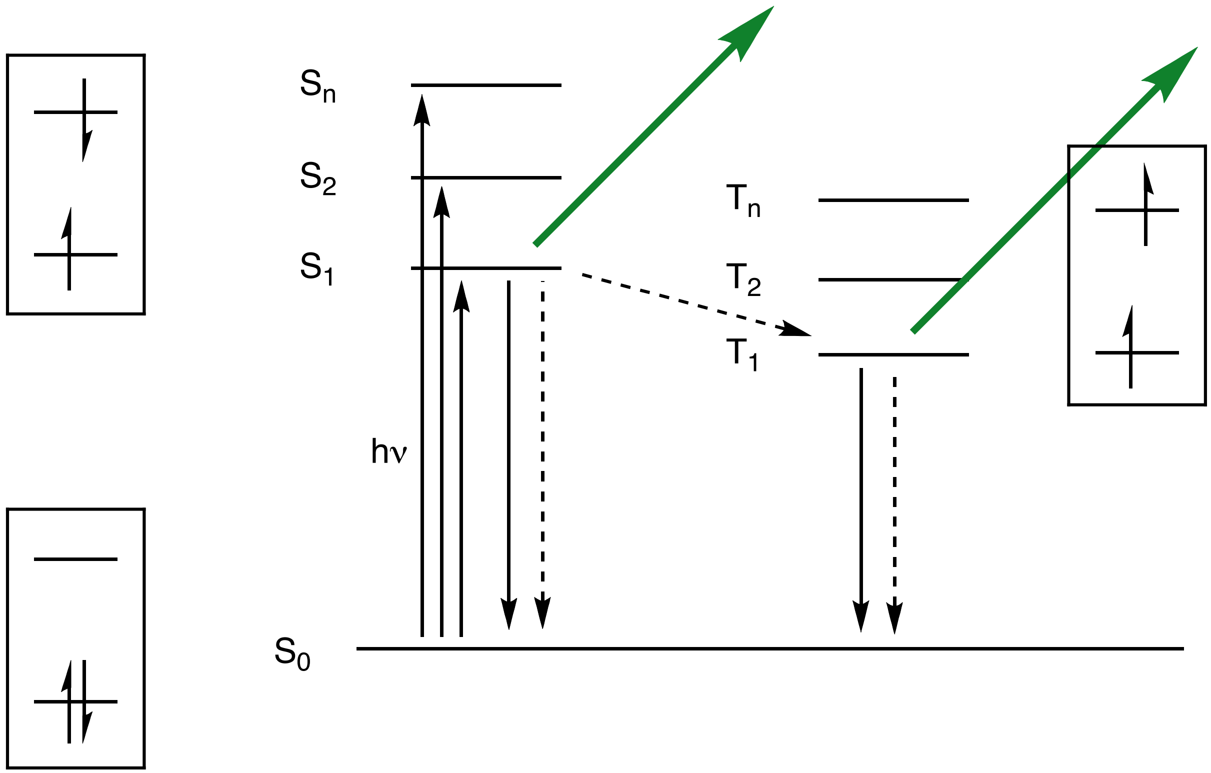


Radiative decay to ground state (fluorescence or phosphorescence)

Non-radiative decay (heat or energy transfer)

Intersystem crossing to different manifold

Jablonski Diagram



- Photochemistry occurs from S_1 (infrequent) or T_1 states
- Photochemistry must compete with photophysical processes

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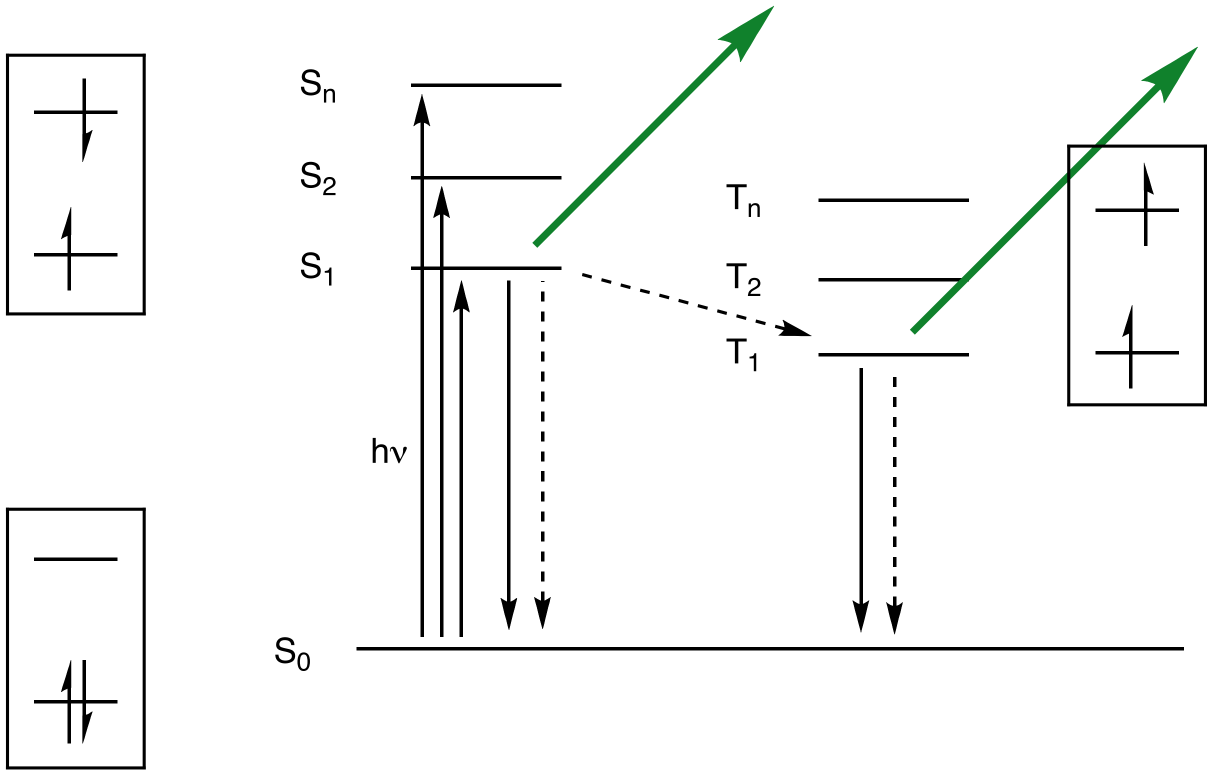
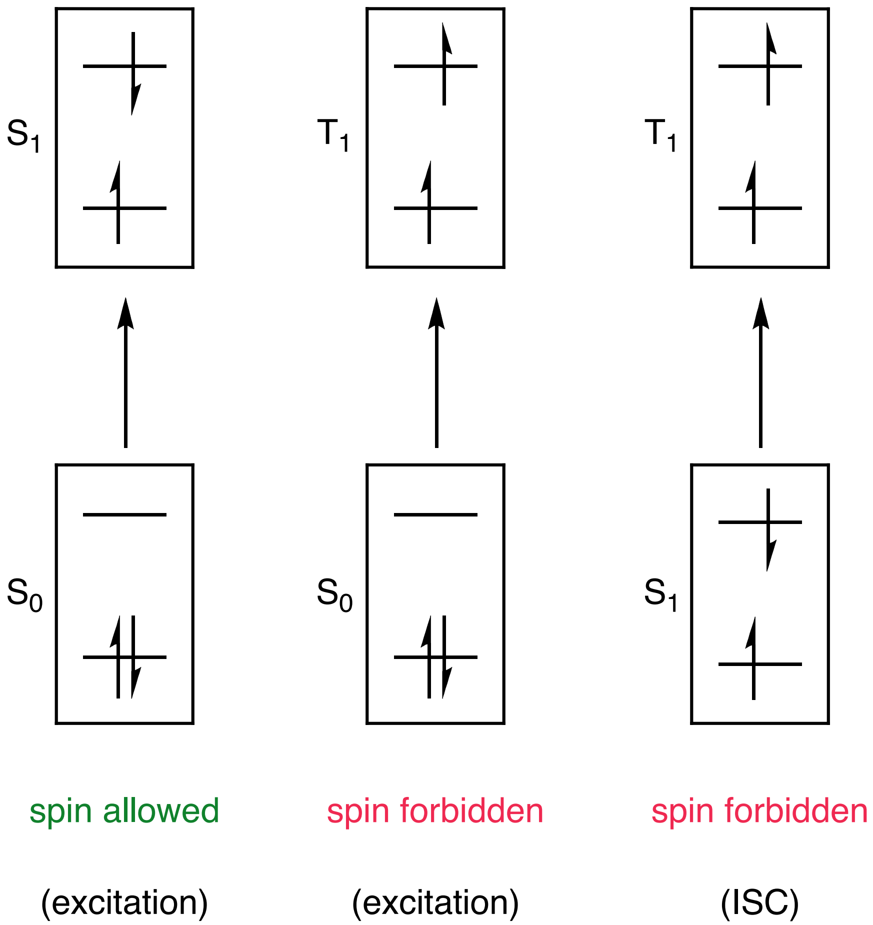


- Photochemistry occurs from S_1 (infrequent) or T_1 states
- Photochemistry must compete with photophysical processes
- If excited state is short-lived, there will be less time for chemistry
- Photoreaction must generally have E_a less than 20 kcal/mol
- S_1 reactions will not outcompete fluorescence if E_a is above 10 kcal/mol

Allowed and Forbidden Processes



- Spin forbidden transitions alter electron spin angular momentum
- Triplet states tend to be more photochemically active b/c they are long-lived

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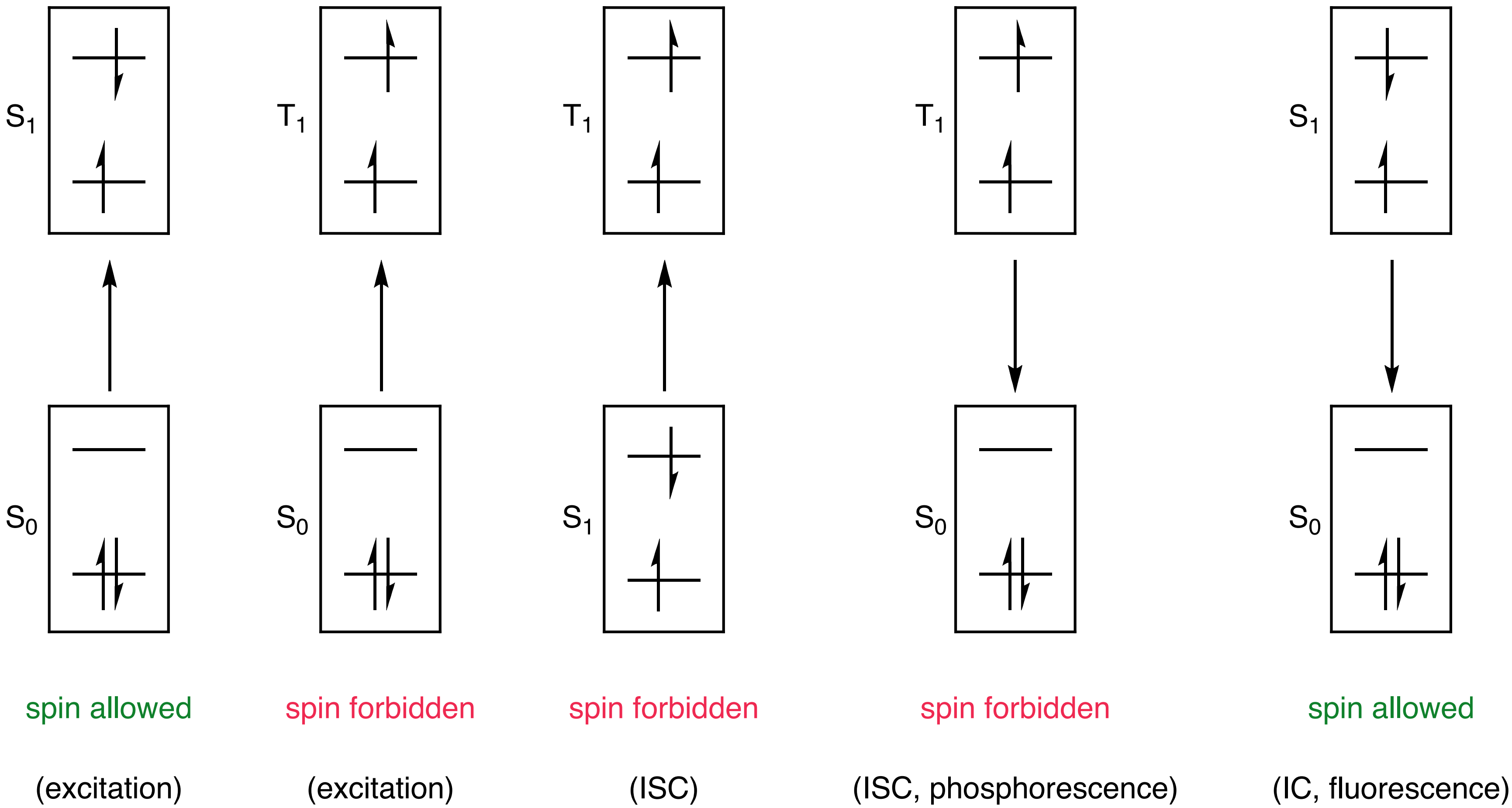

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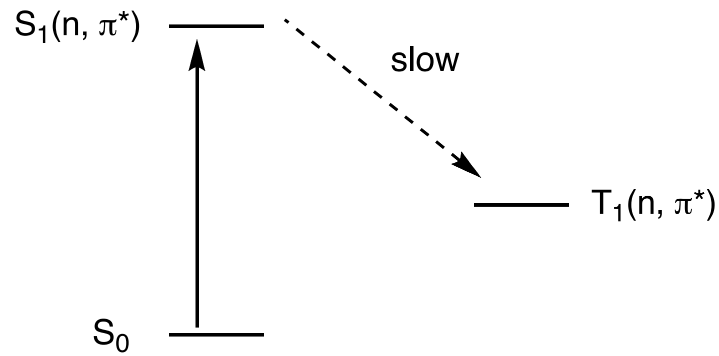
Bimolecular Photophysical Processes

- How could one access T_1 exclusively?



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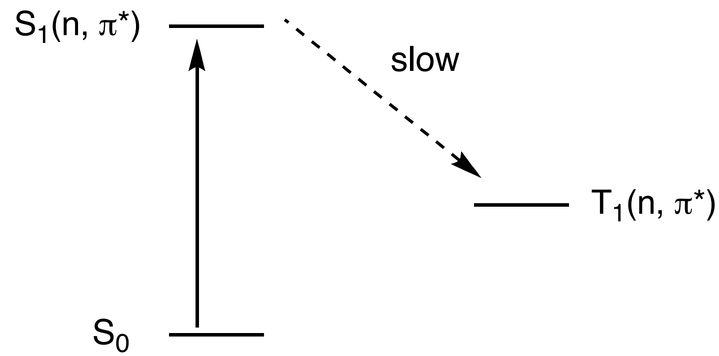

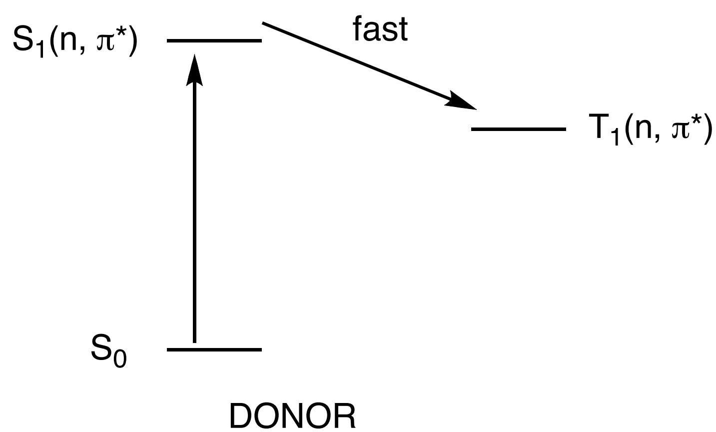

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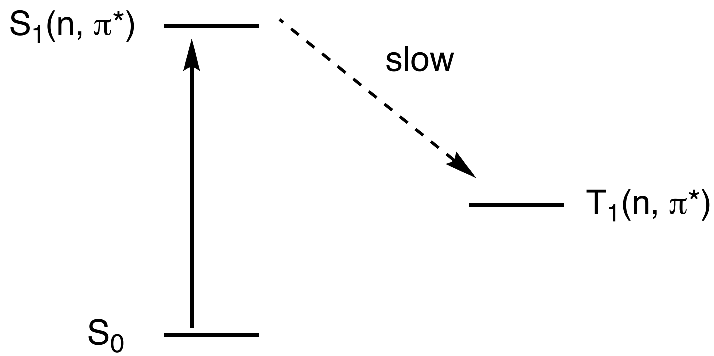

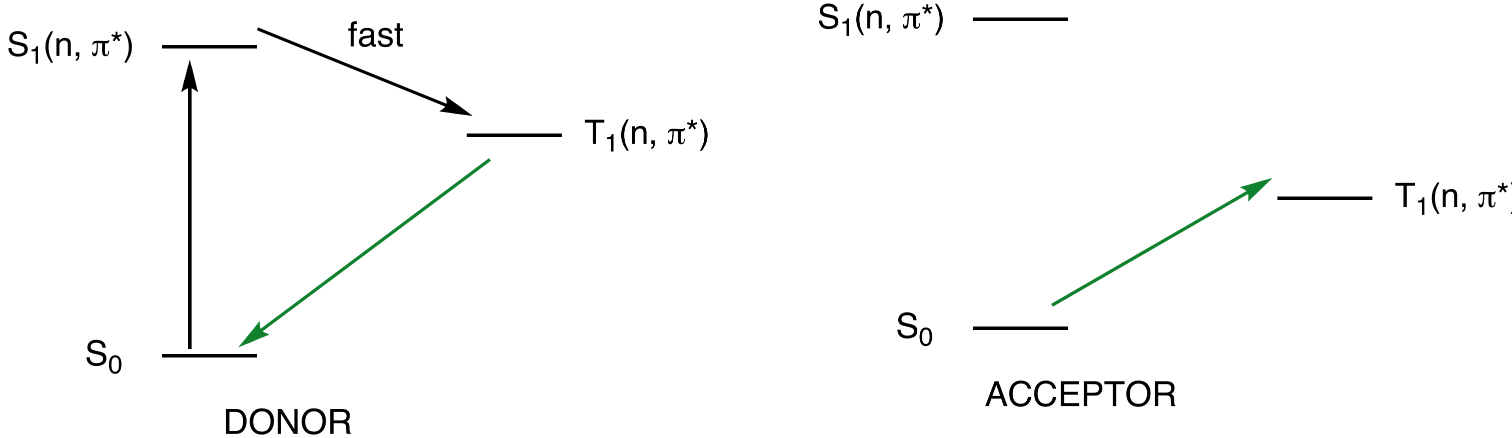

Sensitization

$$D^* + A \longrightarrow D + A^*$$

sensitizer	**triplet energy (kcal/mol)**
acetophenone	73.6
benzophenone	68.5
anthraquinone	62.2
biacetyl	54.9

- Sensitizer should absorb at a different wavelength than acceptor molecule
- Triplet energy of senitizer must be greater than that of acceptor
- Two mechanisms for photosensitization

Bimolecular Photophysical Processes

- Quenching requires close contact between A* and Q
- Olefins and dienes are often used as quenchers

$$A^* \xrightarrow{k_1} A$$

$$Q + A^* \xrightarrow{k_q} A$$

$$1/\tau_2 = 1/\tau_1 + k_q[Q]$$

τ_1 = lifetime of A* without Q

τ_2 = lifetime of A* with Q

- Stern-Volmer quenching kinetics
- Description of quenching efficiency

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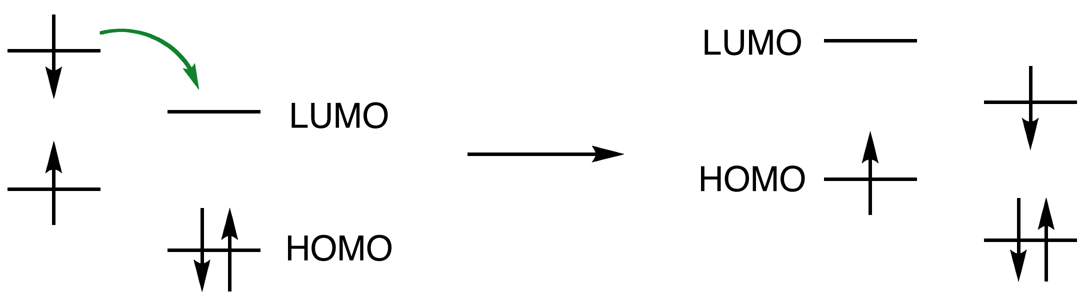

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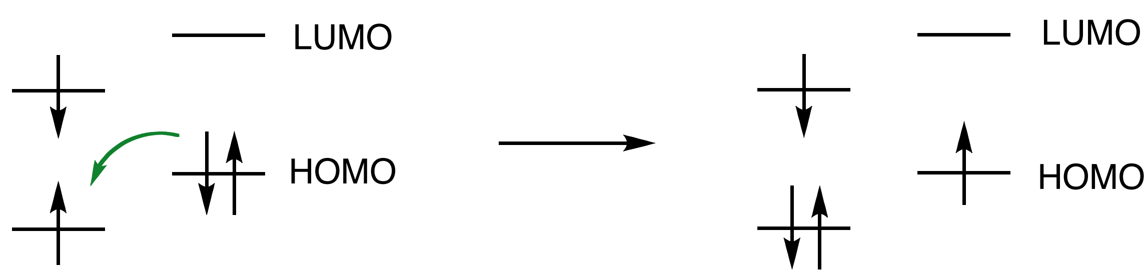
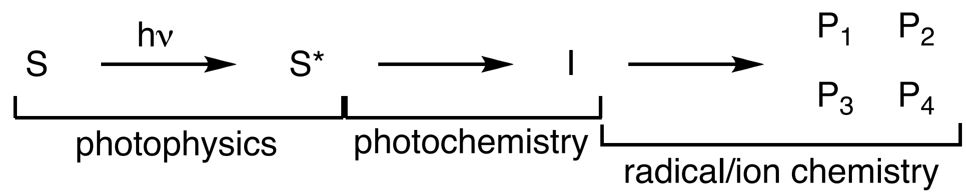


Photochemistry



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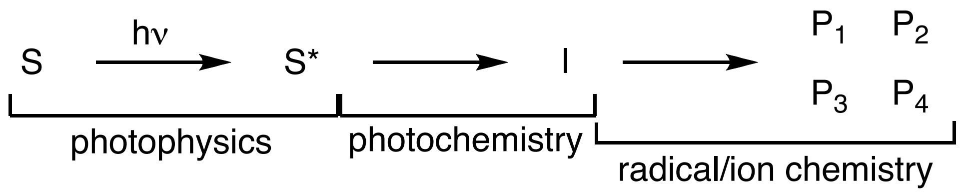

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- Photophysical rates must provide an excited species that persists long enough for photochemistry to occur

Rate of photochemistry from S_1 must outcompete fluorescence

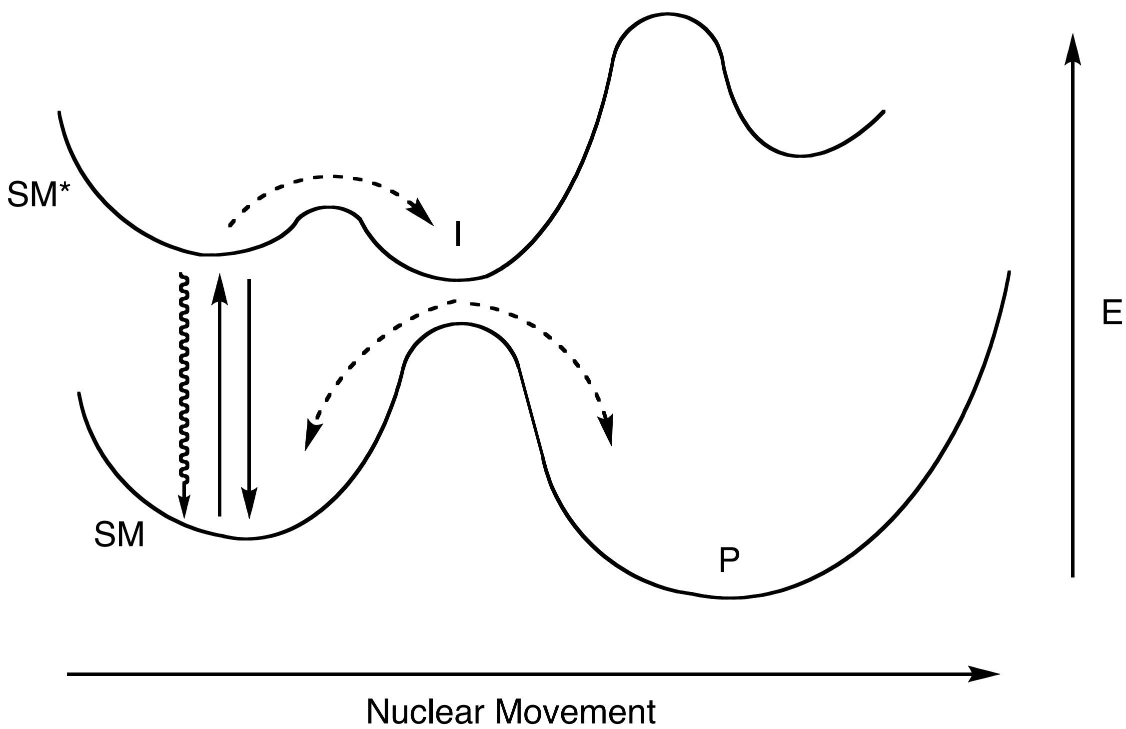
Phosphorescence from T_1 to S_0 must be slow compared to photochemistry

- Two or three energy surfaces are involved due to excited states

- Three types of photochemical reaction diagrams

Photochemistry

Diabatic photoreaction



- Small gap between surfaces promotes crossing
- Minimum on upper surface matches maximum on ground state surface
- Frequent return back to SM results in low quantum yield

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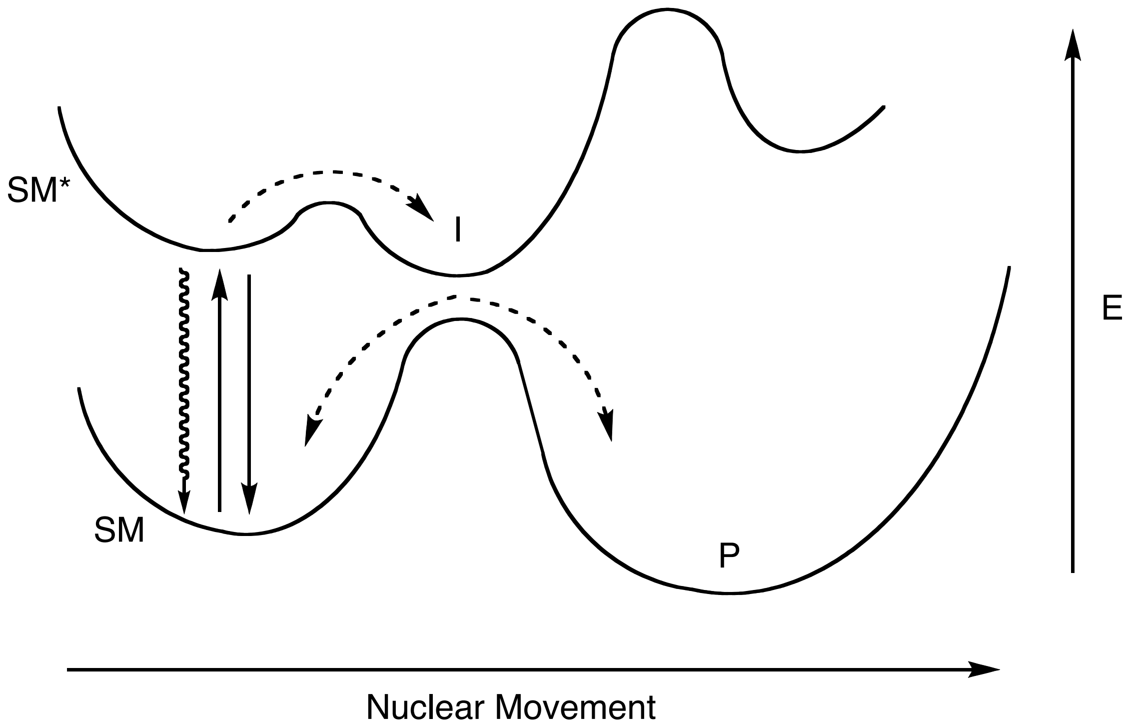

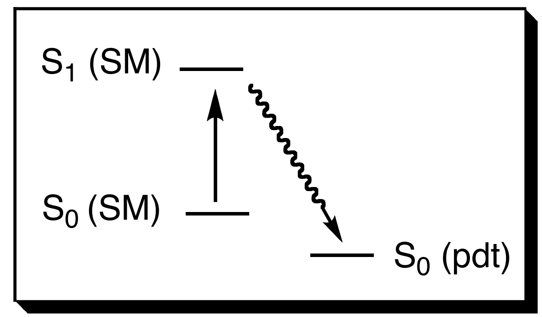

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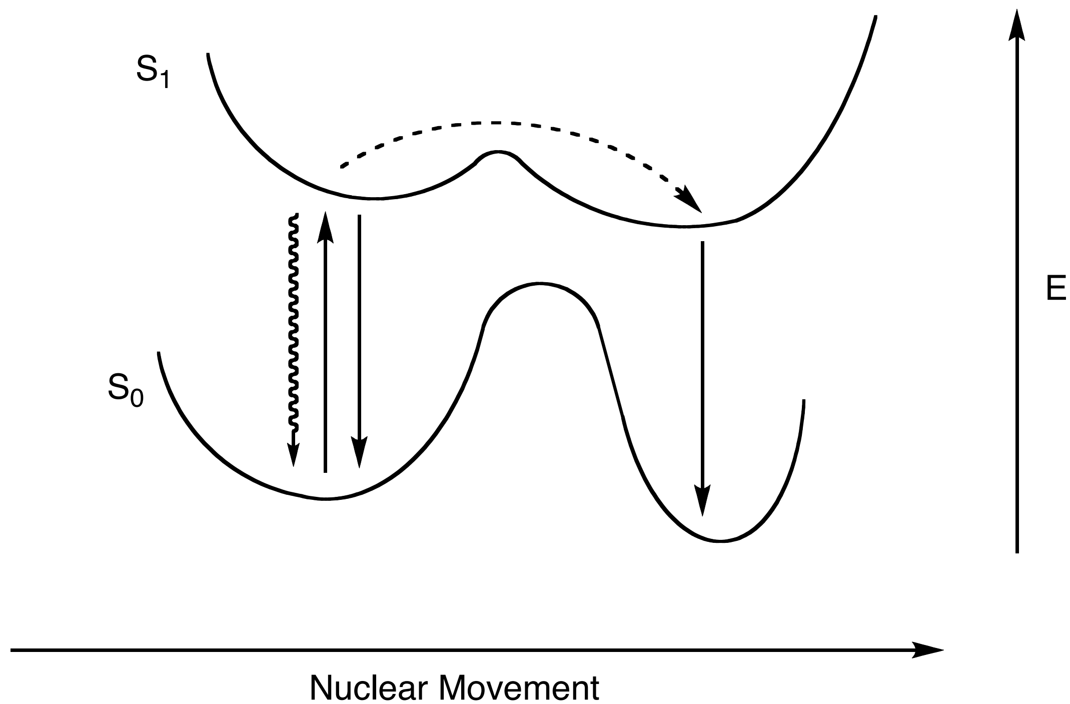

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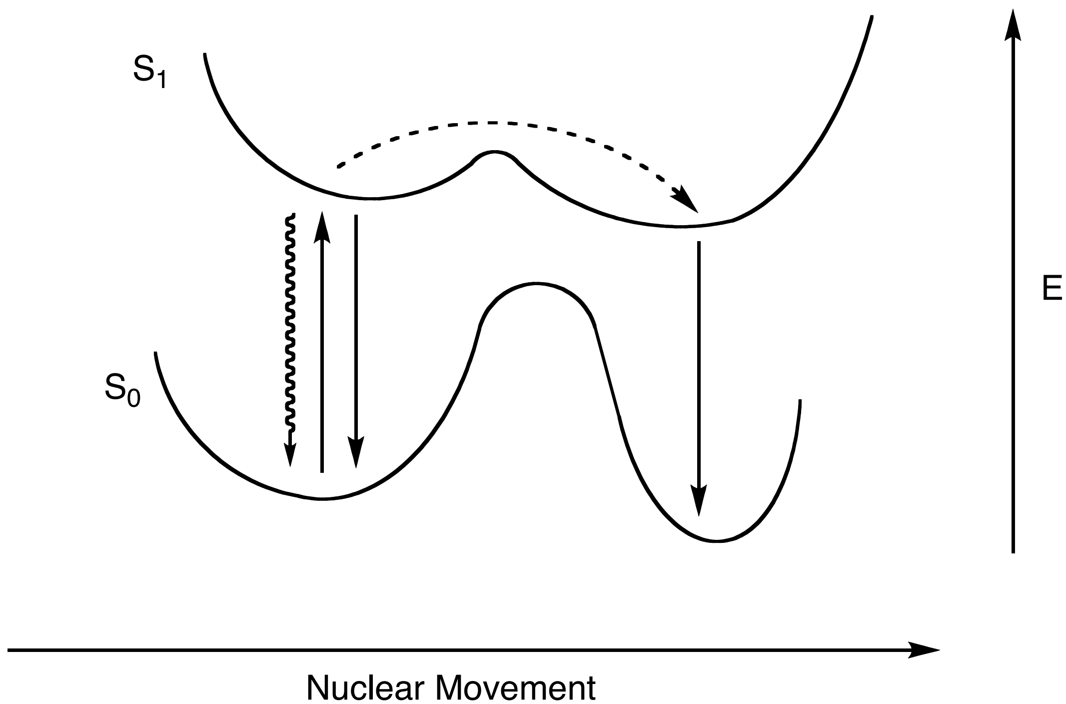

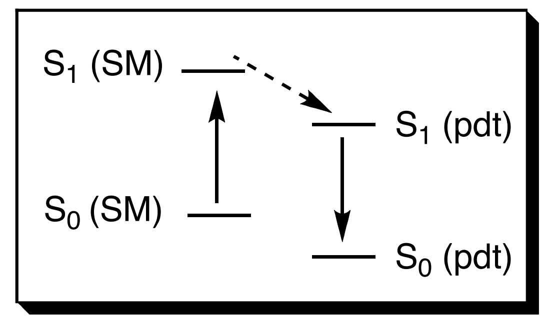

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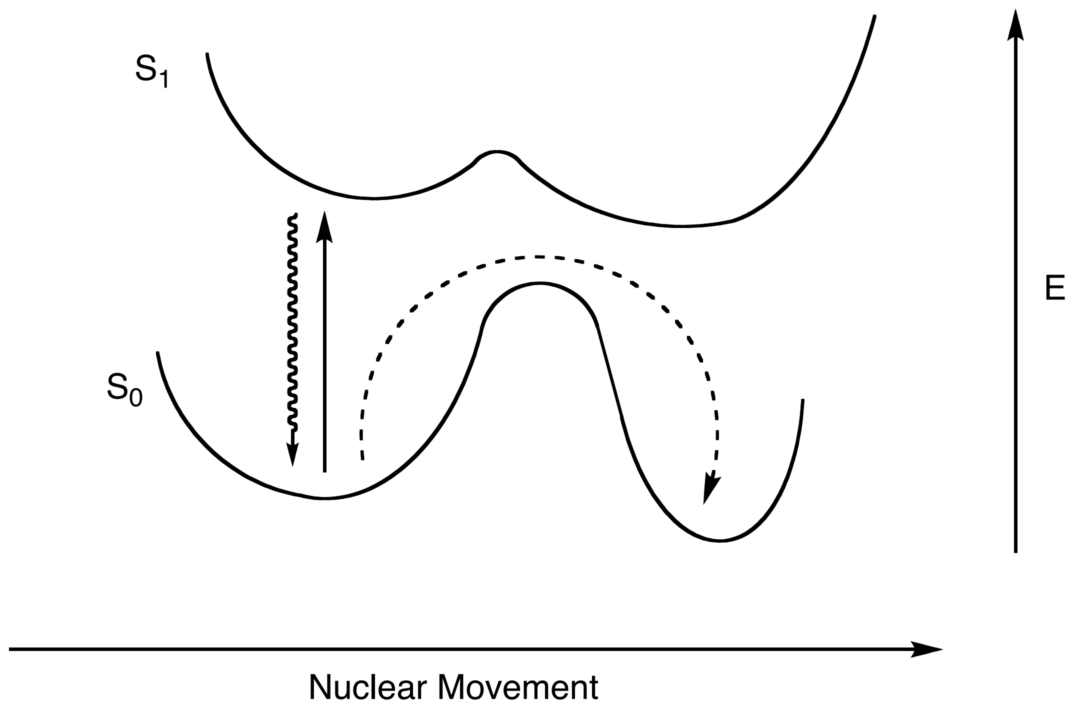
Hot Ground State reaction (thermal)



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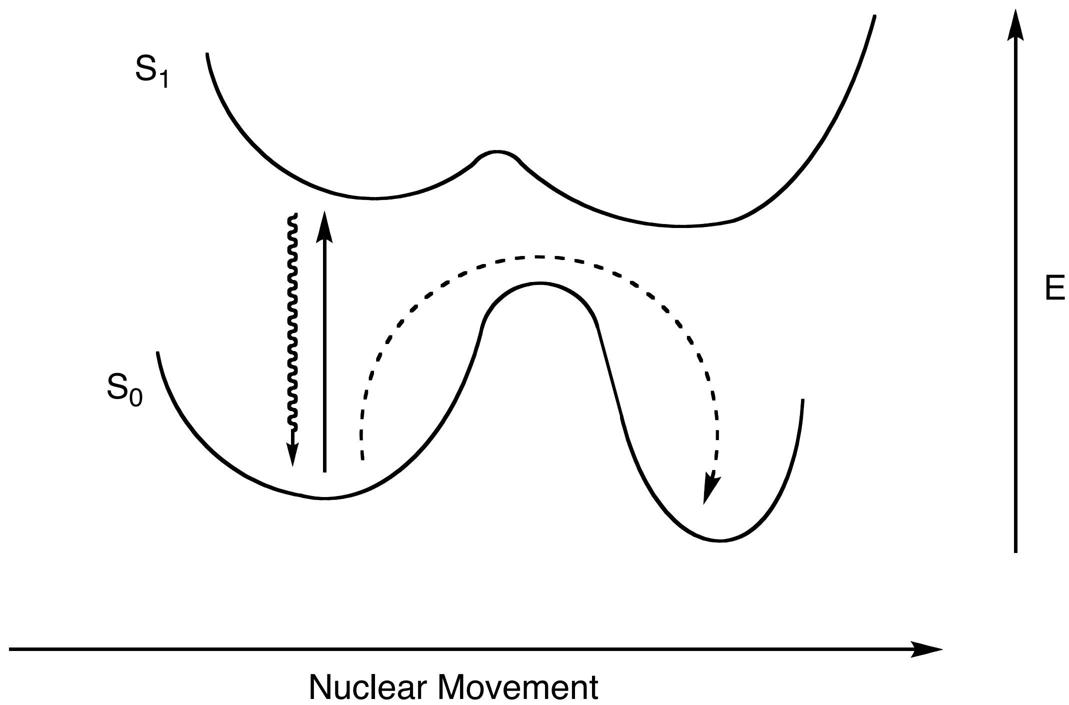

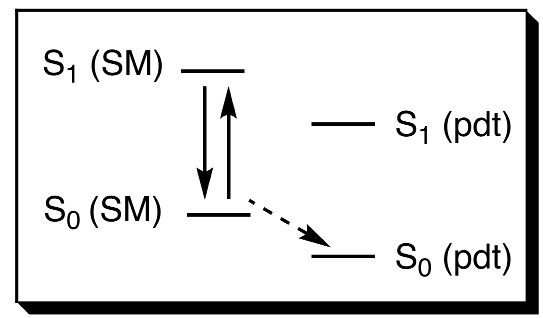

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Tendencies of S and T states

- Singlet and triplet excited states often show different reactivity

Singlet

tend to have considerable zwitterionic character

undergo rapid, concerted reactions

stereospecific

must compete with facile photophysical processes

electrocyclic rearrangements

cycloadditions

sigmatropic rearrangements

Tendencies of S and T states

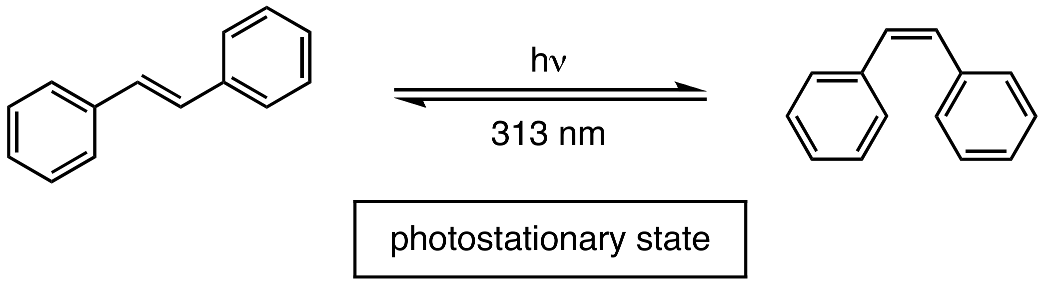
- Singlet and triplet excited states often show different reactivity

Singlet	**Triplet**
tend to have considerable zwitterionic character	tend to have biradical character
undergo rapid, concerted reactions	triplet state is longer lived
stereospecific	stepwise reactions
must compete with facile photophysical processes	no stereospecificity
electrocyclic rearrangements	*hydrogen abstraction*
cycloadditions	*additions to unsaturation*
sigmatropic rearrangements	*homolytic fragmentation*
	radical rearrangements

- Different products due to the fact that the ground state is a singlet state

Olefin Isomerization

- Simple olefins do not absorb at easily-generated wavelengths, so additional chromophores are added



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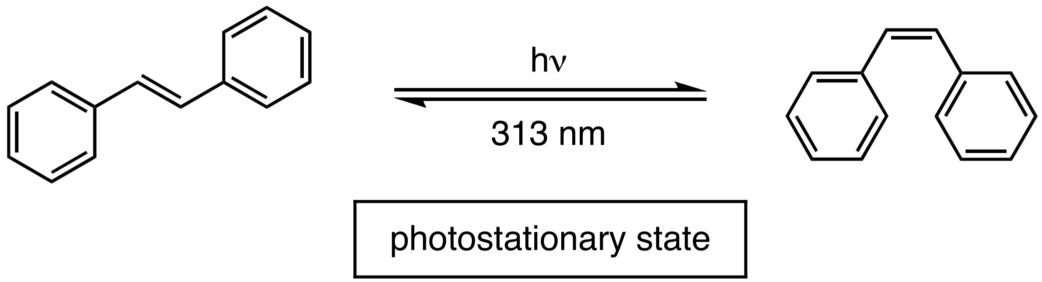

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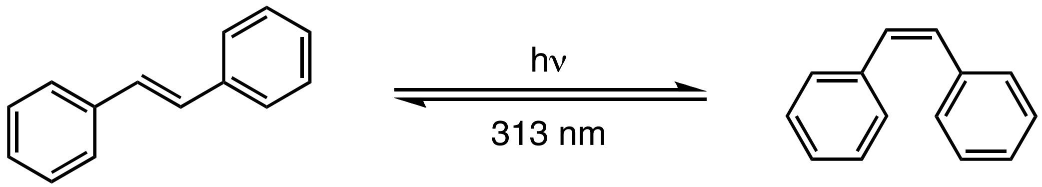

photostationary state

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- Ratio controlled by absorption and quantum yield for isomerization

trans and cis stilbene absorb with the same efficiency at 313 nm

lifetime of S_1(trans) = 68 ps

lifetime of S_1(cis) = 1 ps

Φ (trans to cis) = 0.50

Φ (cis to trans) = 0.35

Olefin Isomerization

- Olefin isomerization is a powerful feature of photochemistry
- The relative energy of two minima on S_o surface does not matter
- Key issue is how system exits from S_1 or T_1 onto S_0

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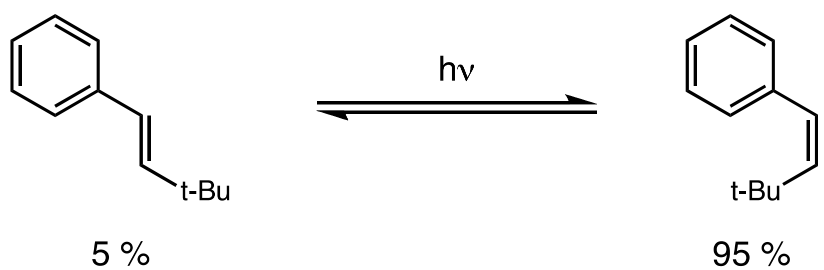

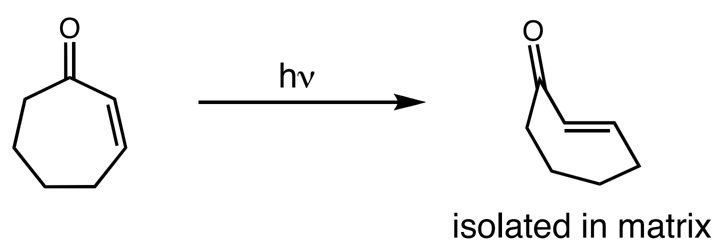

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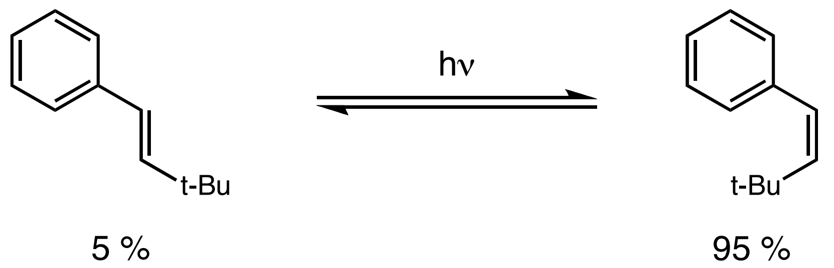
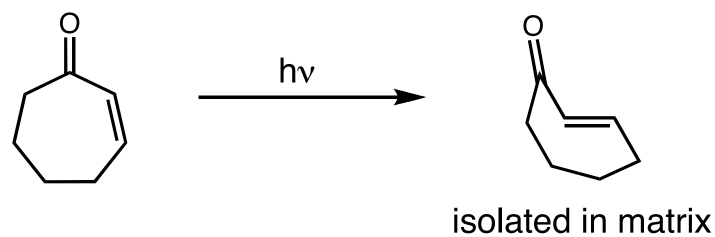
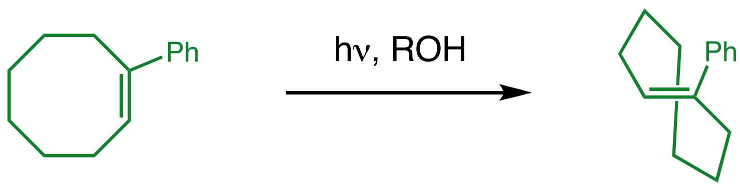


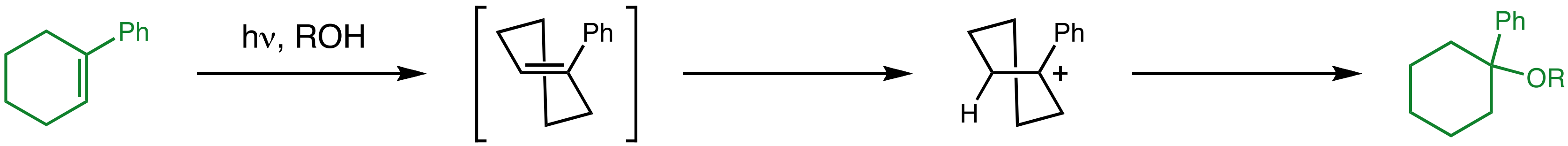


- 3-4 (impossible); 5 (difficult, reactive); 6-7 (facile, reactive); 8 or above (stable)
- Cyclic trans olefins are used *in situ* for functionalization

Olefin Isomerization



isolated



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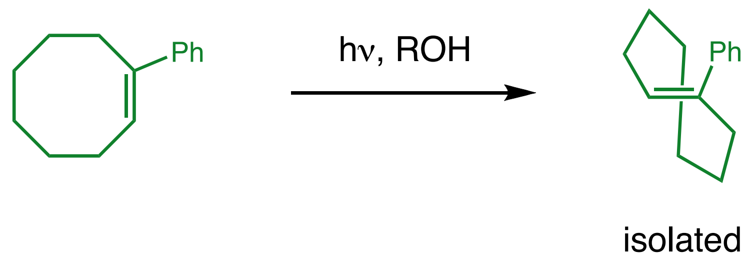

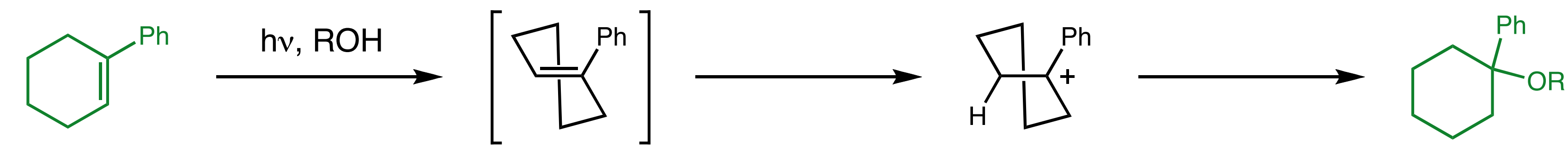

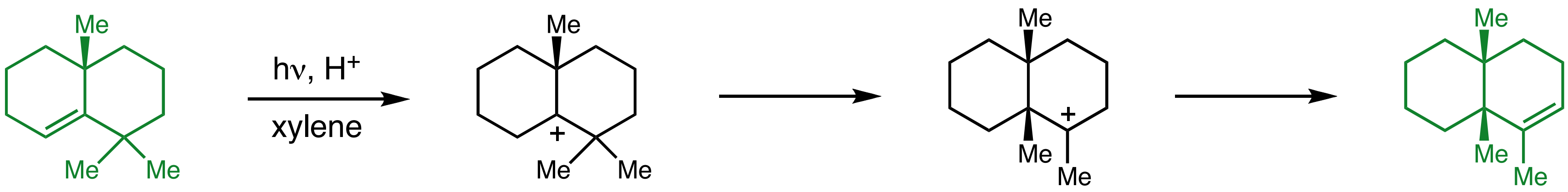

Photoadditions/substitutions

- Hydrogen abstration is frequent in these reactions:

Strength of bond being broken
Strength of bond being formed
Steric effects of approach
Solvent effects on reagent or transition state

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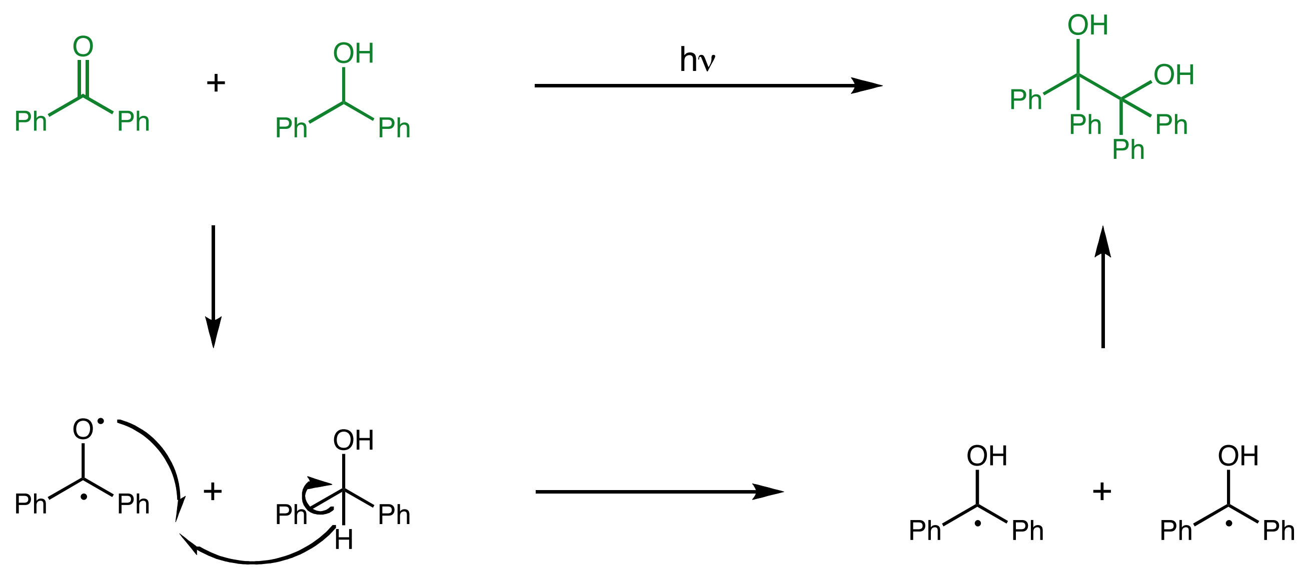
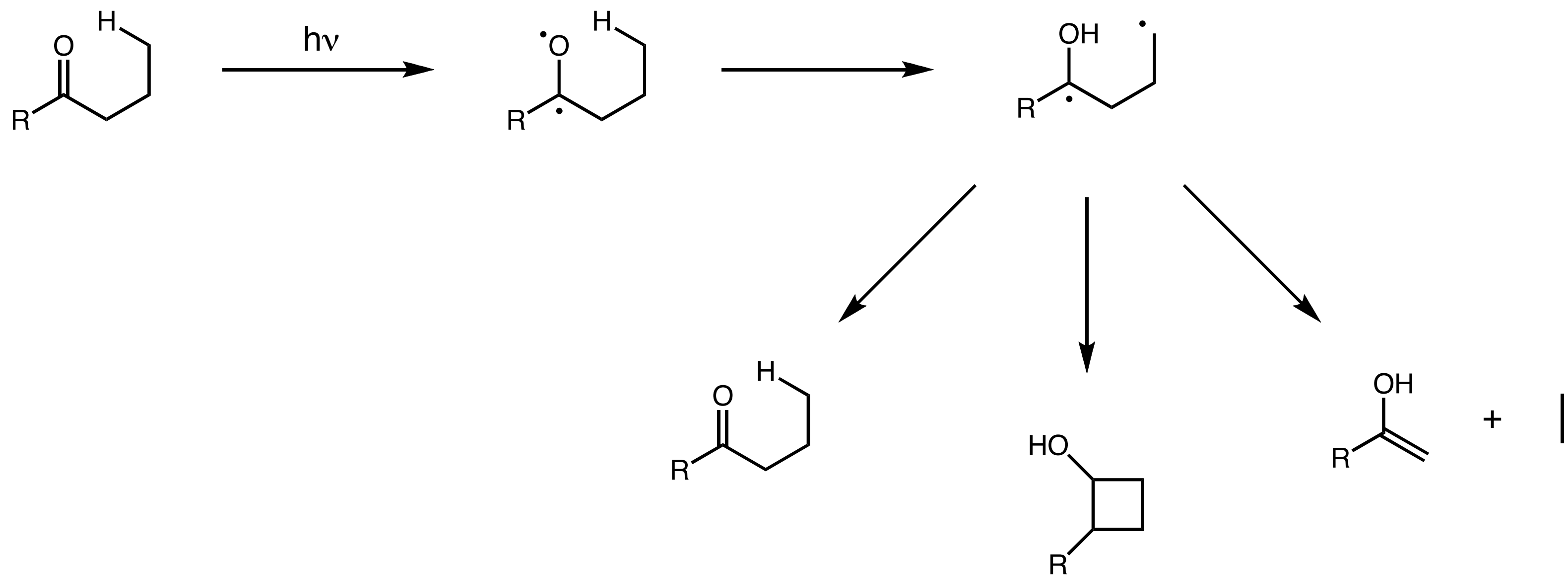


Norrish Type II

- Intramolecular H abstraction



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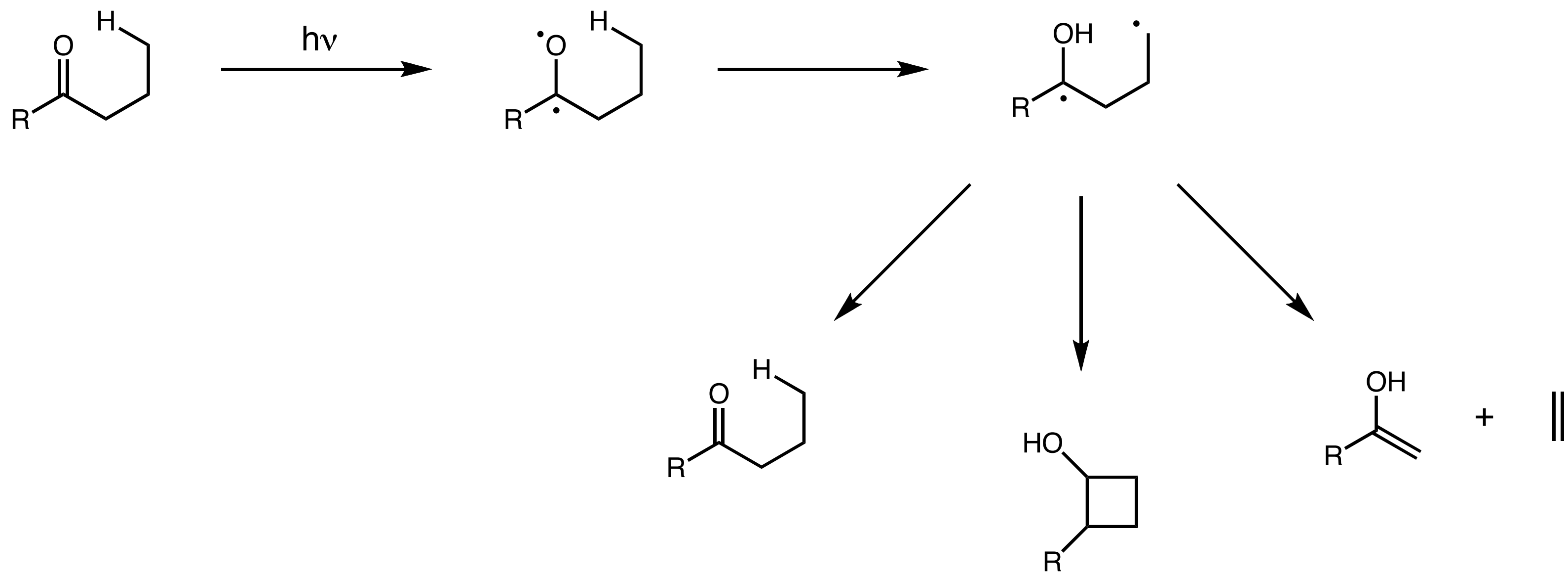
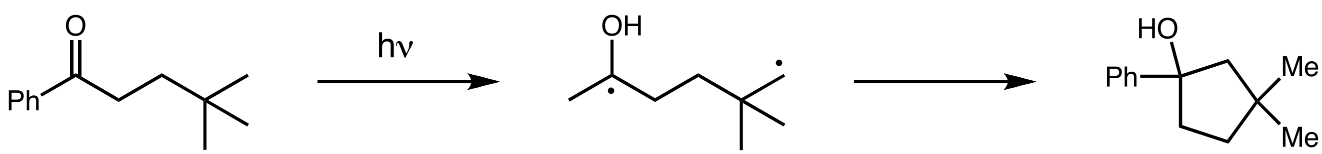


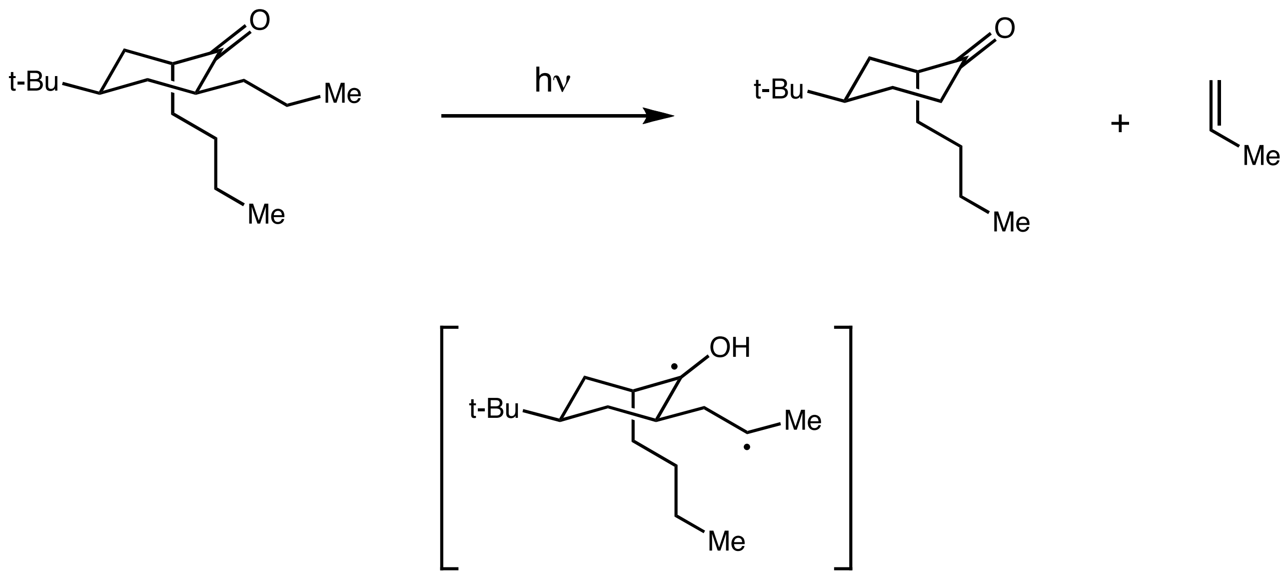
- Six-membered H abstracted preferntially

- Seven- and five-membered H abstraction possible if six-membered position is blocked or disfavored



60%

Norrish Type II



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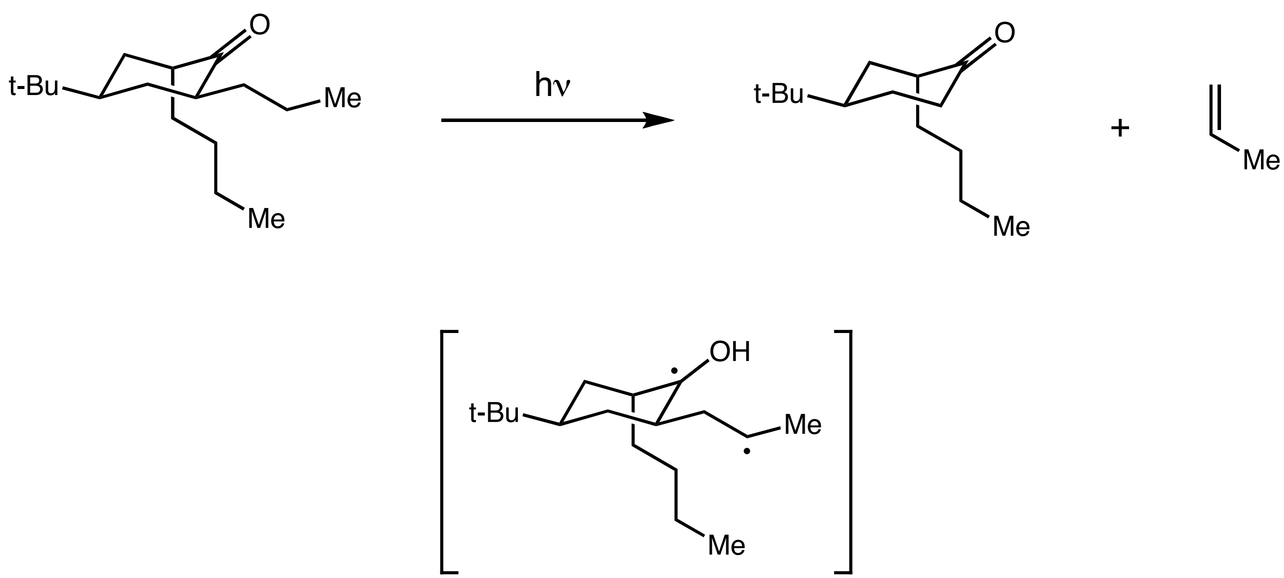
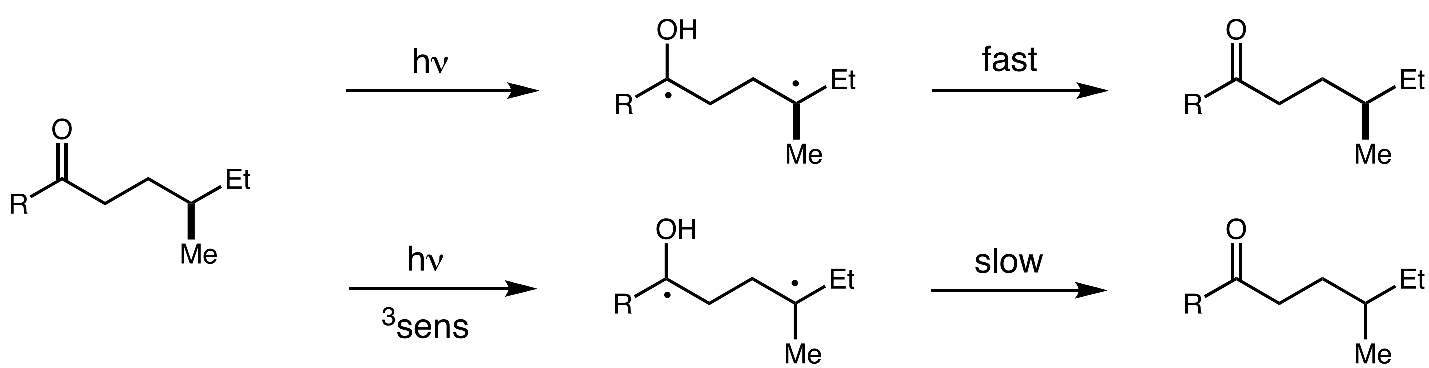
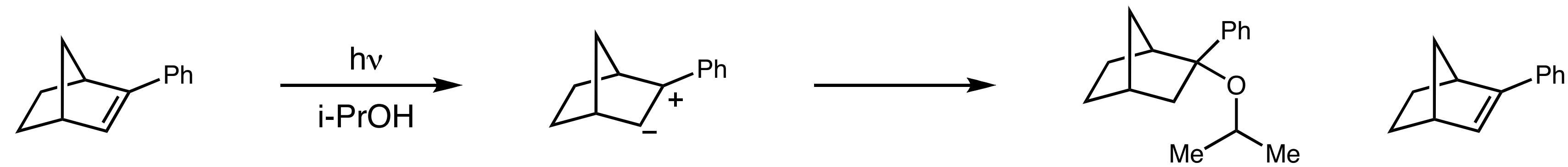


Stereospecificity of singlet and triplet states - Example: disproportionation in Type II reactions



Alkene Hydrogen Abstraction

- Alkenes abstract hydrogens when excited to T_1, but act as zwitterions if excited to S_1 (and cannot isomerize)



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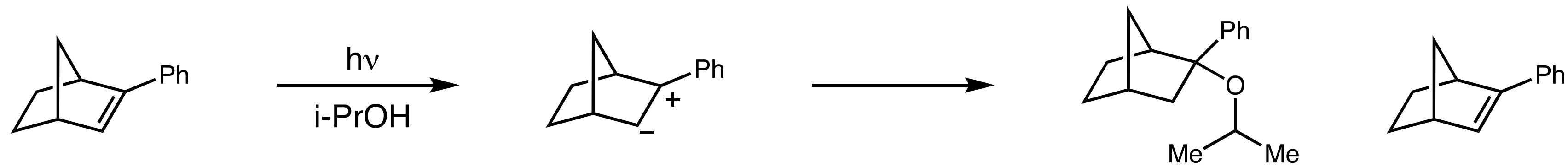

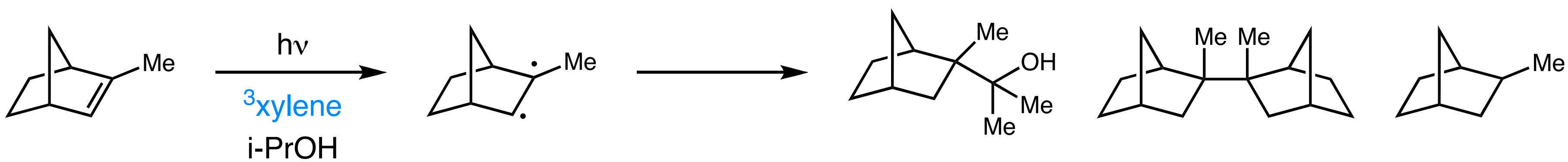

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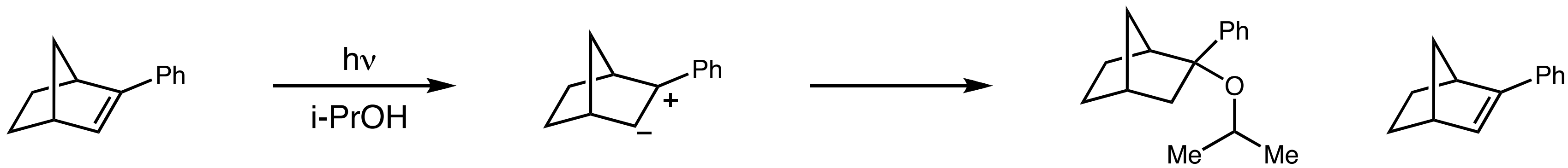
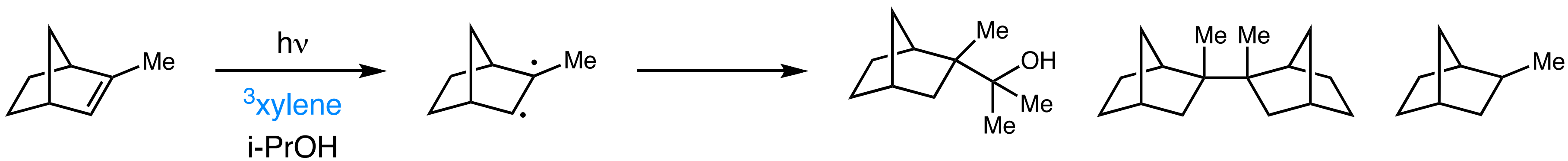
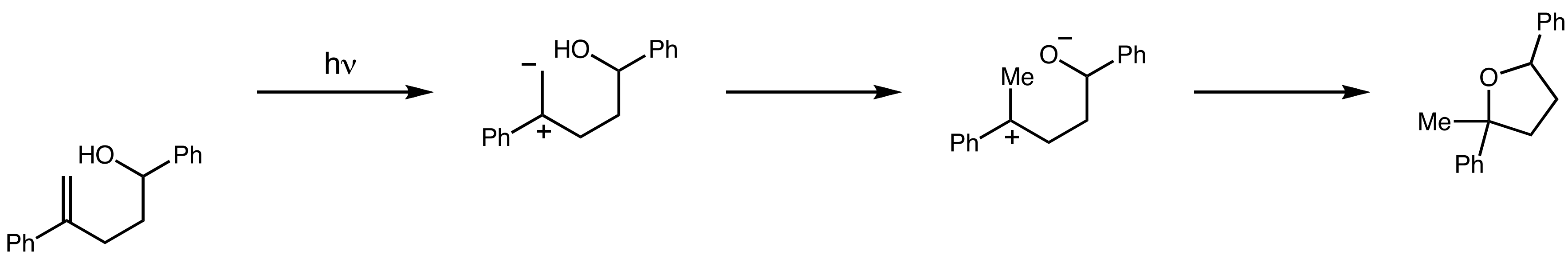
- Alkenes abstract hydrogens when excited to T_1, but act as zwitterions if excited to S_1 (and cannot isomerize)







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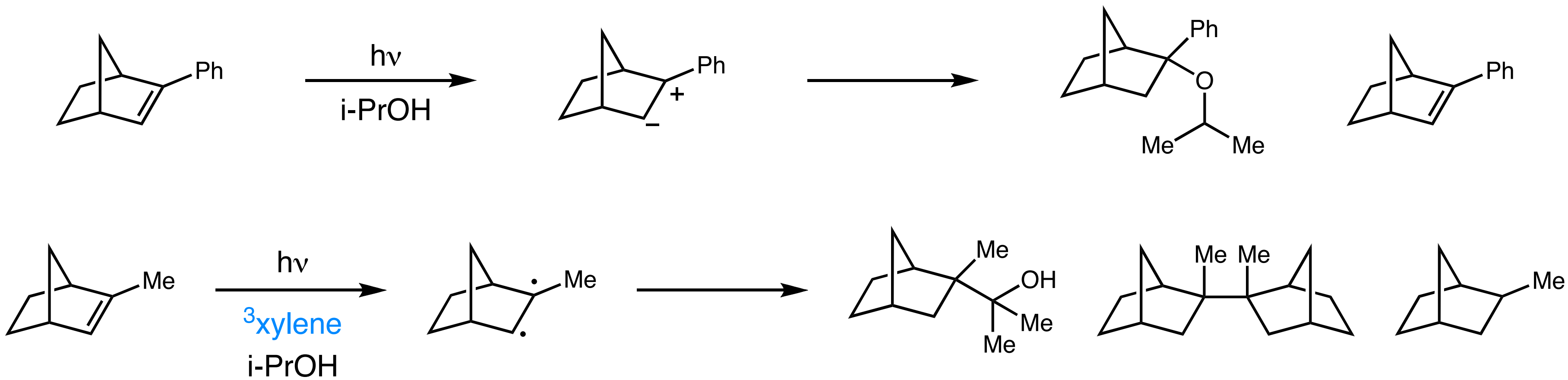
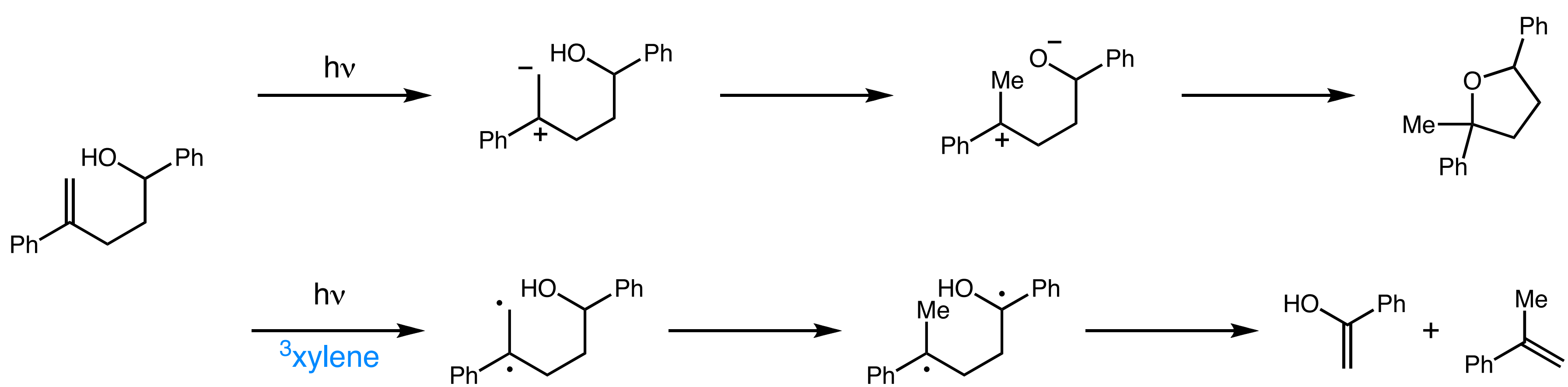
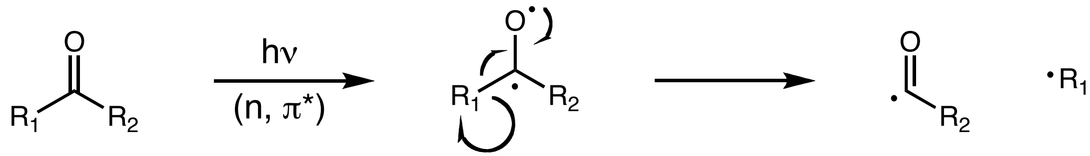




Norrish Type I Fragmentation

- C=O bond is a very strong bond, so there is a considerable driving force to reform it



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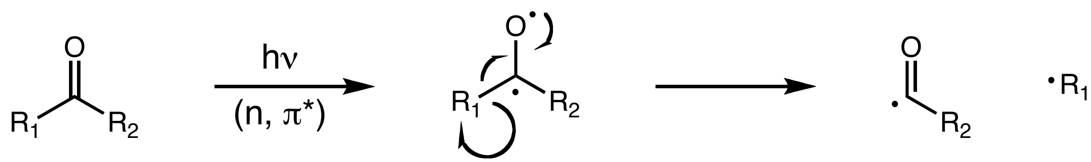


- Several factor control rate of this α-**cleavage** reaction

- Rate of Type II reaction, phosphorescence, or ISC

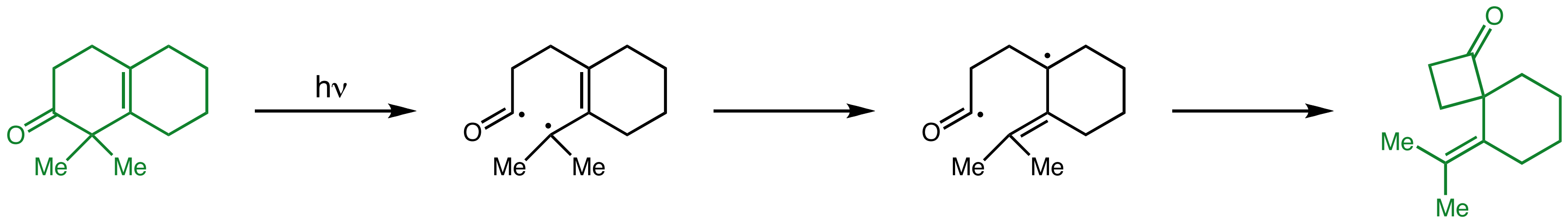
- Nature of R_1 and R_2

Stability of resulting radical

Me = 10^3 s^{-1}
1^o alkyl = 10^7 s^{-1}
Benzyl = 10^{10} s^{-1}

- Ring strain

Norrish Type I Fragmentation



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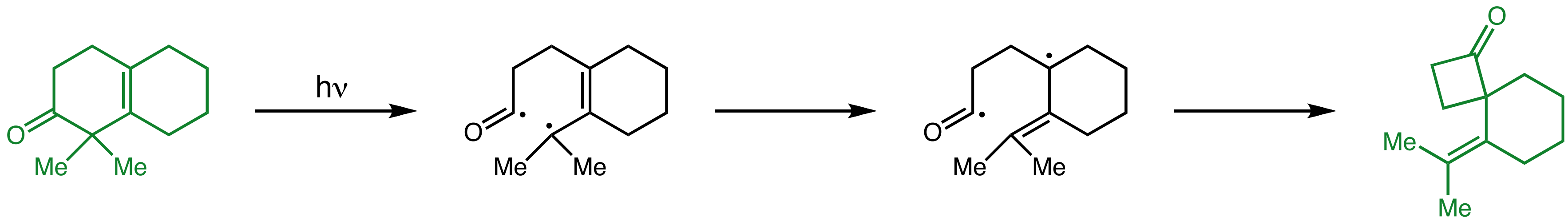

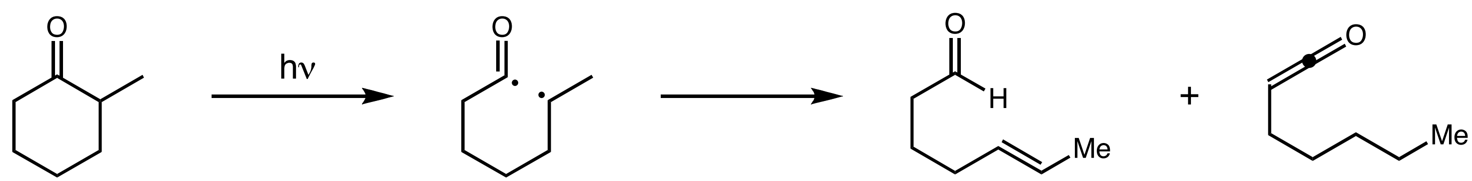

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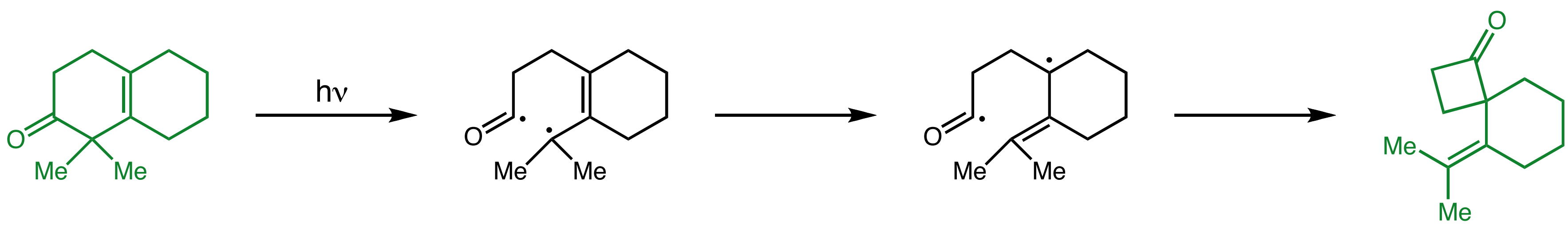
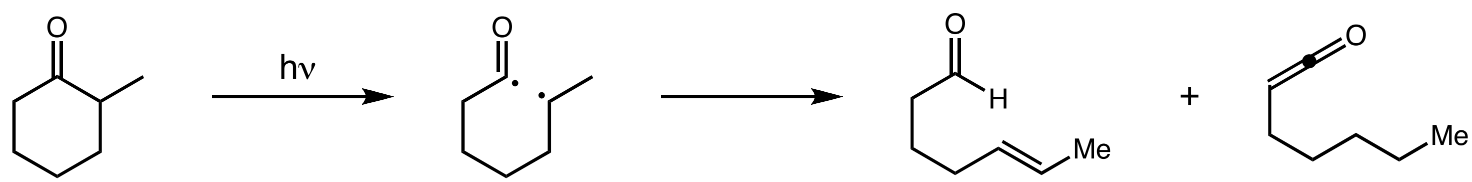
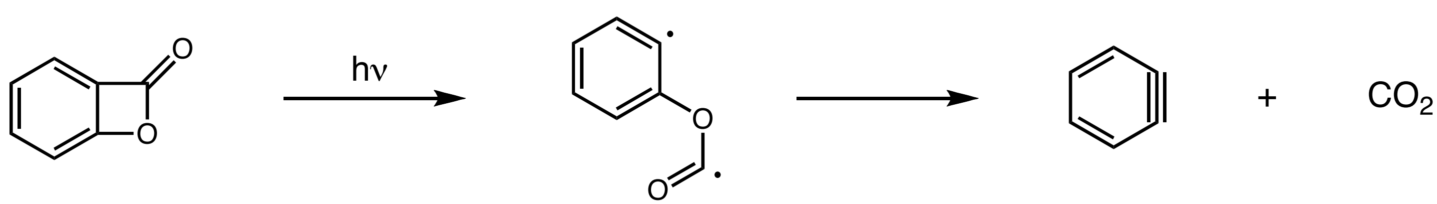


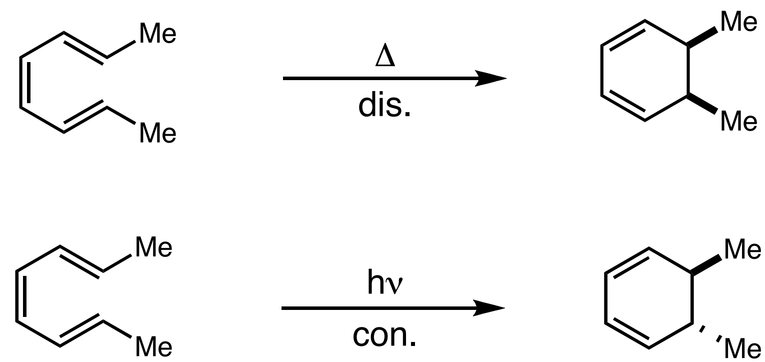




Electrocyclic Reactions

Reversal of Pericyclic Selection Rules

	D	C
2	Δ	hν
4	hν	Δ
6	Δ	hν
8	hν	Δ



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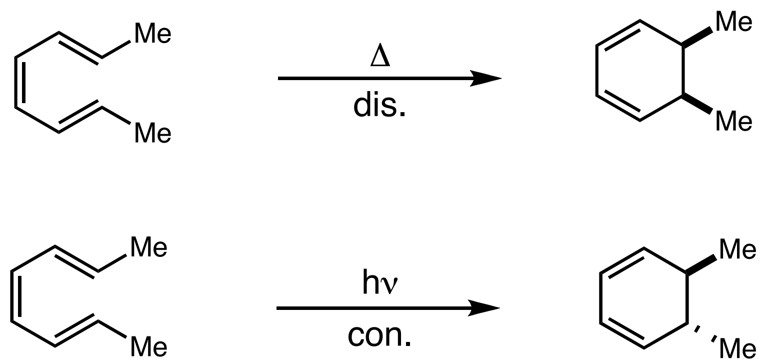

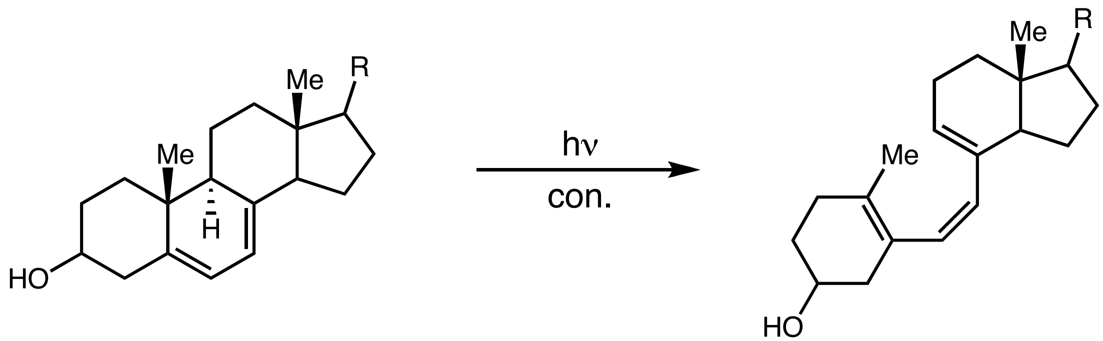

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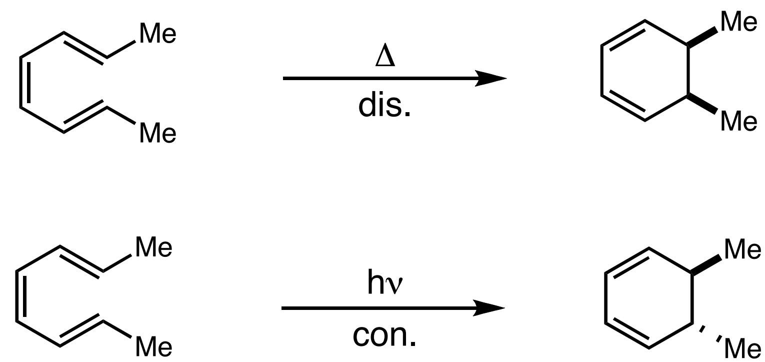
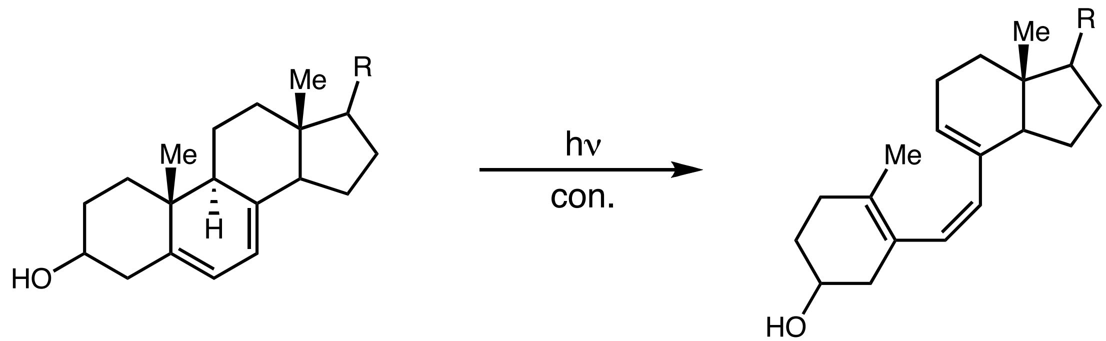
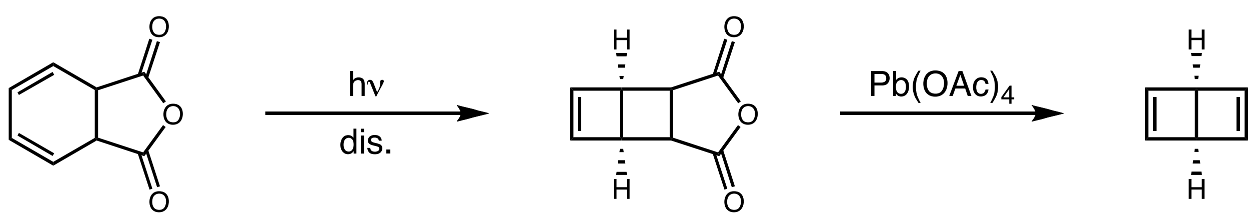
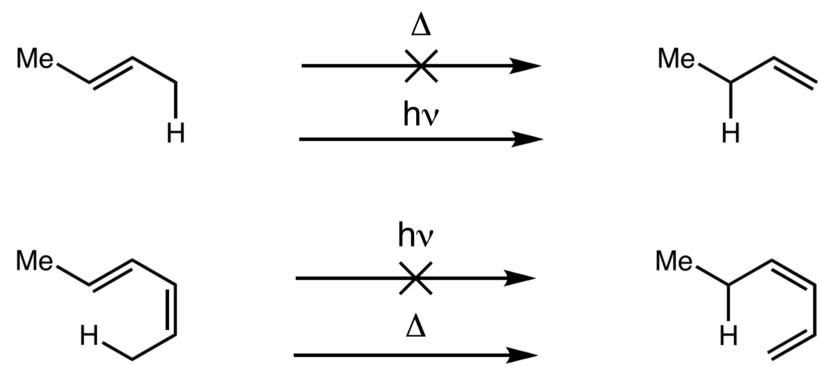






Sigmatropic Rearrangements

- Orbital Symmetry Rules control what rearrangements are allowed



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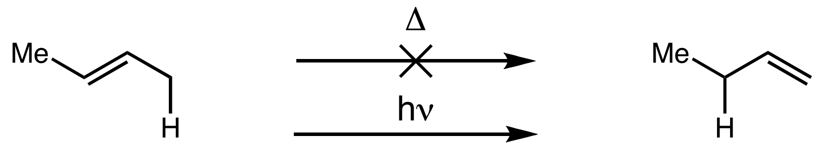

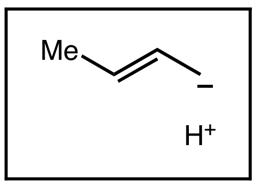

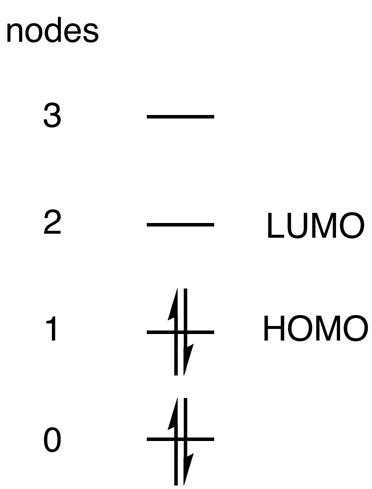

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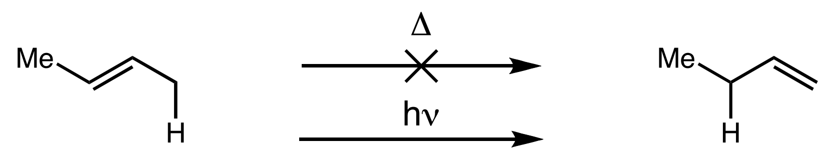
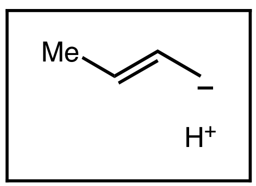
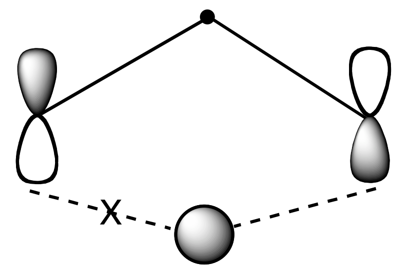
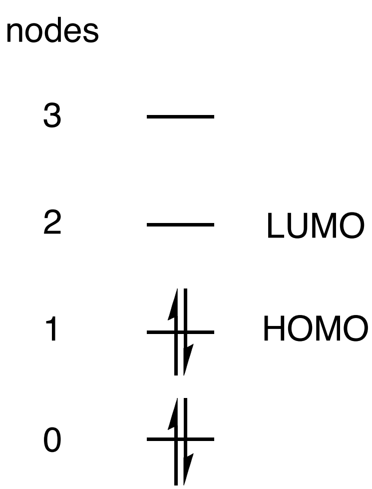






Thermally disallowed



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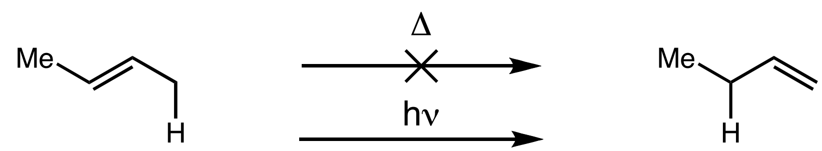

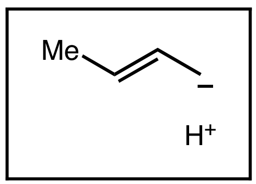

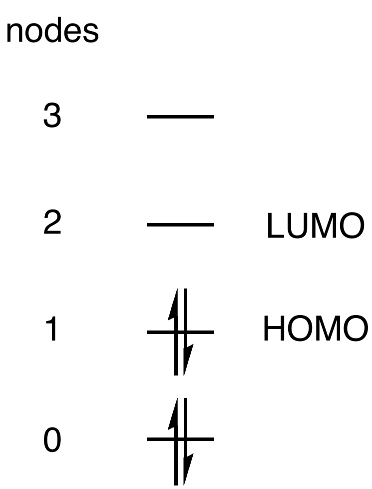

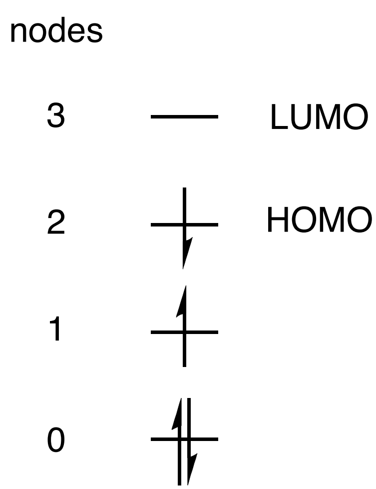

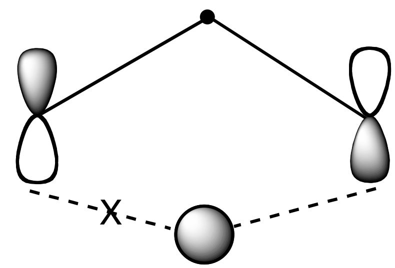

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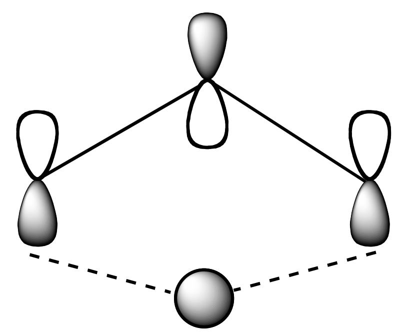
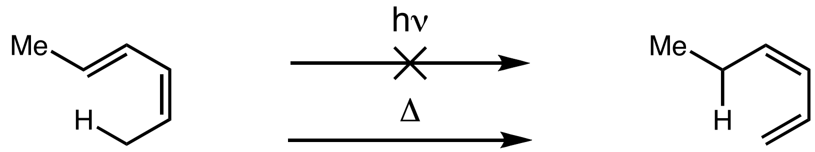
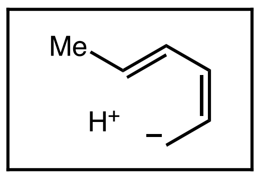
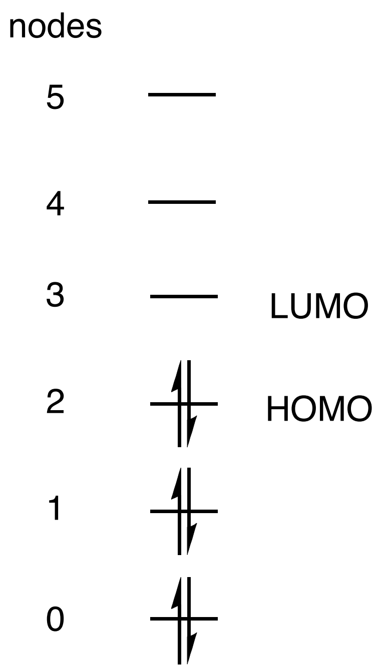


Photochemically allowed

Sigmatropic Rearrangements







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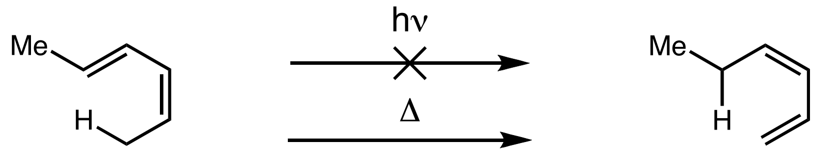

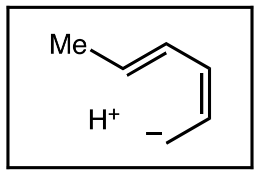

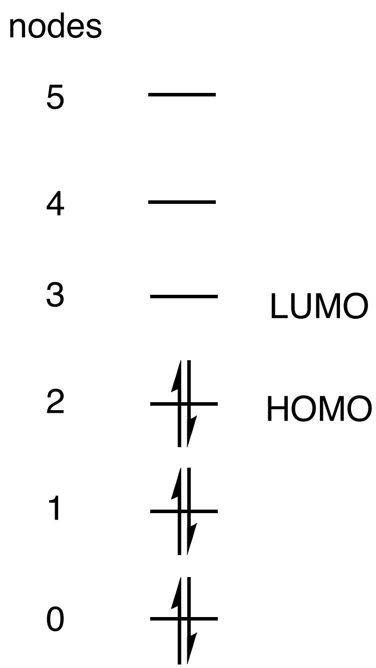

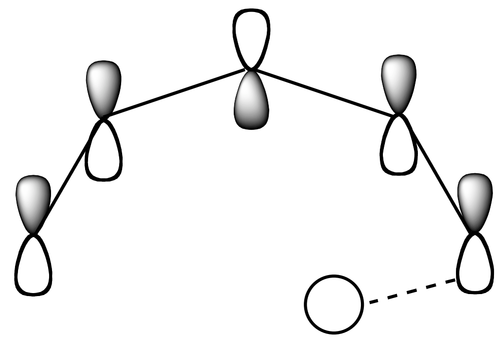

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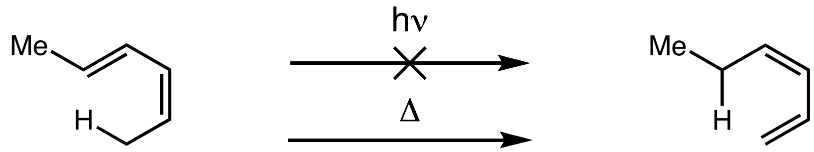
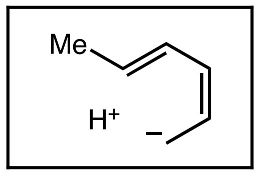
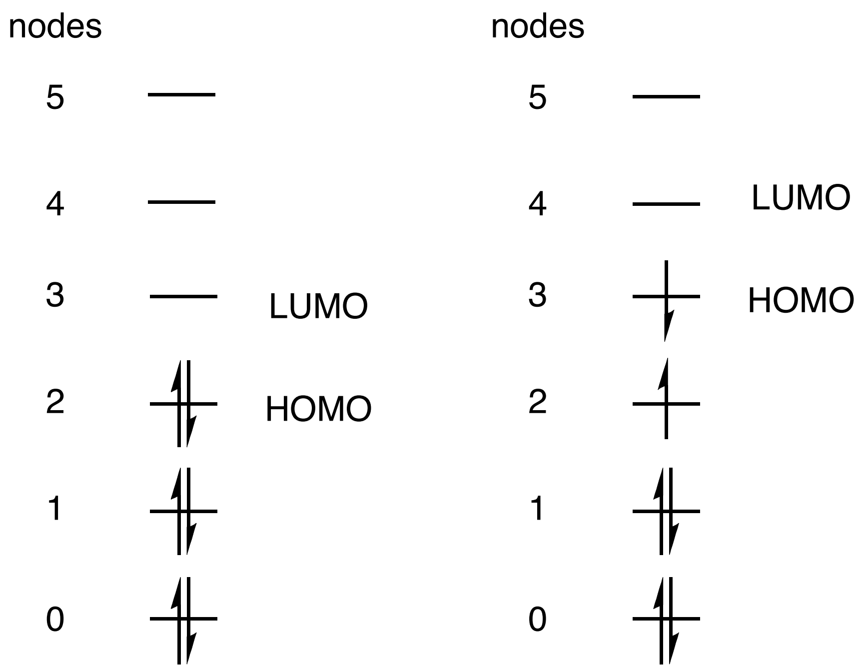
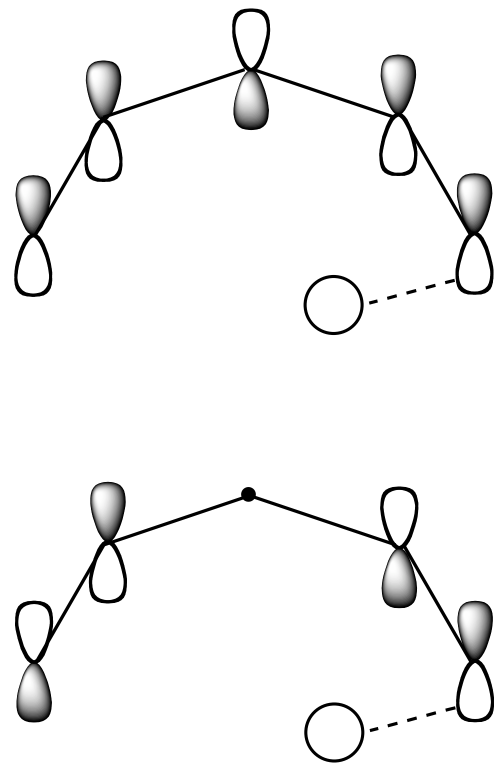




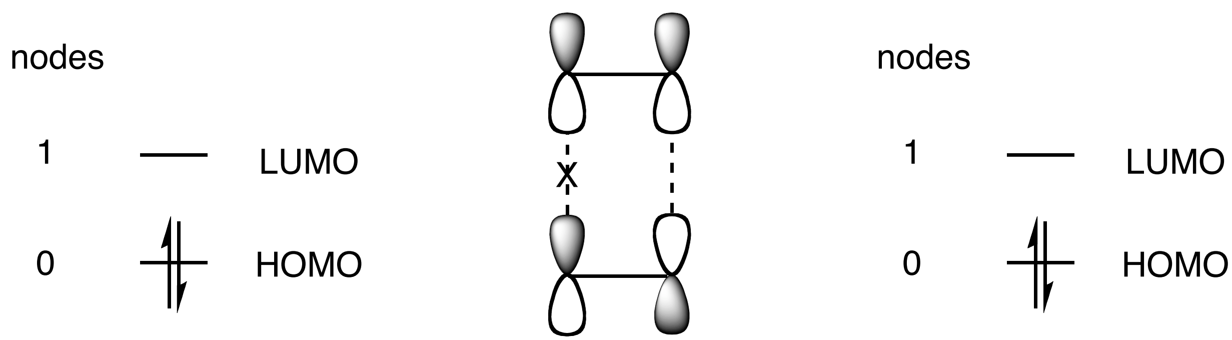




rare for antarafacial shift to occur

Cycloadditions

■ Photochemical [2 + 2] cycloaddition



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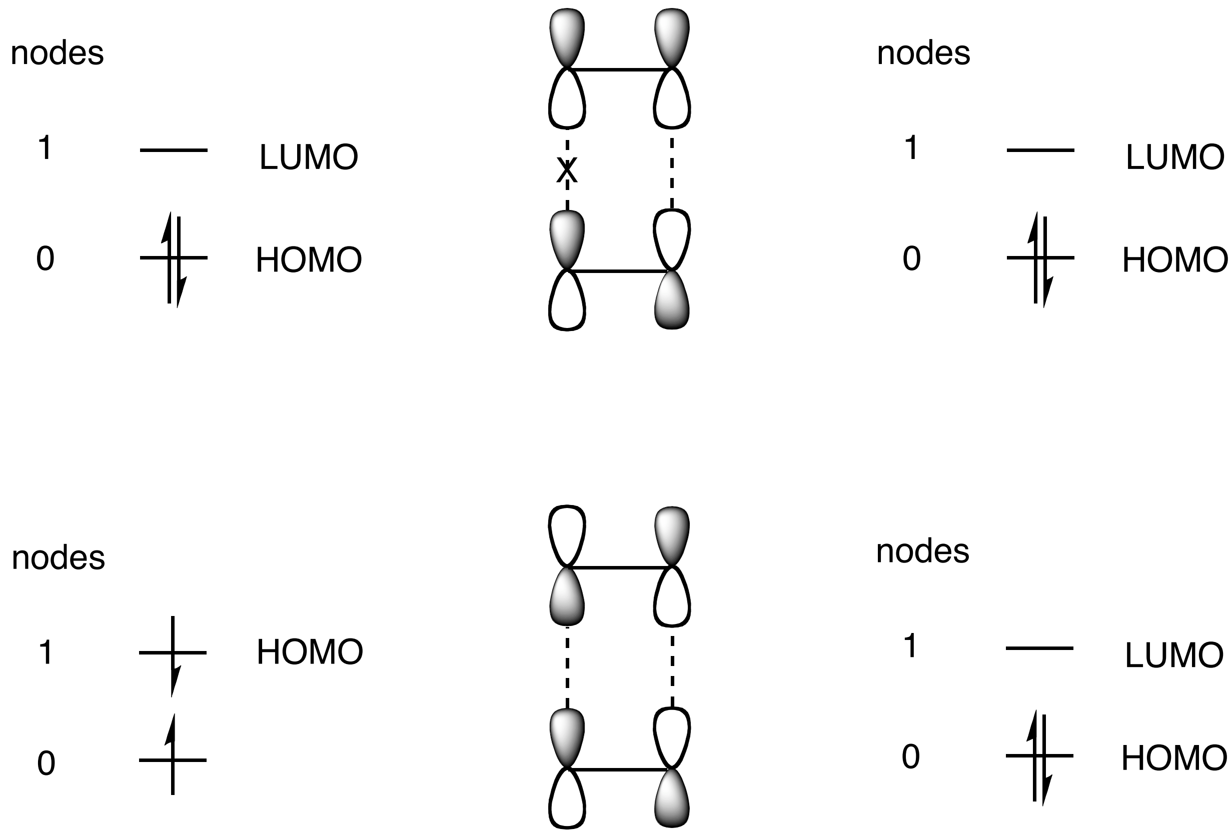
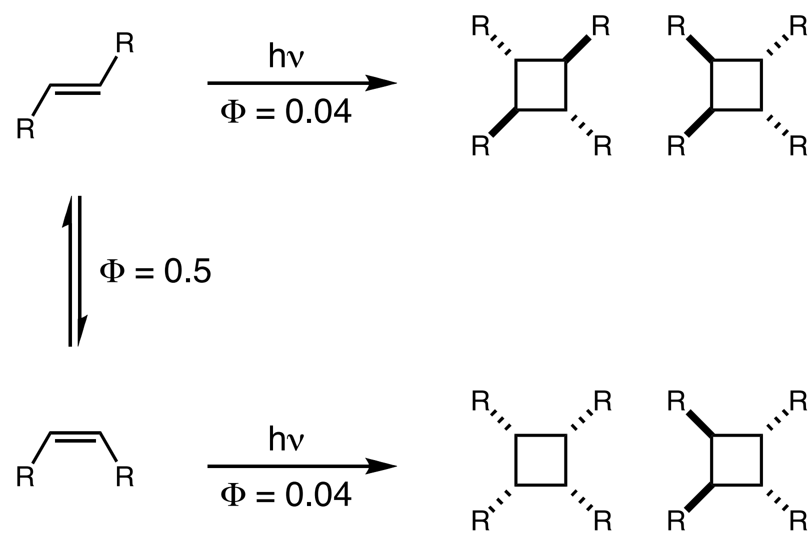


Cycloadditions

- Acyclic olefins tend to undergo isomerization rather than [2 + 2]



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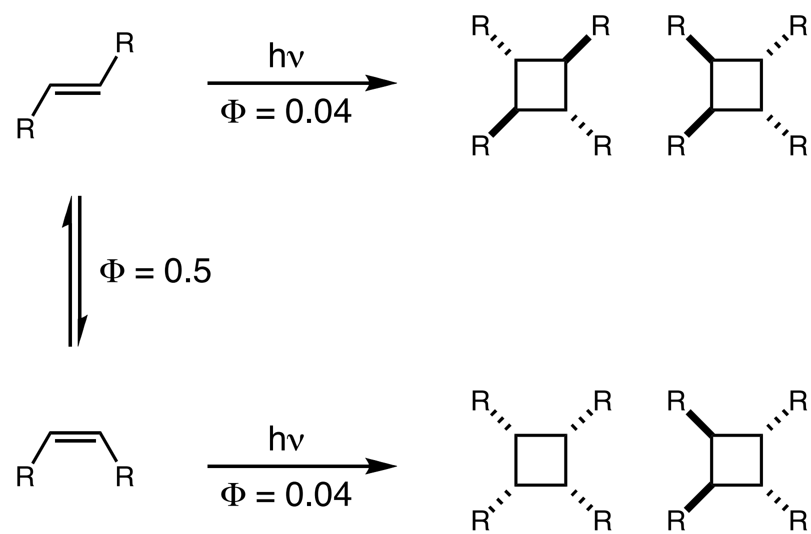
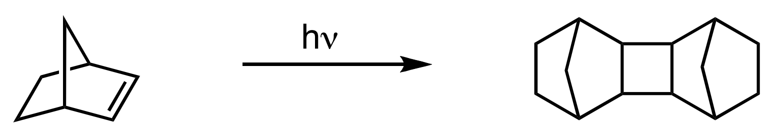
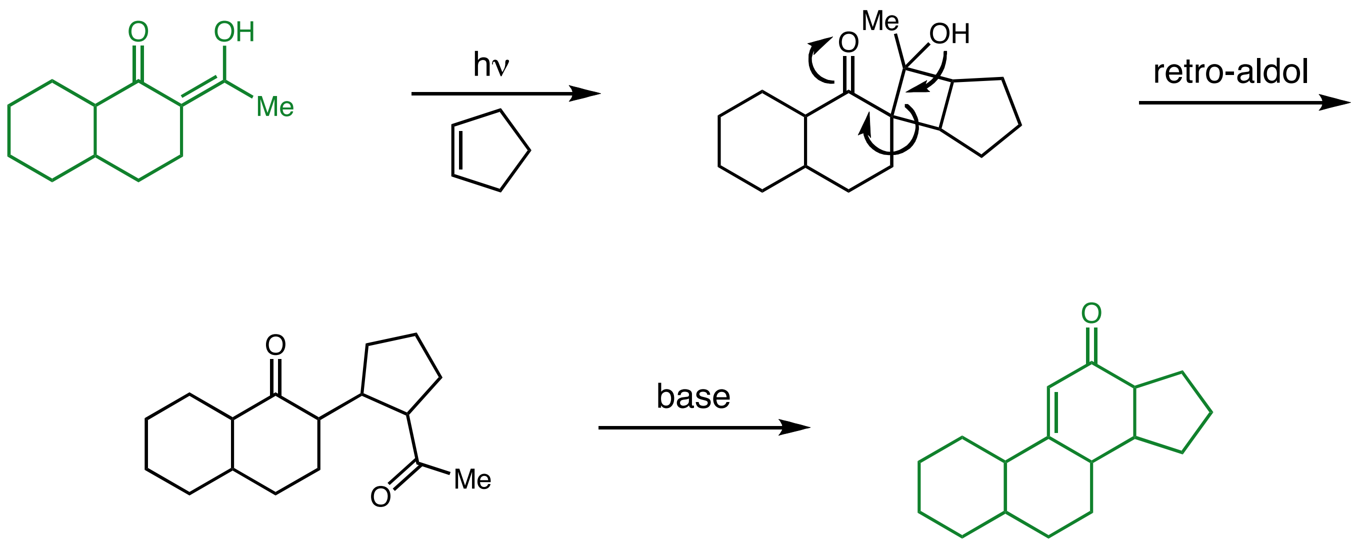


- Small and medium ring cyclic olefins do, however, generally undergo facile [2 + 2]



Cycloadditions

DeMayo reaction - [2 + 2] with 1,3-diketone followed by retro-aldol



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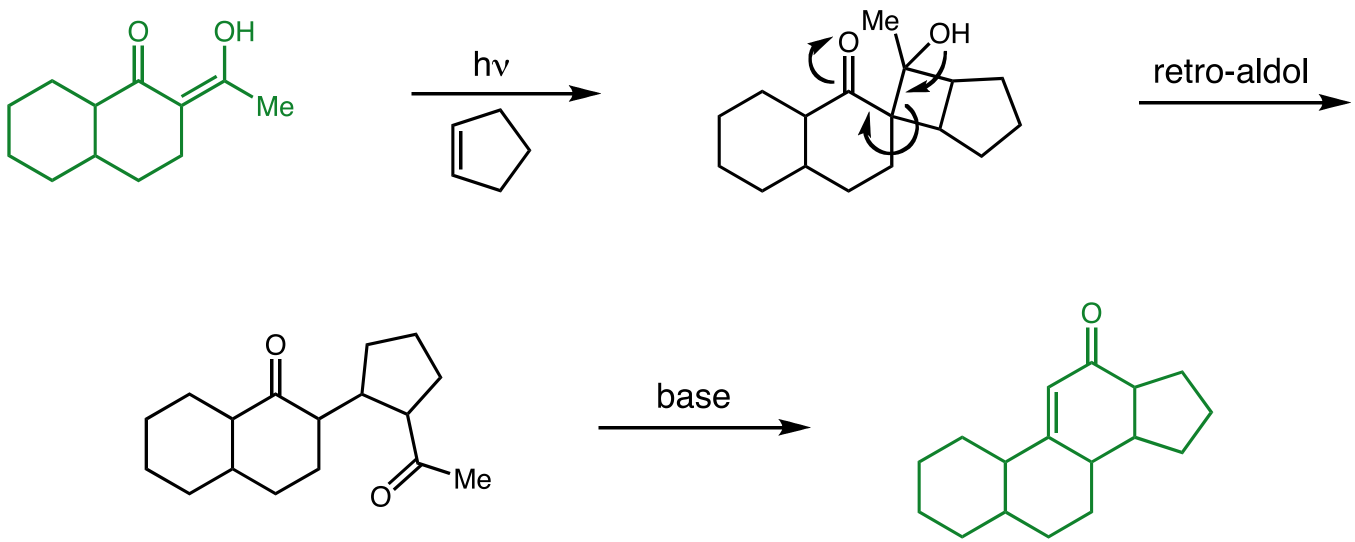
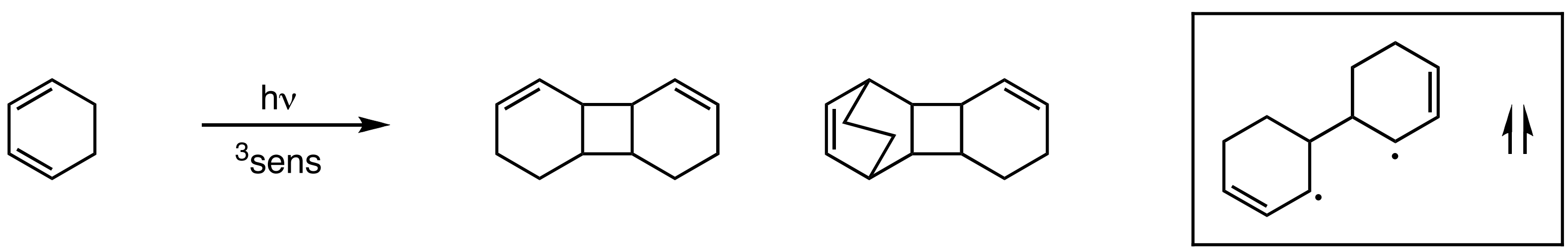
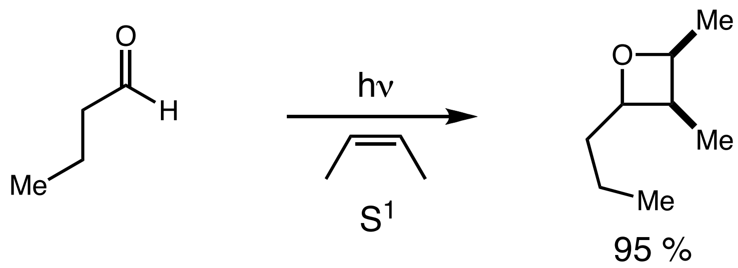


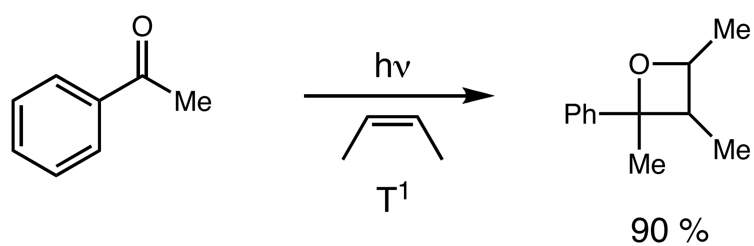
- S_1 [4 + 2] is not allowed by orbital symmetry, but radical T_1 undergoes stepwise addition



Cycloadditions

- Paterno-Büchi reaction - stereospecificity





Note that carbonyl/alkene [2 + 2] occurs from both S_1 and T_1 states

Cycloadditions

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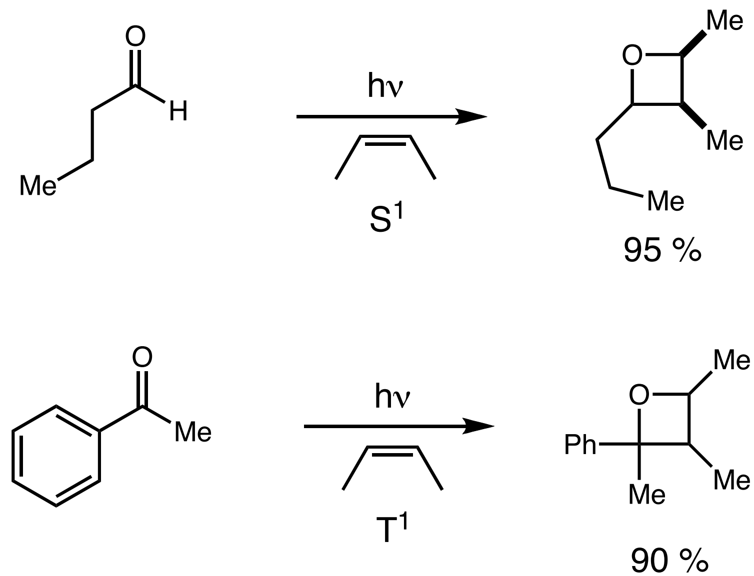

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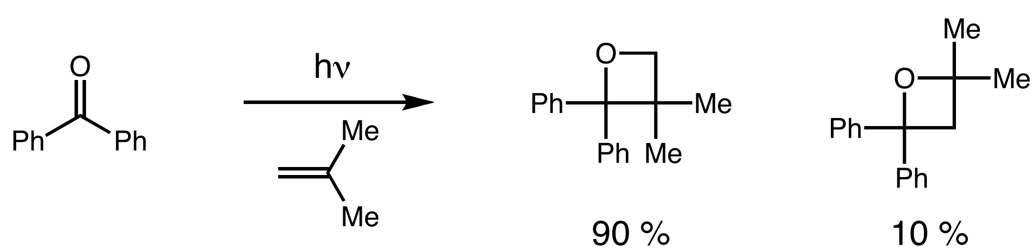
Paterno-Büchi reaction - regioselectivity with electron rich olefins



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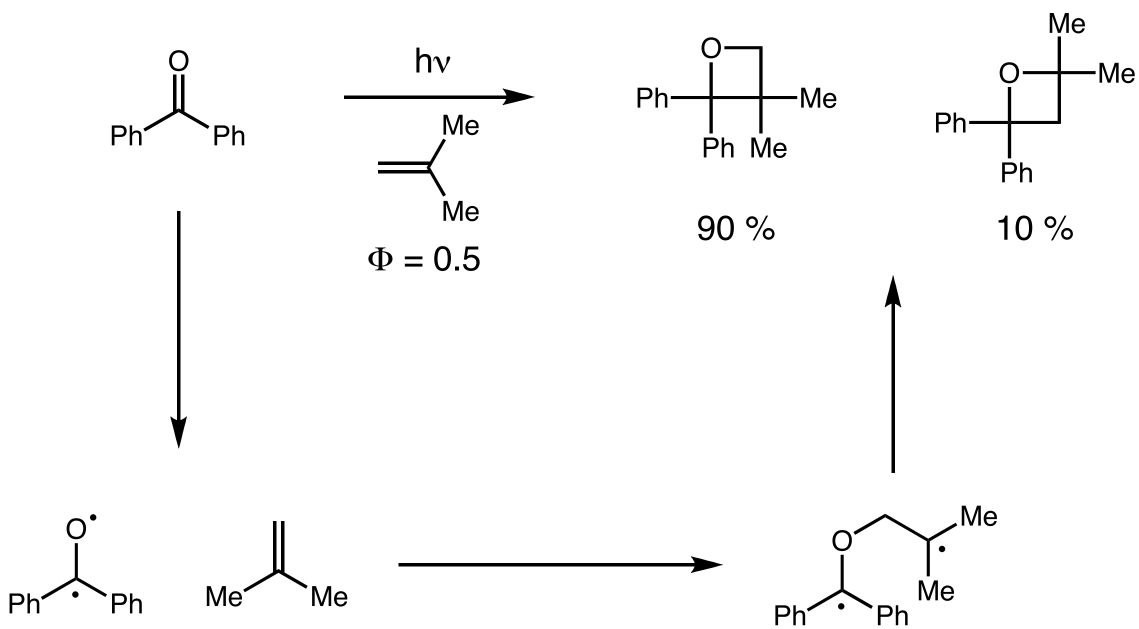
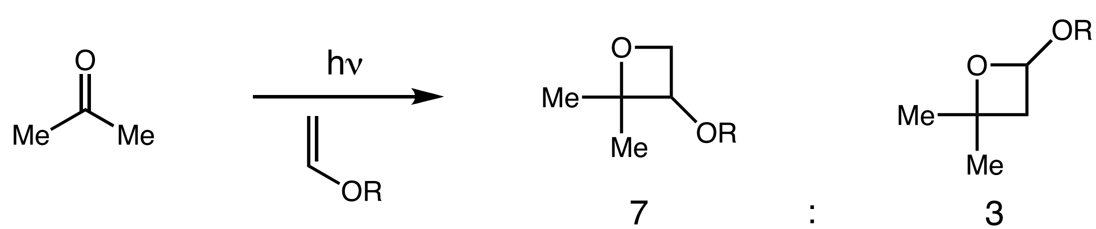
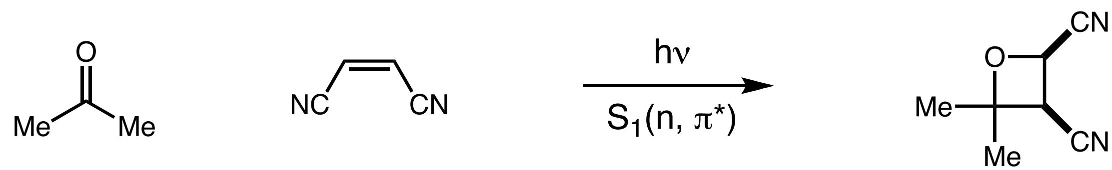


- Oxygen radical is more electrophilic than carbon radical, so it adds first to form the more stable biradical



Cycloadditions

- Paterno-Büchi reaction - electron poor olefins
  - Only occurs from S_1 state, so reactions are complete stereospecific
  - Products are not the expected adducts based on electron-rich alkene mechanism



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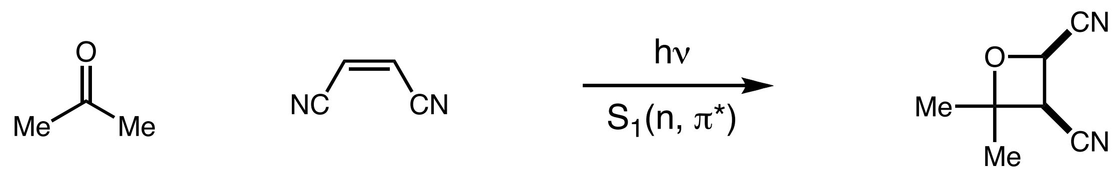

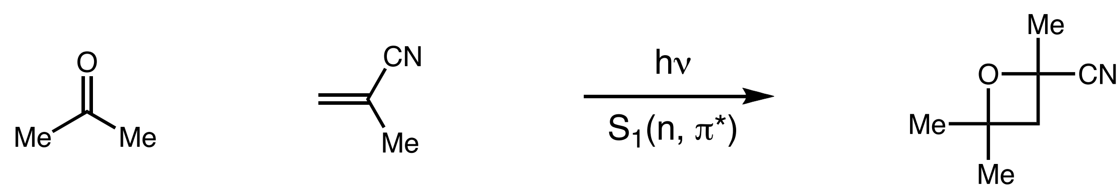

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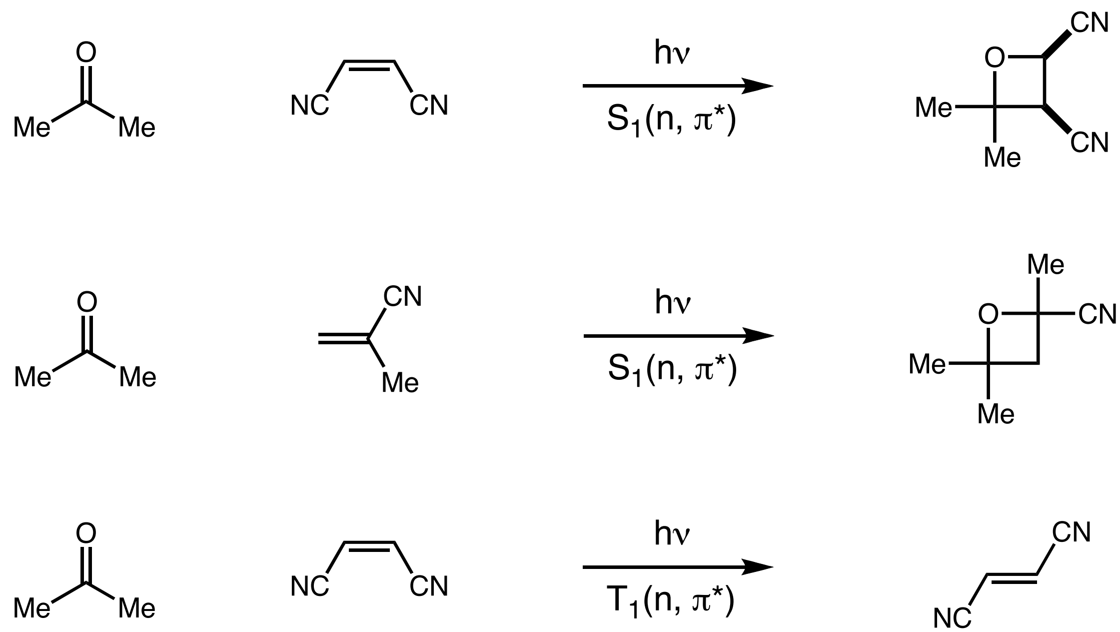

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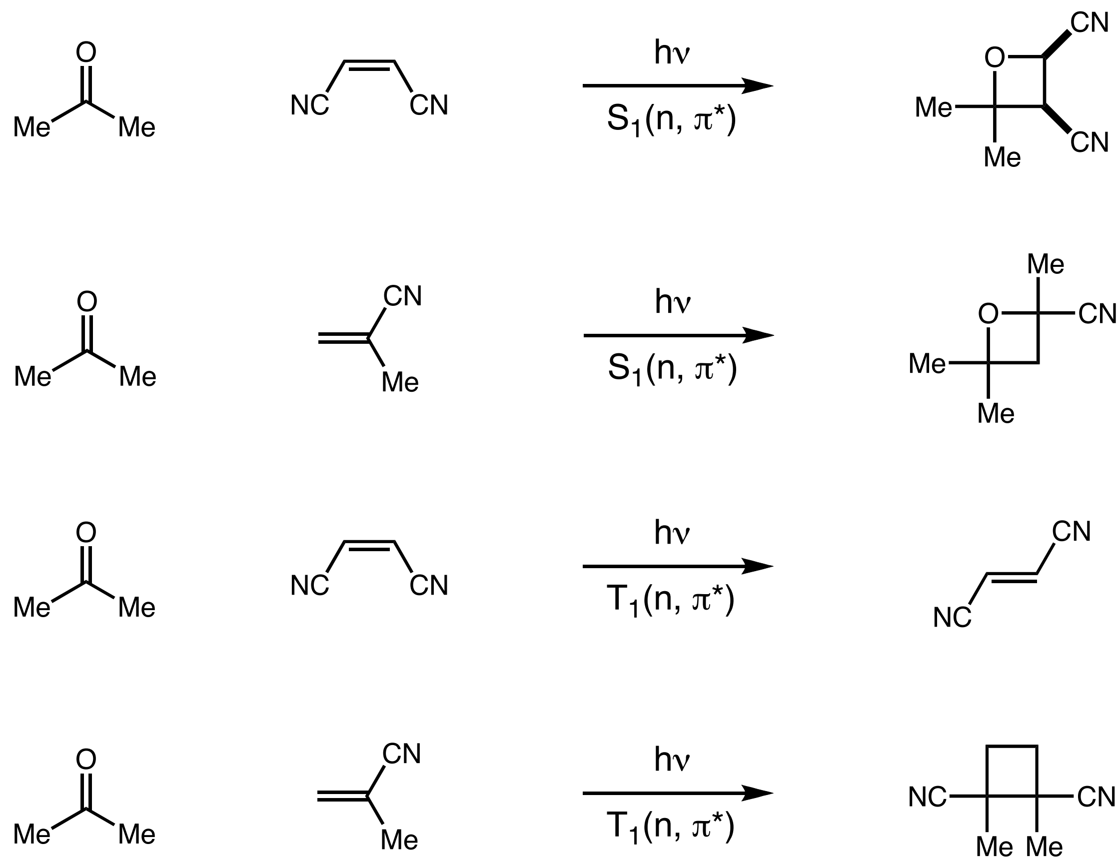

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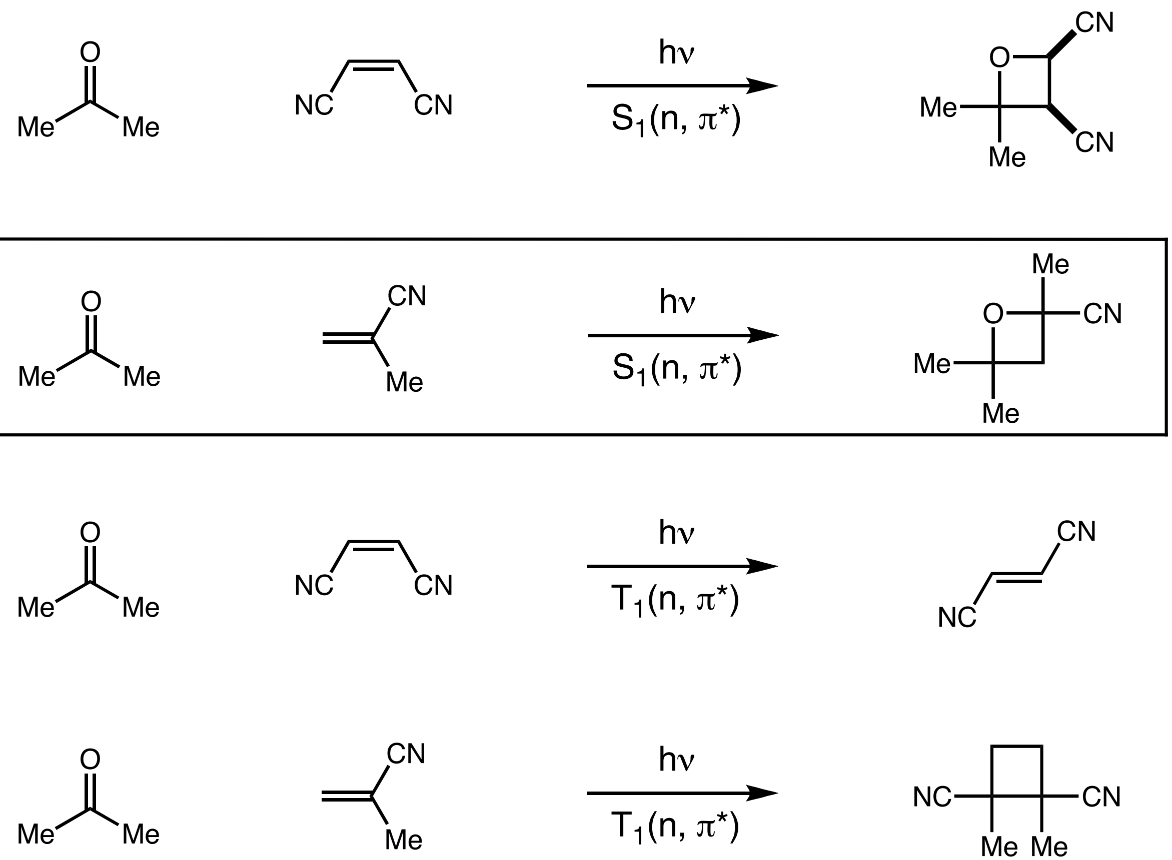

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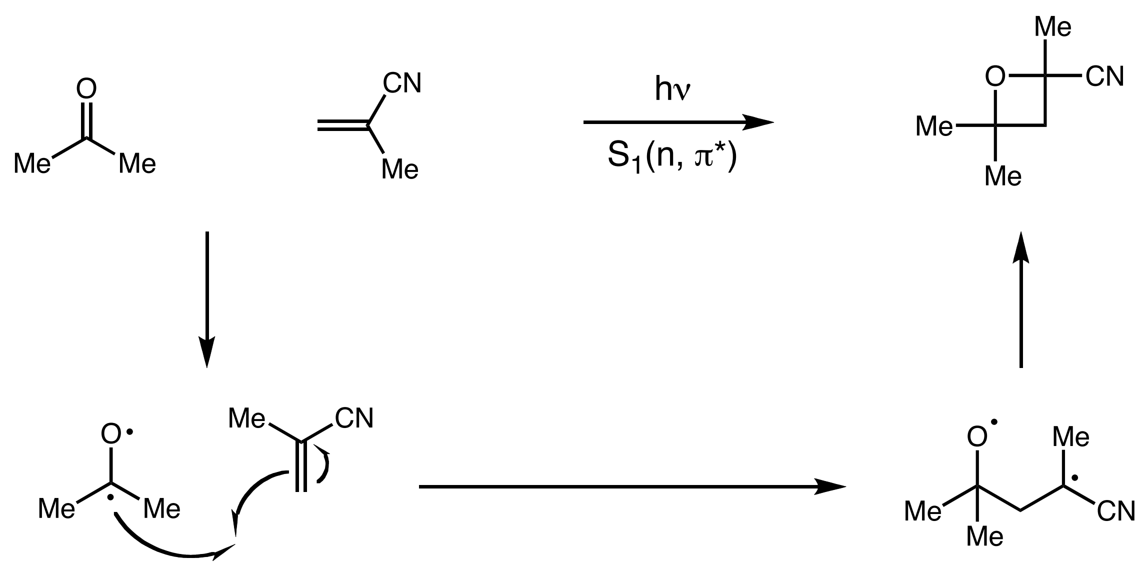
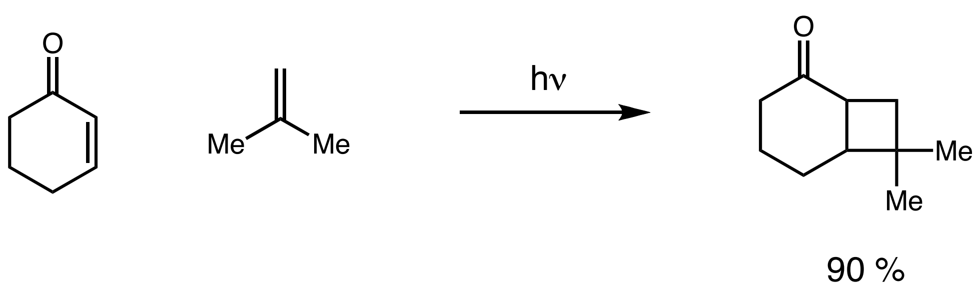
    - Products are not the expected adducts based on electron-rich alkene mechanism

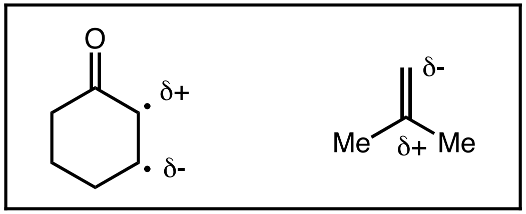


- Carbon radical is more nucleophilic than oxygen, so it adds first to make the more stable biradical

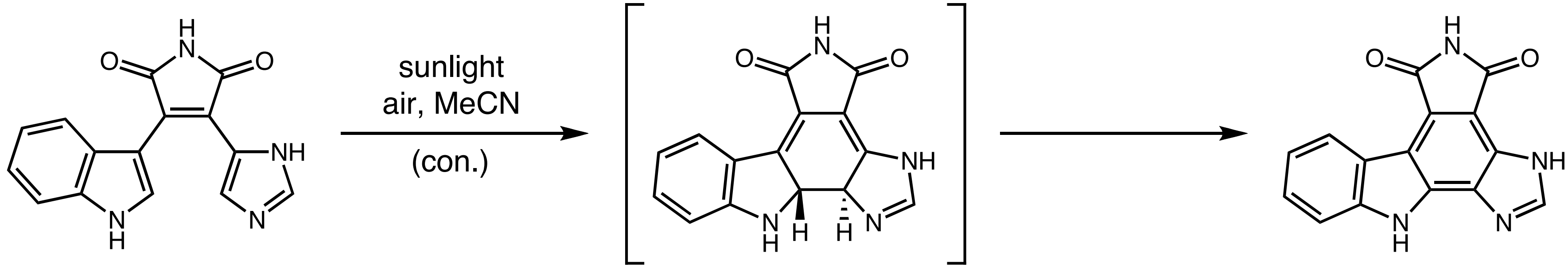
Cycloadditions

- Cycloadditions of alkenes with enones are efficient reactions as well

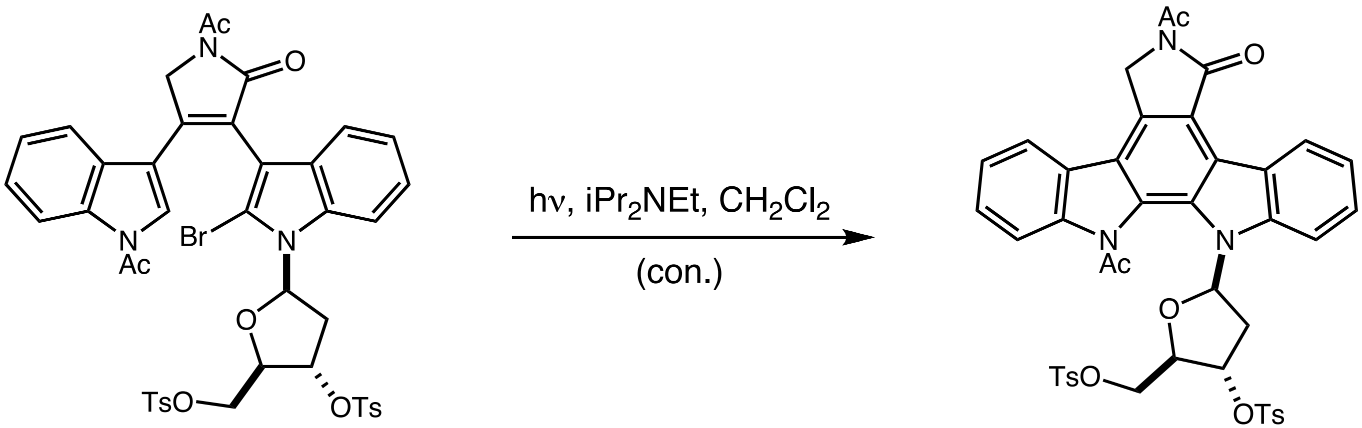




Examples in Synthesis



91%



96%

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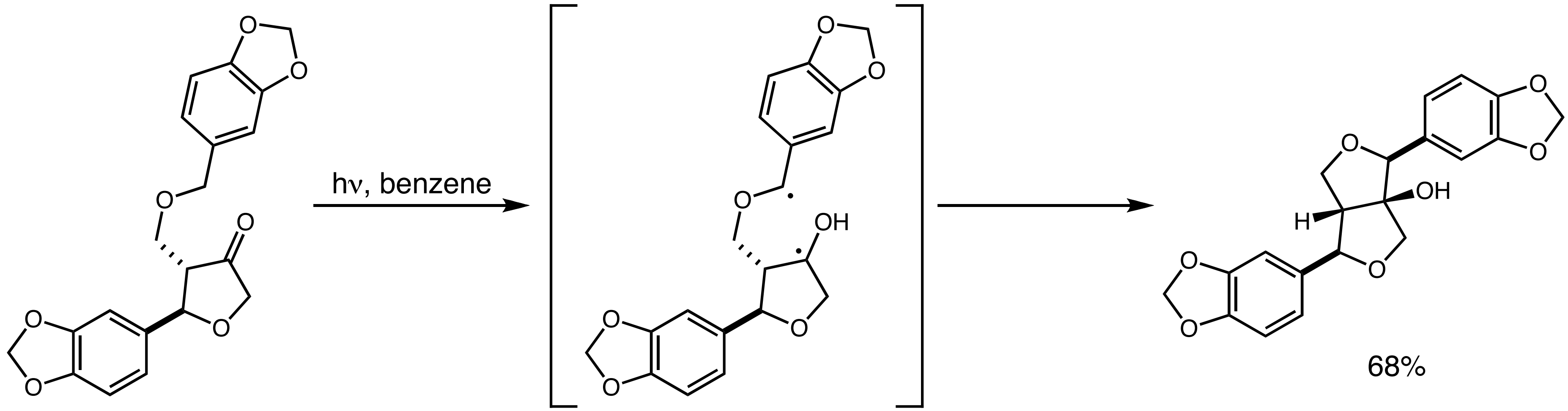
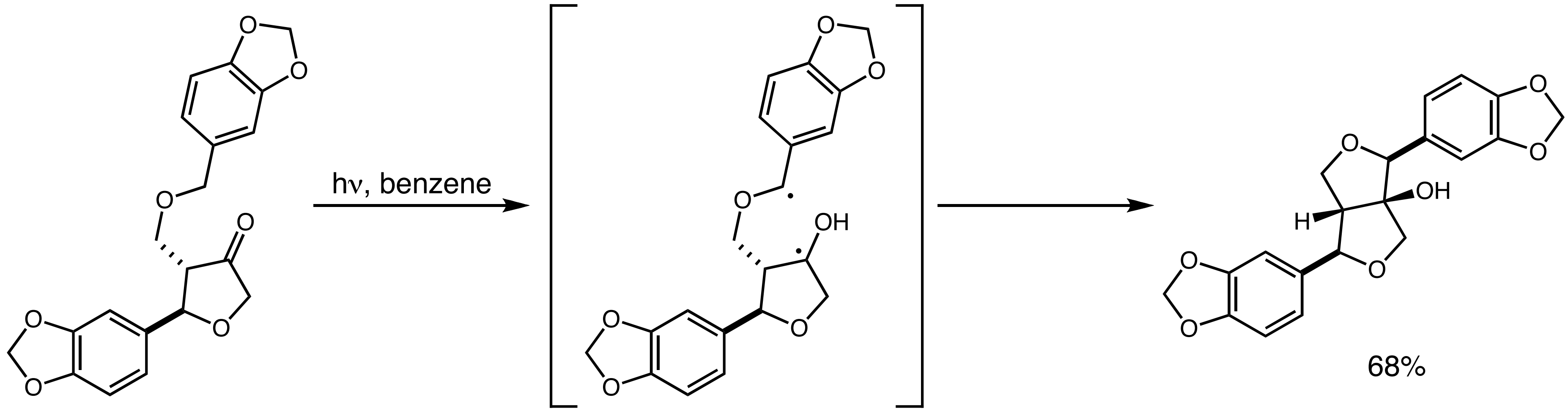
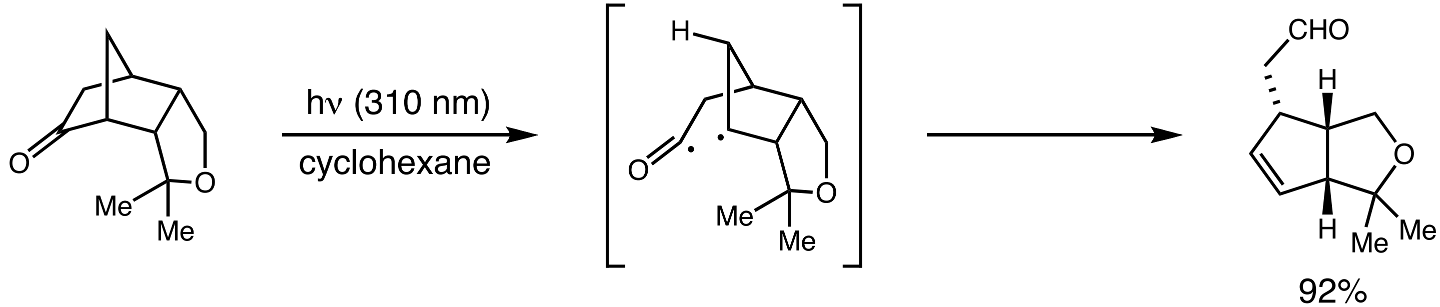
Examples in Synthesis



Kraus, G. A., Chen, L. *J. Am. Chem. Soc.* **1990**, *112*, 3464.

Examples in Synthesis





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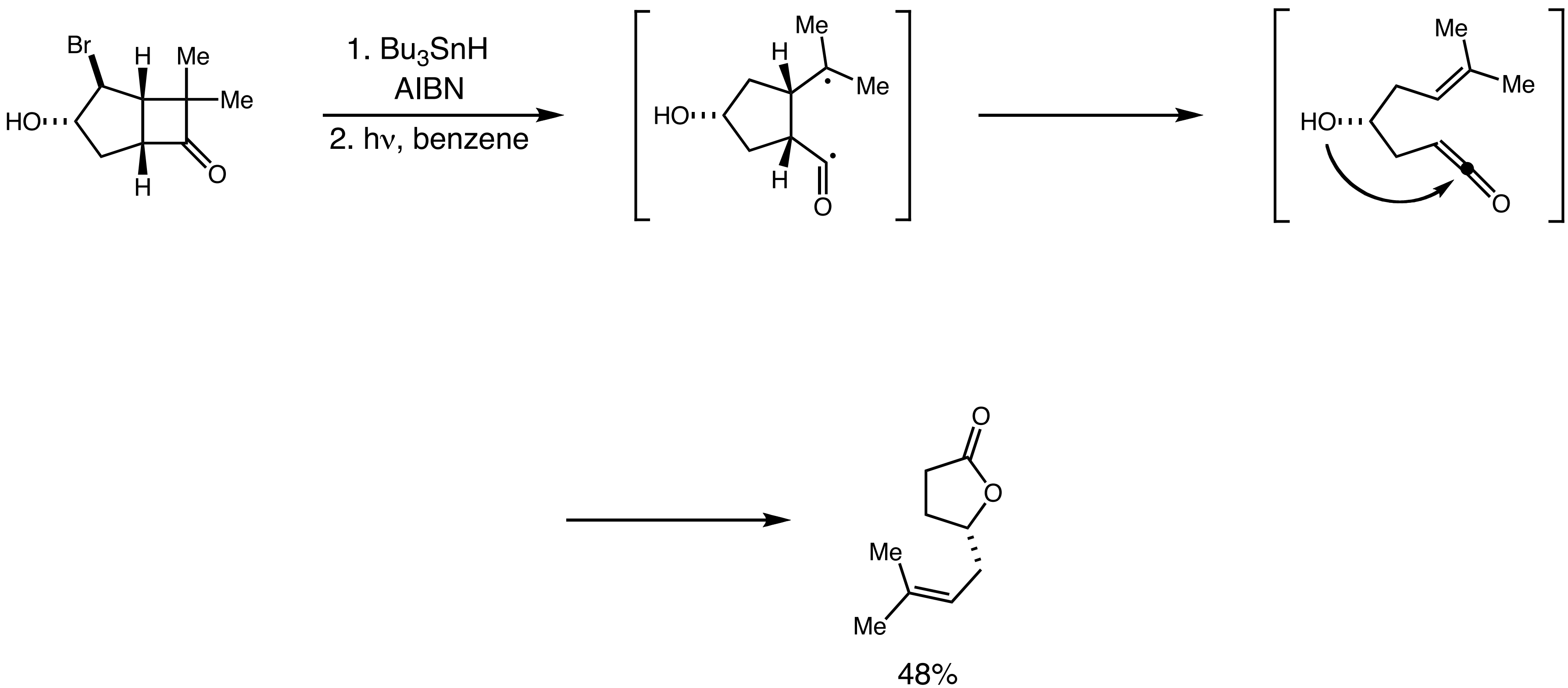
Examples in Synthesis



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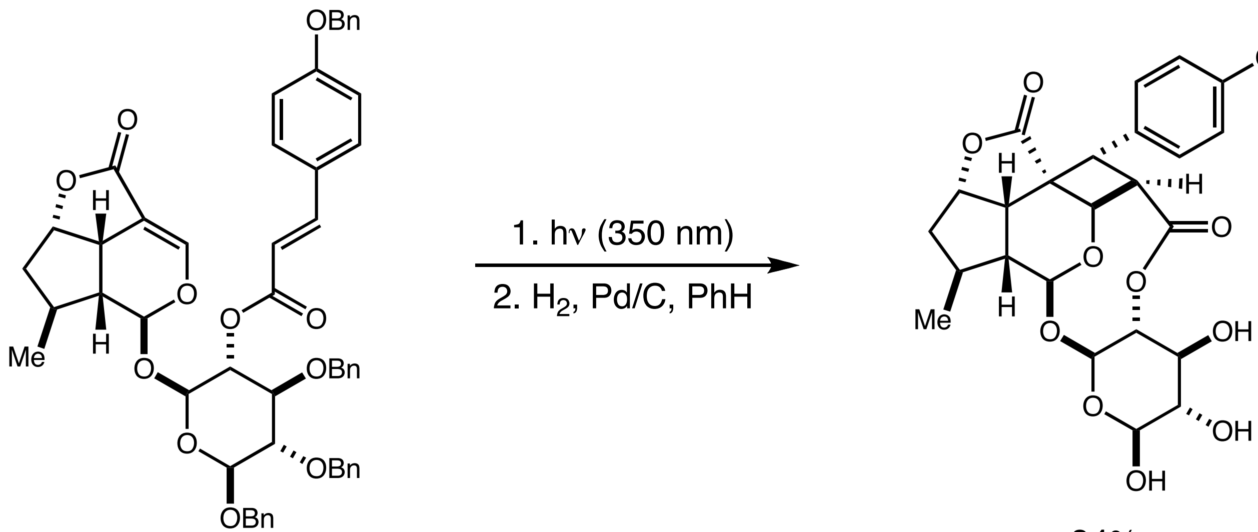
Examples in Synthesis



84%

(–)-littoralisone

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