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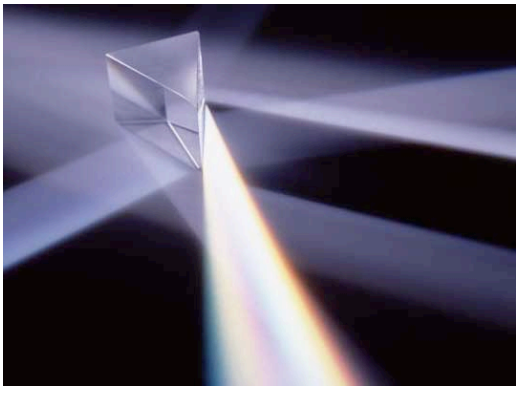
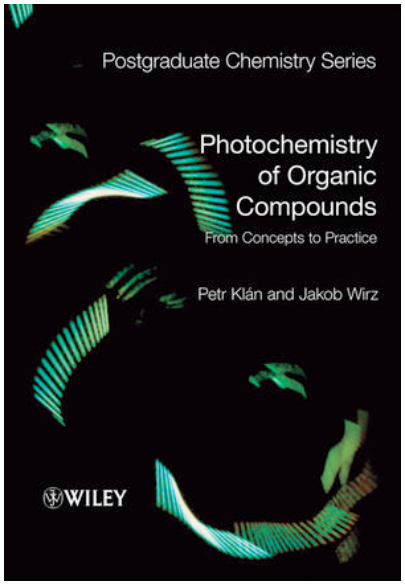
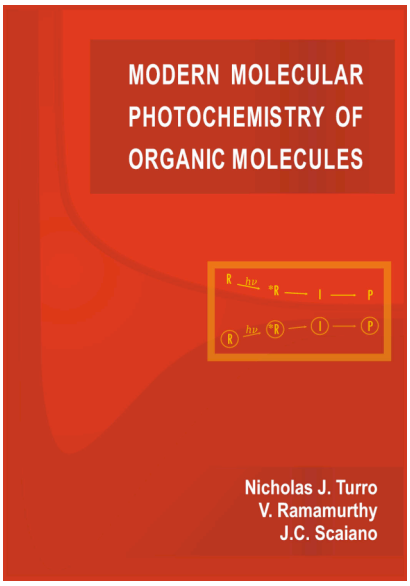
Controlling Photochemical Reactions Through Weak Interactions and Confinement



Supramolecular Photochemistry





References

"Supramolecular Photochemistry: The Control of Organic Photochemistry and Photophysics Through Intramlecular Interactions"

Chapter 13 in "*Modern Molecular Photochemistry of Organic Molecules*", N. J. Turro, V. Ramamurthy and J. C. Scaiano, 2010.

"Reaction Control by Molecular Recognition – A Survey from the Photochemical Perspective" by C. Yang, C. Ke, Y. Liu and Y. Inoue,

Chapter 1 in "*Molecular Encapsulation: Organic Reactions in Constrained Systems*", U. H. Brinker and J. -L. Mieusset, 2010.

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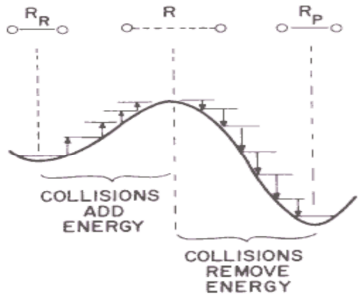
Thermal Chemistry
Photochemistry
What is the difference?

- Mode of activation
- Selectivity in activation
- Energy distribution

Visualization of Thermal Reactions



- Transition state connects a single reactant to a single product and it is a saddle point along the reaction course.
- Collisions are a reservoir of continuous energy (~ 0.6 kcal/mol per impact).
- Collisions can add or remove energy from a system.
- Concerned with a single surface.

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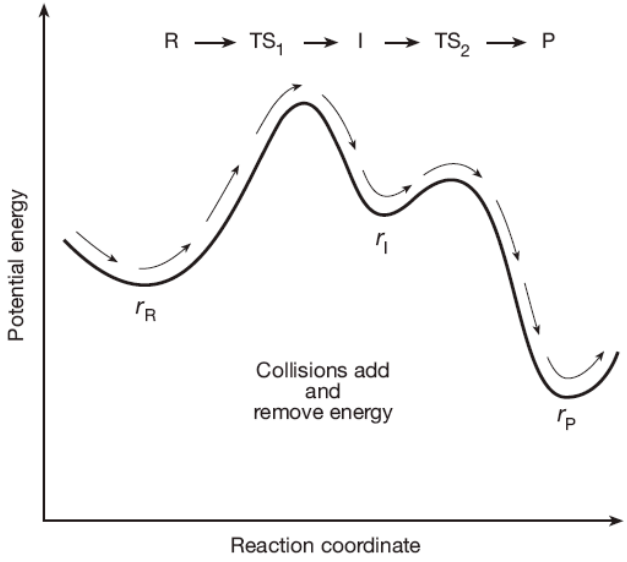
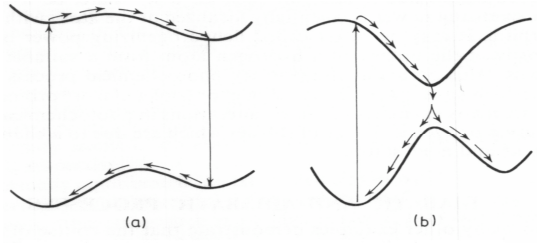
Visualization of Thermal Reactions



Visualization Photochemical Reactions

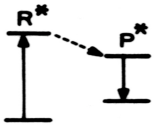
Two surfaces are involved

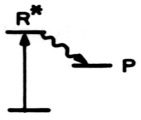
Adiabatic



Diabatic

Pathways of photochemical reactions: (a) adiabatic, (b) diabatic.





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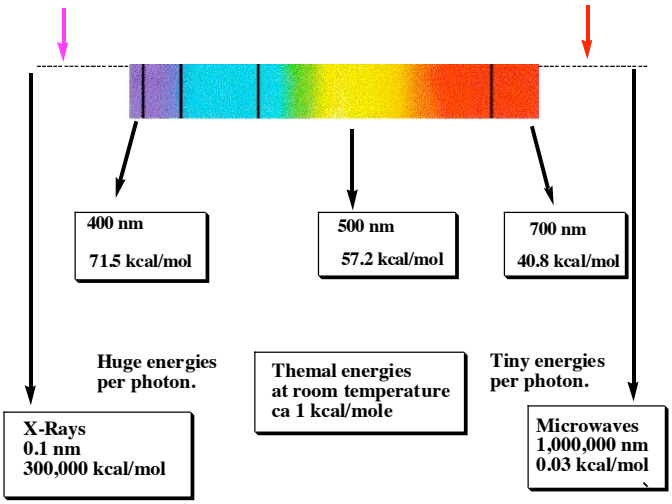
Light and Energy Scales

Ultraviolet Region
Chemical Bonds of DNA and Proteins Damaged

Infrared Region
Chemical Bonds Energy too low to make or break chemical bonds.



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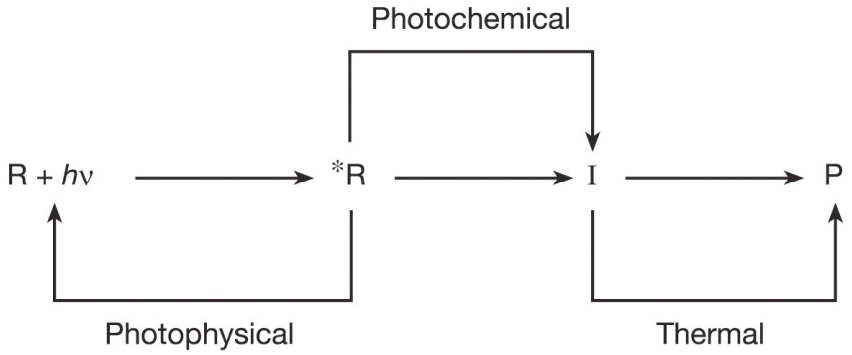
Photochemistry consists of two parts

- Photochemical
- Photophysical



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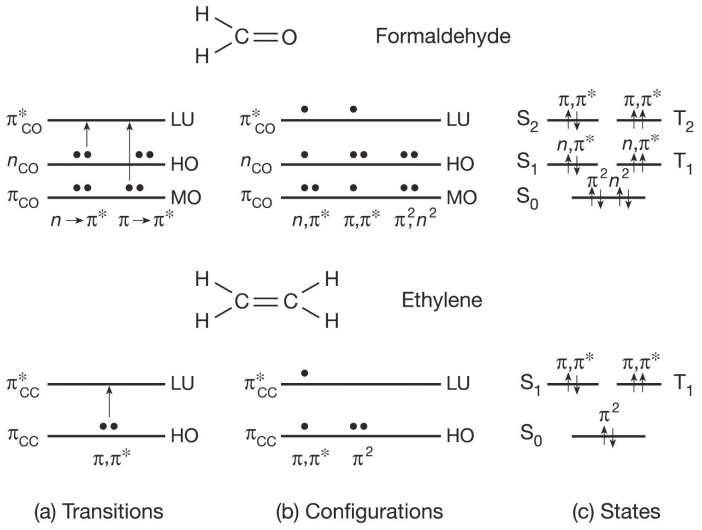
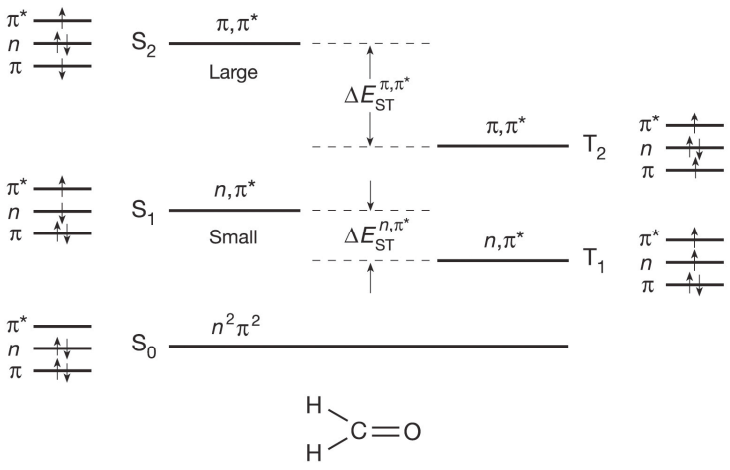
Points to Remember

- Electronic Configuration of States, nπ*; ππ*
- Spin Configuration of States (S and T)
- Singlet-Triplet Gap (ΔE (S-T)
- Rules of Intersystem Crossing (El-Sayed's Rule)
- Absorption and Emission
- Fluorescence and Phosphorescence
- Radiative and Radiationless Transitions
- Kasha's Rule

Electronic and Spin Configuration of States



Singlet-Triplet Gap and Intersystem Crossing



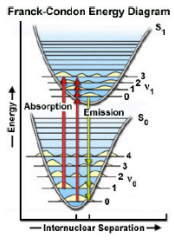
El-Sayed's Rule

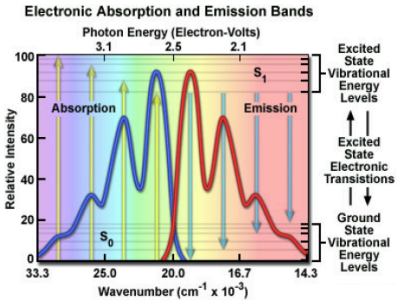
Absorption and Emission

Mirror Image rule

Emission spectrum is typically a mirror image of the absorption spectrum of the S_0-S_1 transition, but shift to higher wavelength.

Stokes Shift



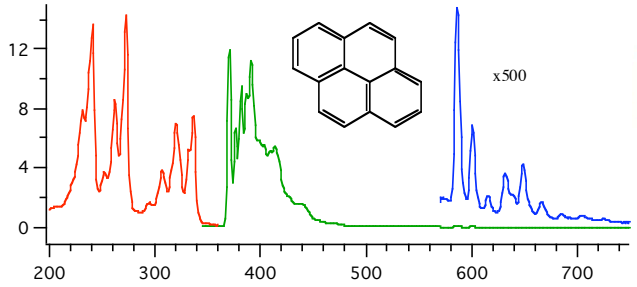


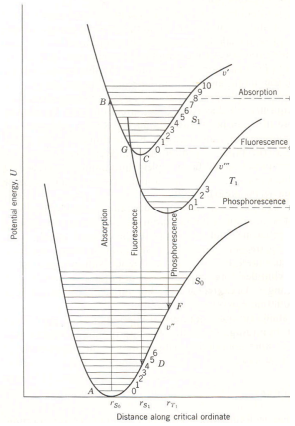
This similarity occurs because-

Same electronic tranisiton being involved in both absorption and emission and the similarities of the vibrational energy levels of S_0 and S_1.

In many molecules vibrational energy levels are not significantly altered by the different electronic distributions of S_0 and S_1.

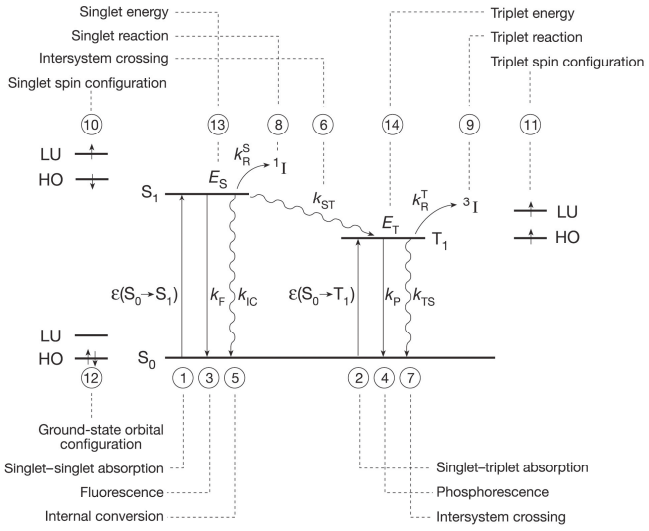
Fluorescence and Phosphorescence





Photochemists' handy horoscope of a molecule

Jablonski diagram: Radiative and Radiationless Transitions



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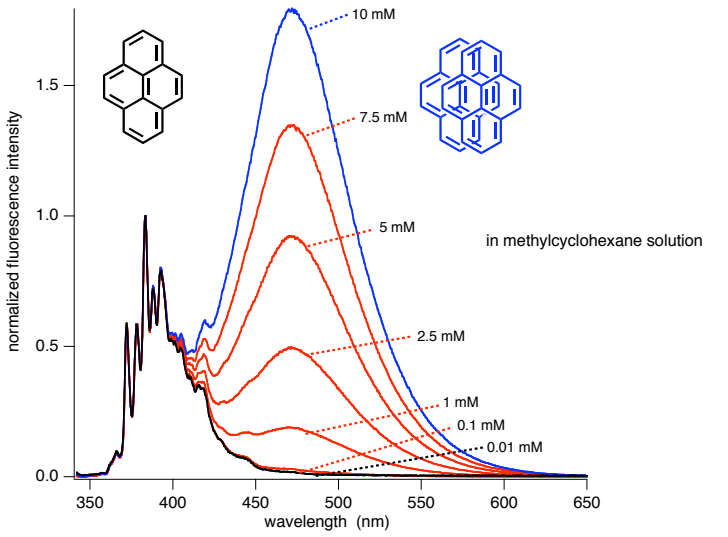
Photophysics: Excimer Emission



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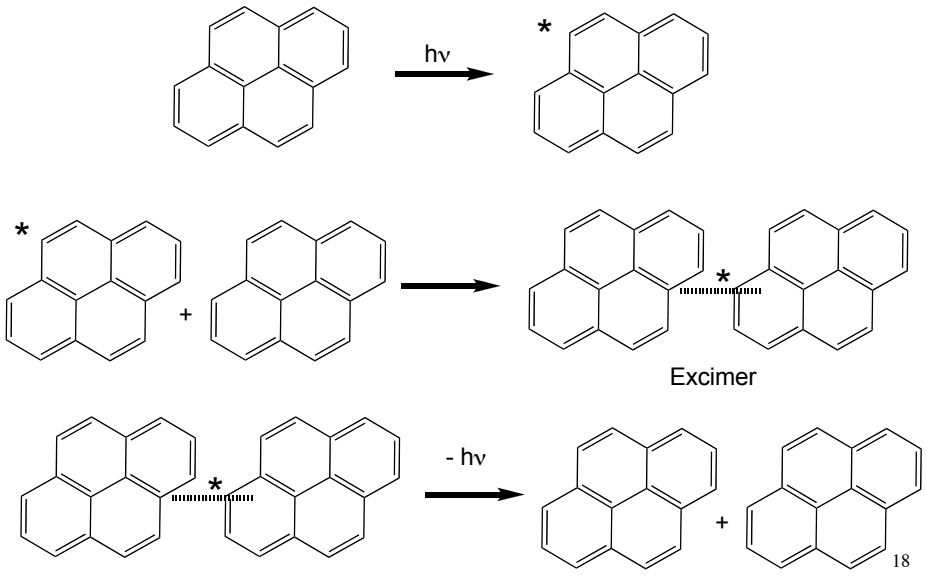
Pyrene as an exemplar of excimer formation



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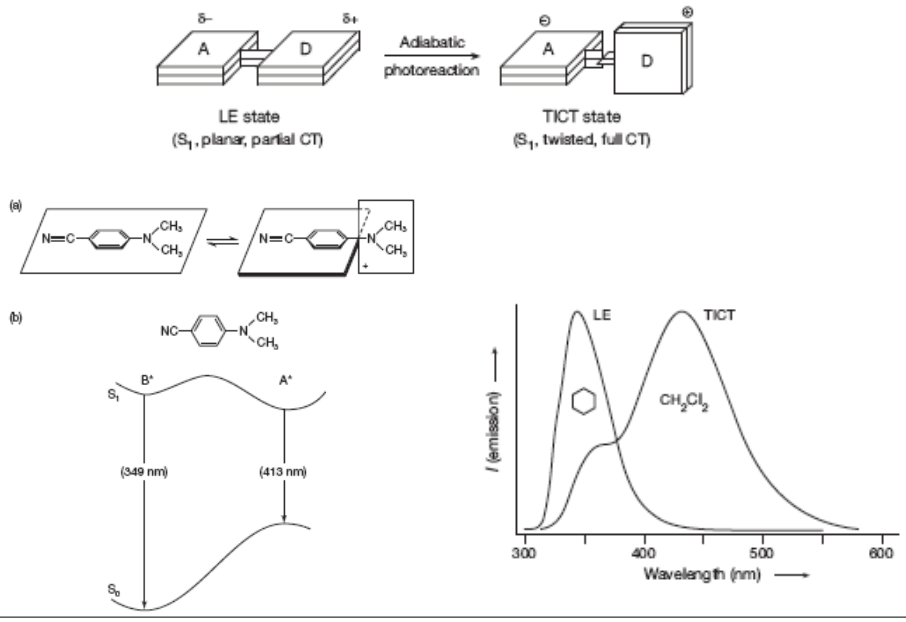
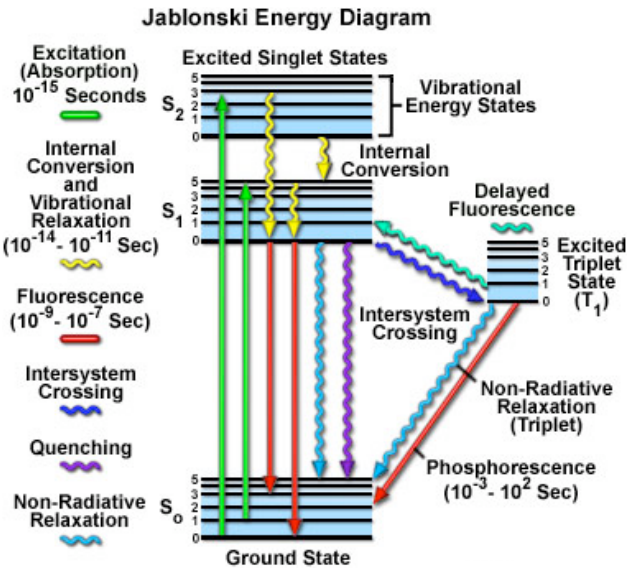
TICT Emission



Kasha's Rule



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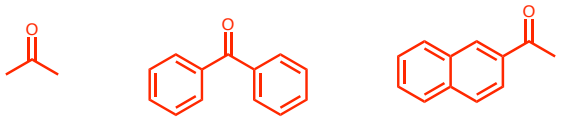
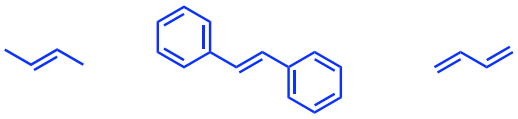
Examples of Common Organic Chromophores

Carbonyls



Olefins



Enones

Aromatics

How does 'light energy' compare with chemical bonds?

Bond	Dissociation energy kcal/mol	Wavelength nm
O-H	104	275
C-H	95	300
C-C	82	350
C-Br	66	435
O-O	38	750

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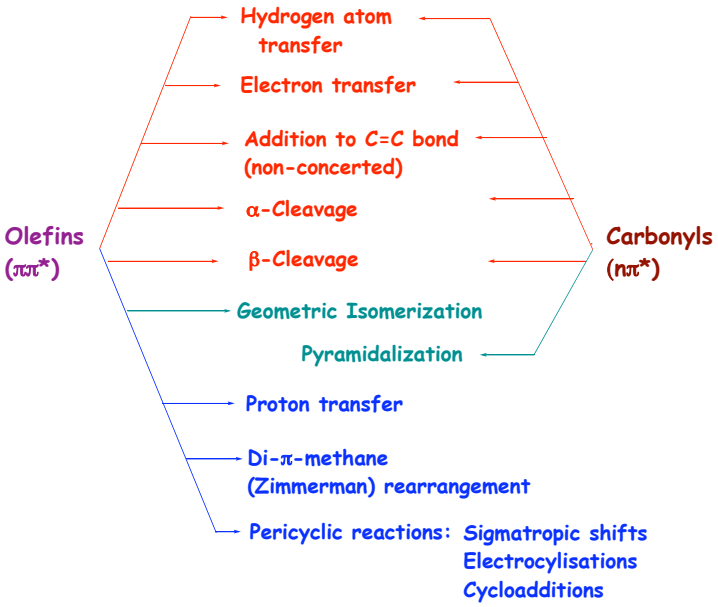
Photochemistry: Common Photoreactions



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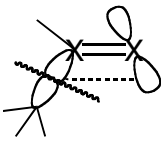
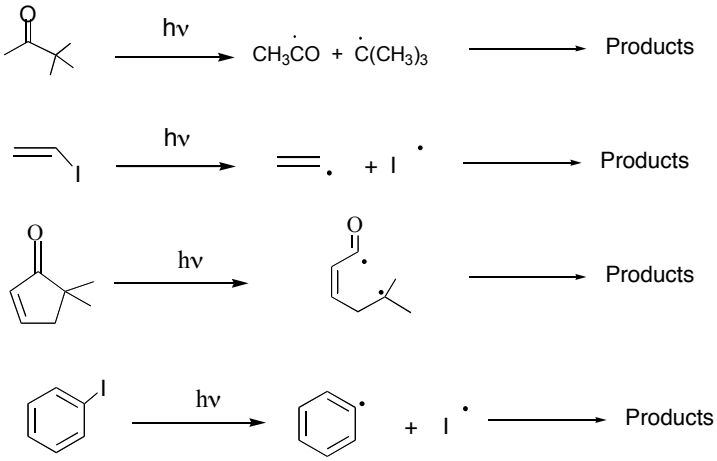
Photochemistry: Primary Photoreactions (1)

α-Cleavage





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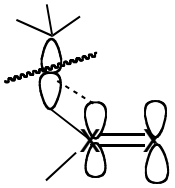
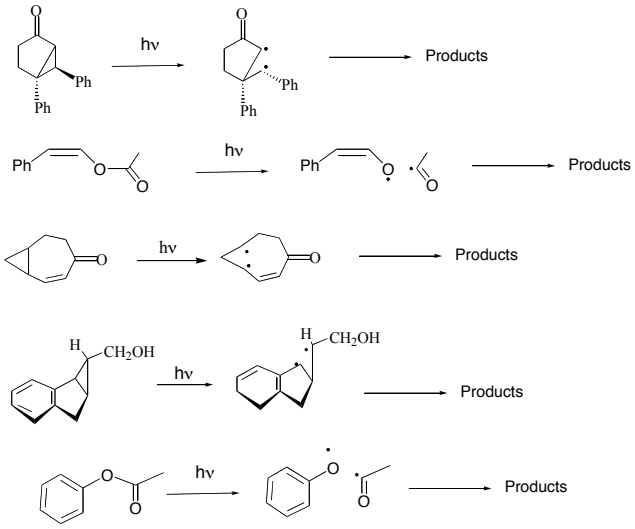
Photochemistry: Primary Photoreactions (2)

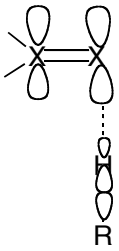
β-Cleavage

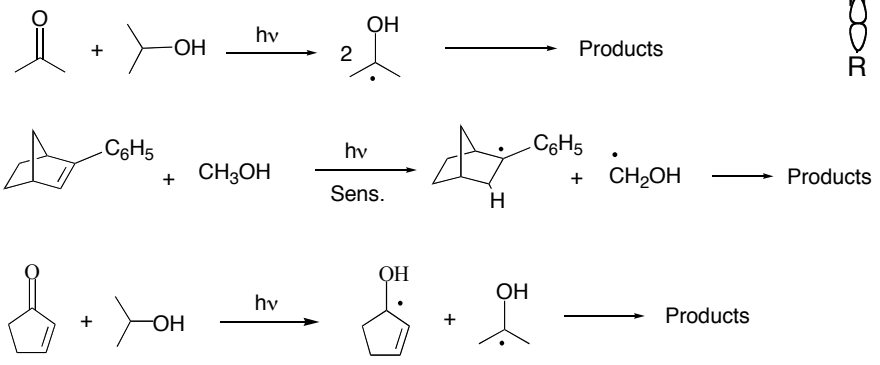




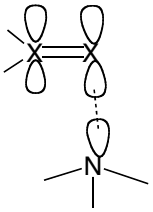
Photochemistry: Primary Photoreactions (3)

Hydrogen Abstraction

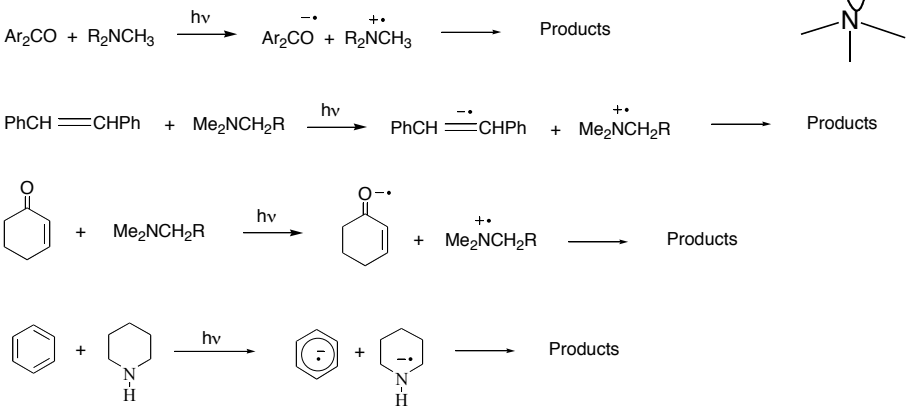




Photochemistry: Primary Photoreactions (4)



Electron Transfer



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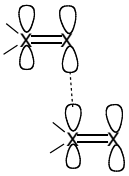
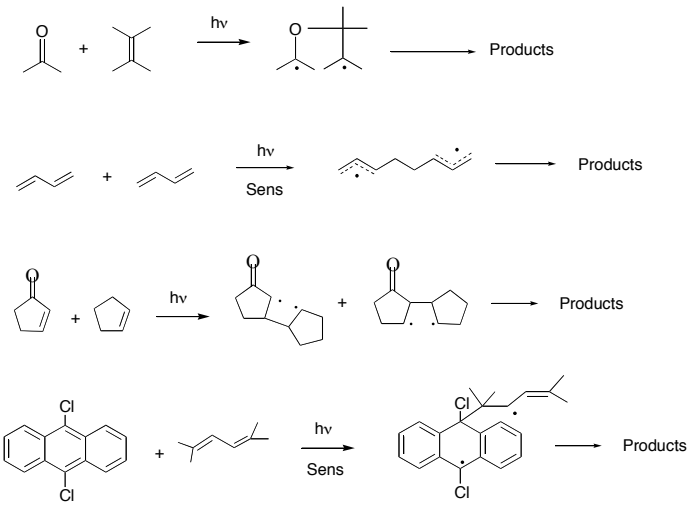
Photochemistry: Primary Photoreactions (5)

Addition to C=C bond, triplet, non concerted





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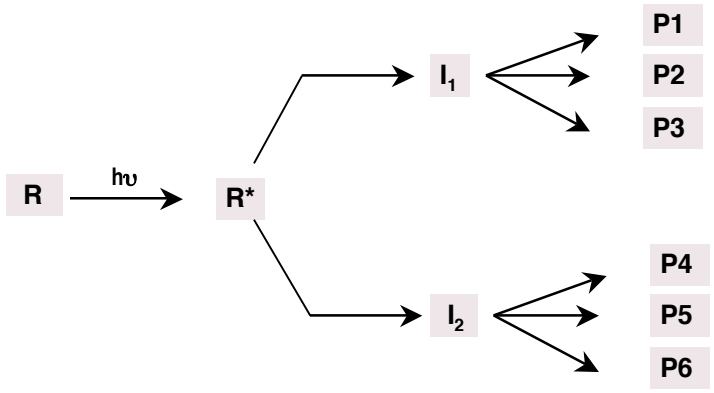
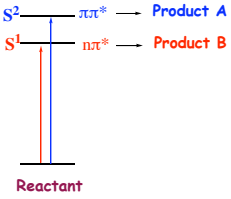
Photochemistry often yields multiple products

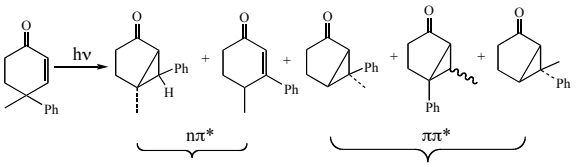


Controlling Photochemical Reactions Through Conventional Means

- Nature of the excited state, $n\pi^*$ and $\pi\pi^*$
- Nature of the spin state, S_1 and T_1
- Level of the excited state, S_1 and S_2; T_1 and T_2

Nature of the excited state, nπ* and ππ* control through solvents





Benzene	100	0
Acetonitrile	58	42
Formamide	38	62

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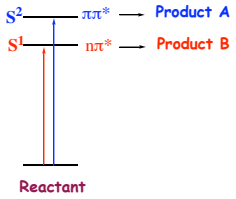
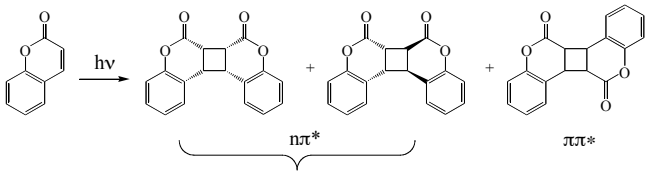
Nature of the excited state, nπ* and ππ* control through additives





None	20	71	10
In presence of BF_3	0	10	90

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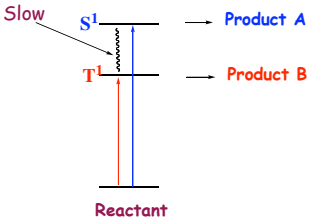
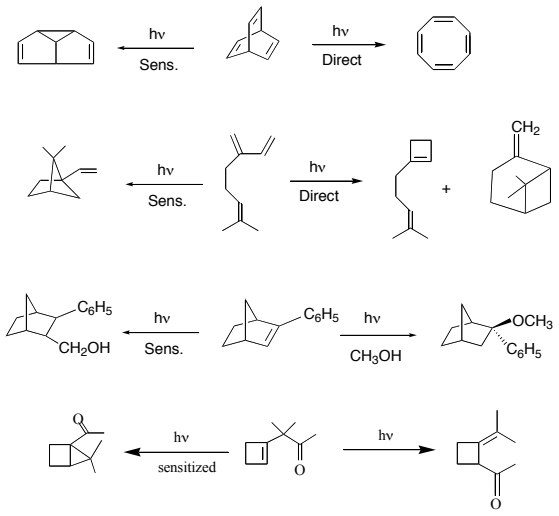
Spin state control through sensitization





Spin control

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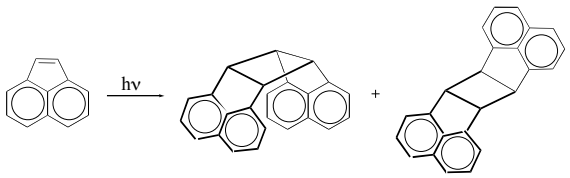
Spin state control through heavy atom effect



S_1 : 100 : 0

T_1 : 1 : 9

Solvent	Cis/trans dimer
Cyclohexane	4.97
n-Butyl chloride	2.37
n-Propyl bromide	0.41
Ethyl iodide (10% mole %)	0.25

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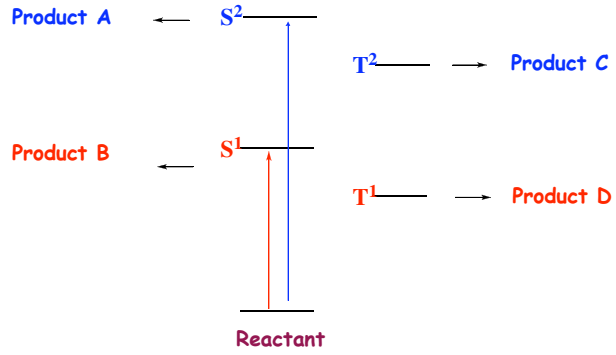
Large energy gap and violation of Kasha's Rule



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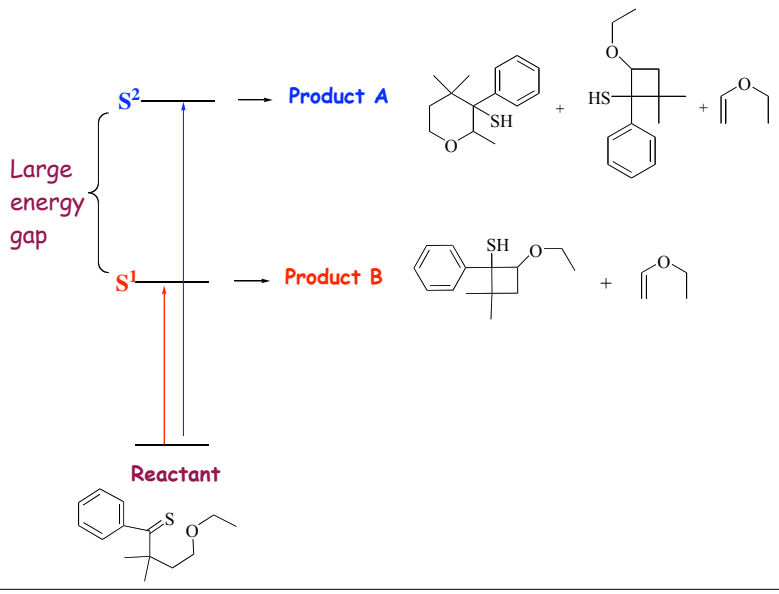
Controlling nature of reactive state with wavelength of irradiation

Reaction from upper excited singlet states



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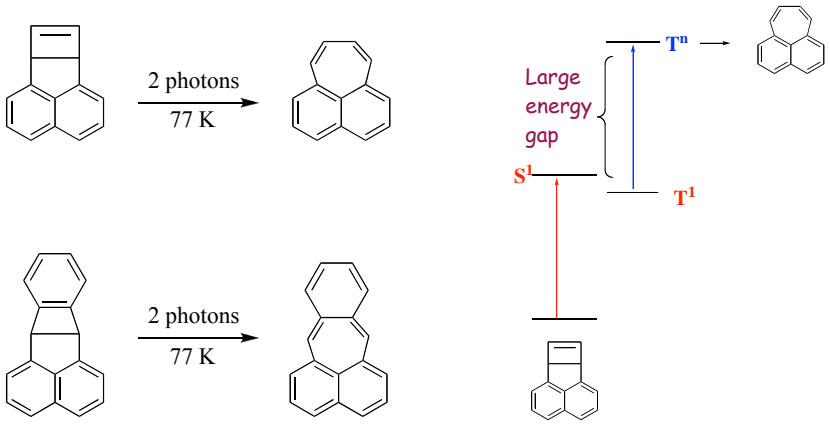
Controlling nature of reactive state with wavelength of irradiation: Reaction from upper excited triplet states



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Controlling Photochemical Reactions

- **Electronic barrier:** Electronic configuration ($n\pi^*$ *vs.* $\pi\pi^*$)
- **Spin barrier:** Spin configuration (S^1 *vs.* T^1)

$$\Delta F^{\#} = \Delta H^{\#} - T\Delta S^{\#}$$

- **Enthalpic barrier:** Presence of activation energy
- **Entropic barrier:** Changes in conformational, rotational and translational freedom

$$\Phi_p = k_r/\Sigma k$$

- **Competition:** Radiative, radiationless and other reactive modes

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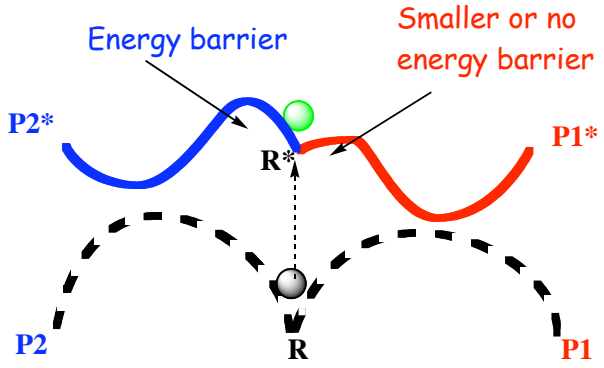
Overcoming the enthalpic barrier with temperature control



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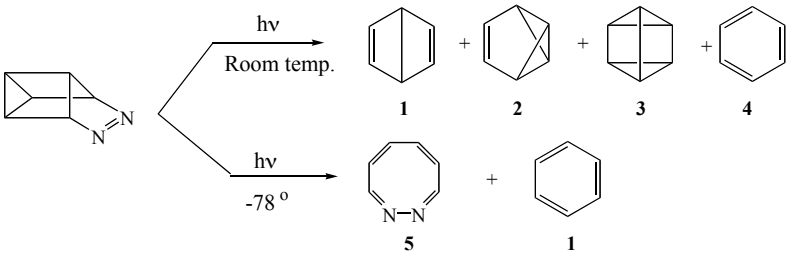
Overcoming the enthalpic barrier by controlling temperature of photoreaction



Temperature °C	4	1	2	3	5
22	30	45	6	11	8
0	30	34	3	5	31
- 35	20	5	-	-	75
- 78	10	-	-	-	90

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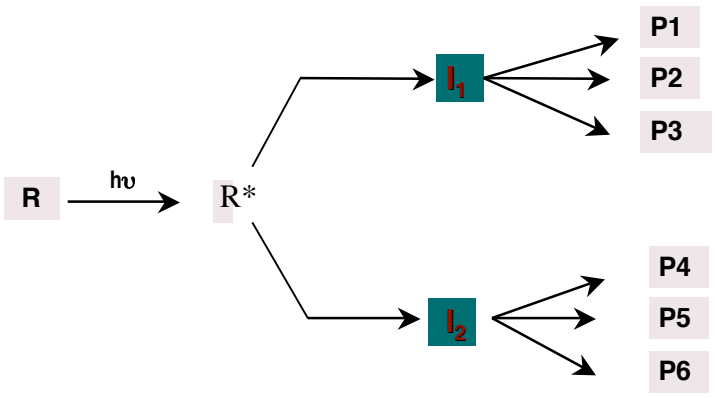
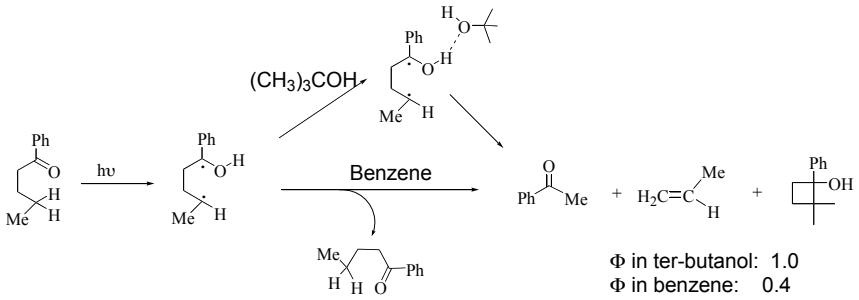


Cutting cut down competition with choice of solvent



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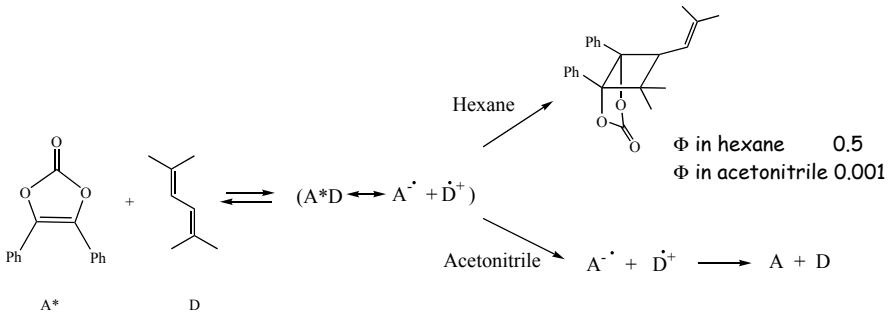
Cutting cut down competition with choice of solvent



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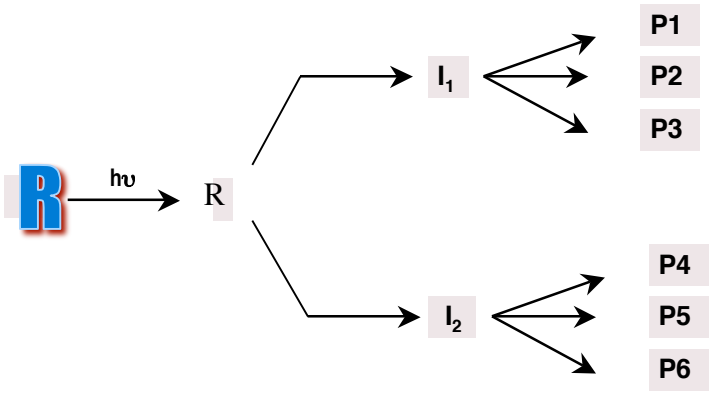
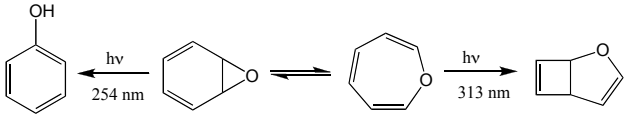
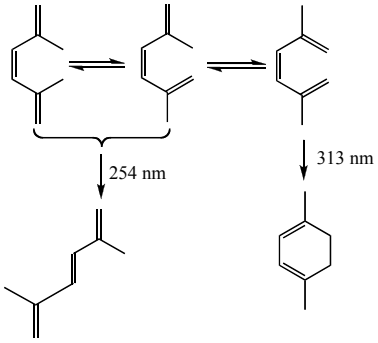


Controlling chemistry with wavelength of excitation





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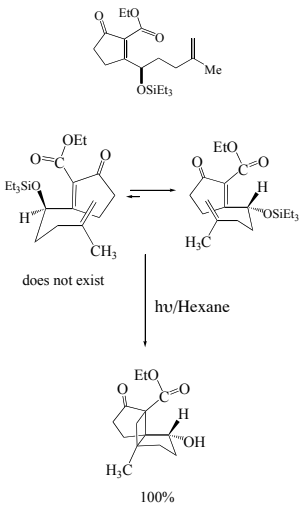
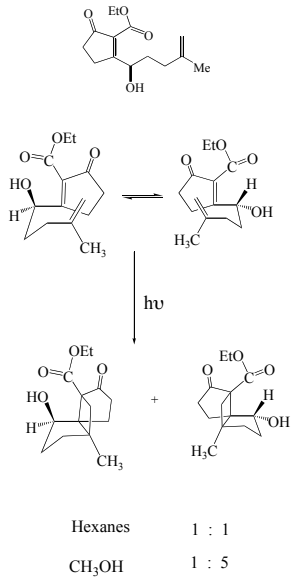
Conformational control through choice of solvent





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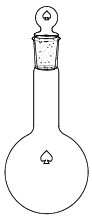
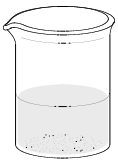
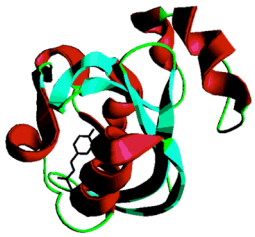
Medium Matters



Gas phase



Solution
(solvent + solute)



Protein

Reaction more selective

Why reactions in biological media are highly selective compared to gas phase and solution?

Are there any other media with some of the features of biological media?

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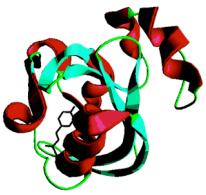
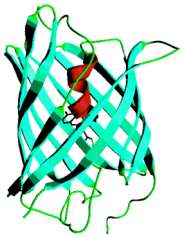
Highly selective geometric isomerization occurs within a protein medium

Rhodopsin

Bacteriorhodopsin



Photoactive yellow protein



Green fluorescent protein

How do a biological media enforce selectivity?

- by restricting the rotational and translational motions
- by pre-organizing the reactants
- by controlling the extent and the location of free space within a reaction cavity

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Controlling Photochemical Reactions Through Weak Interactions and Confinement