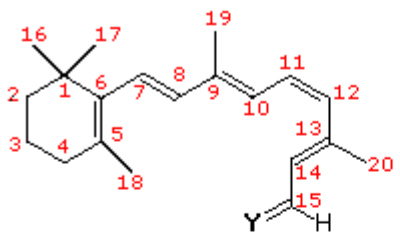
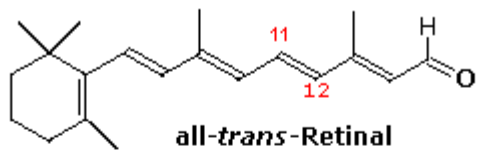
Chem. 862

Photochemistry



hv → Several Transient Intermediates →



all-*trans*-Retinal
+ Opsin

11-*cis*-Retinal Y = O

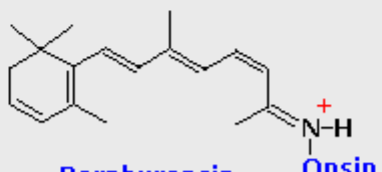
Rhodopsin Y = $\overset{+}{N}H(CH_2)_4CH(\tilde{N}H)CO-$

a Schiff Base

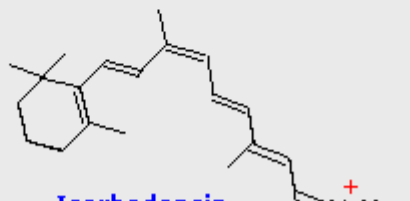
λ_{max} = 504 nm

Opsin

Retinal has 16 configurational isomers
4 are mono-cis; 6 are di-cis; 4 are tri-cis
one is all-cis and one is all-trans



Porphyropsin
λ_{max} = 519 nm
Opsin



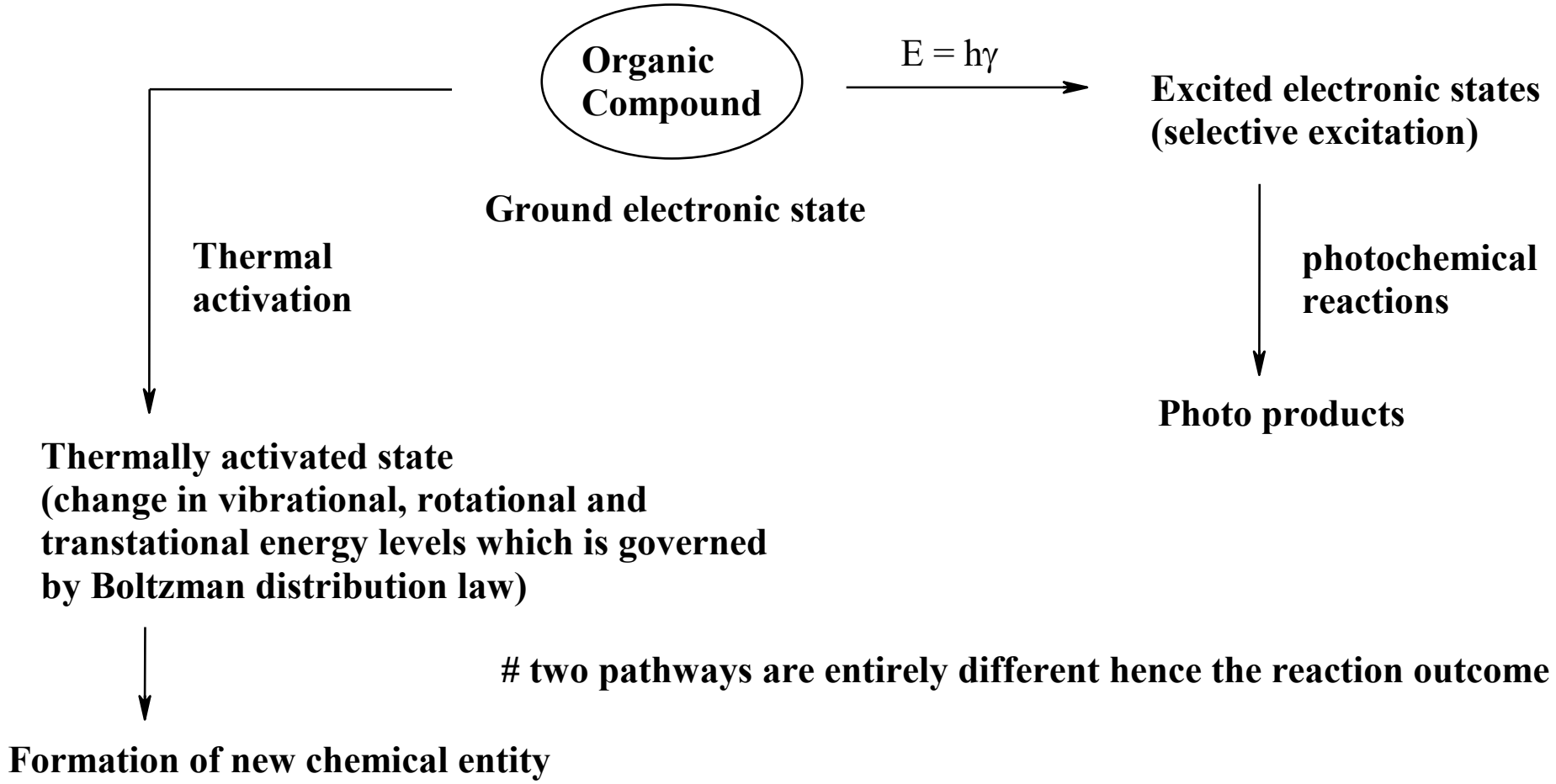
Isorhodopsin
λ_{max} = 487 nm
Opsin

Contents expected on this course will be:

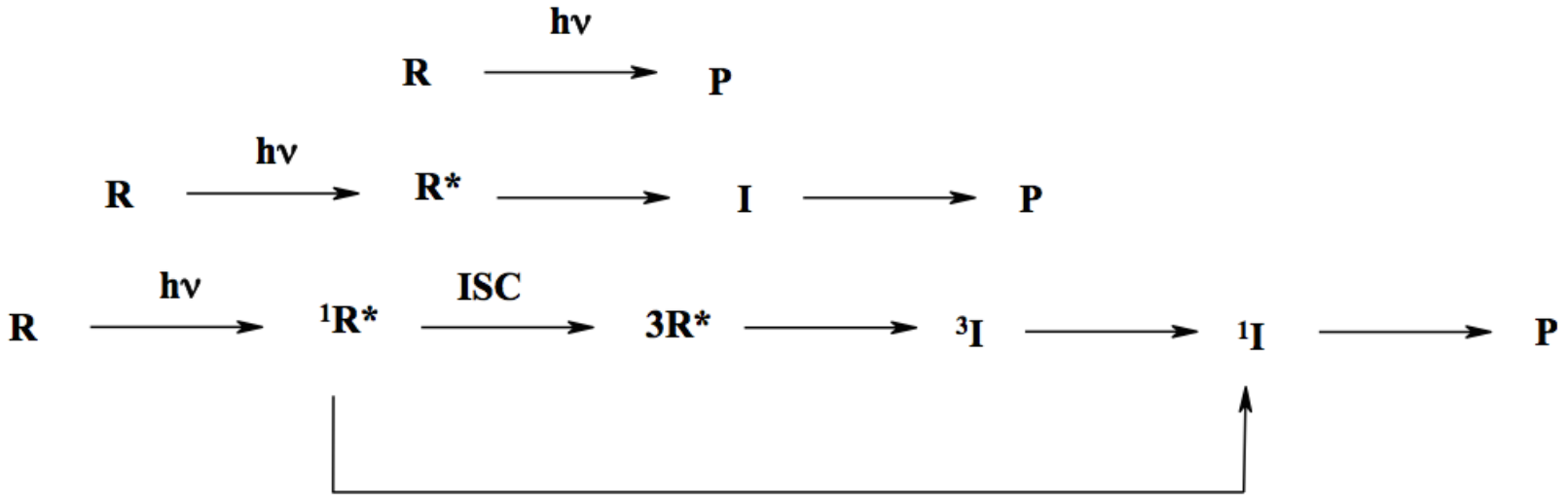
1. Principles of photochemical reactions
2. Excited states and their properties
3. Several useful photochemical reactions and their applications in organic synthesis (isomerization, Patterno-Buchi reaction, Norrish type I and II reaction, Photoreduction, Rearrangements: di-π-methane, oxa di-π- and aza di-π-methane rearrangements, Photocycloaddition
4. Photochemistry of biological systems
5. Pericyclic reactions

Recommended books:

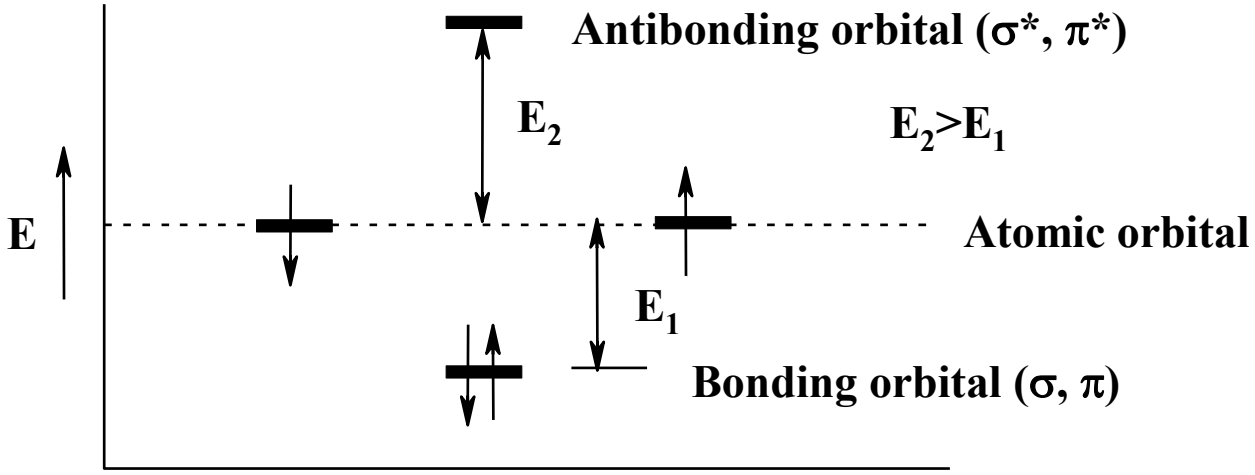
- CRC Handbook of Photochemistry and Photobiology. Eds by. William M. Horspool and Pill-Soon Song. 1994. CRC Press. ISBN: 0-8493-8634-9.
- Synthetic organic photochemistry. Eds by. William M. Horspool, Plenum press. 1984. ISBN: 0-306-41449-X.
- Organic Chemistry by Prashar.
- https://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/photchem.htm


Organic Compound
E = hγ
Excited electronic states (selective excitation)
Ground electronic state
Thermal activation
photochemical reactions
Photo products
Thermally activated state (change in vibrational, rotational and transtational energy levels which is governed by Boltzman distribution law)
two pathways are entirely different hence the reaction outcome
Formation of new chemical entity

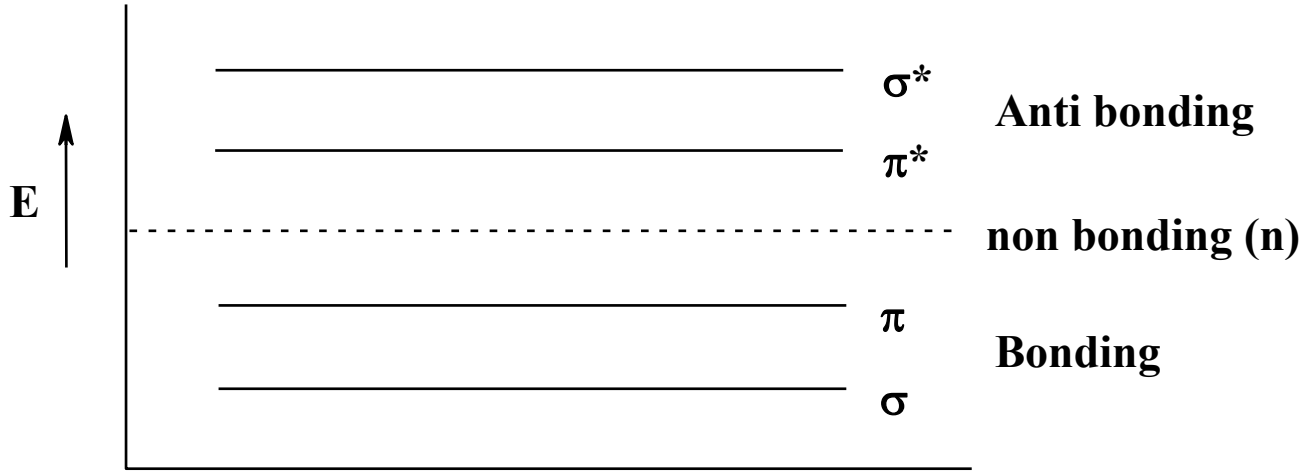
Events in a photochemical reaction:



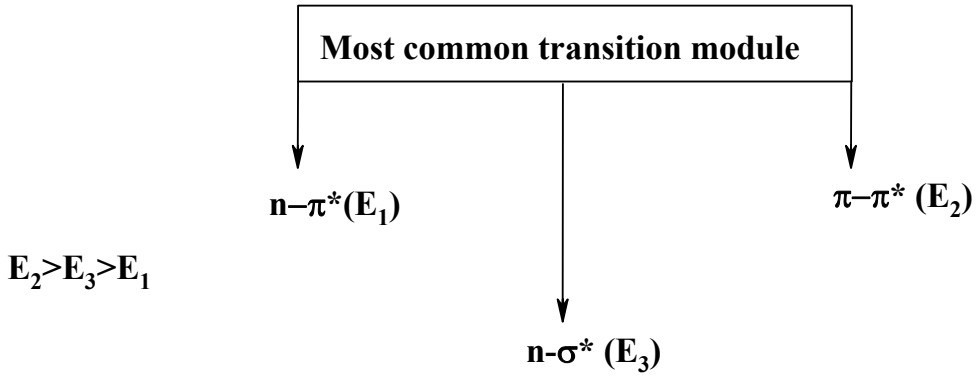
Products? Ionic or radical reaction? Spin orientations of excited states? Intermediates involved? Orbitals involved?



Relative energies of atomic and molecular orbitals

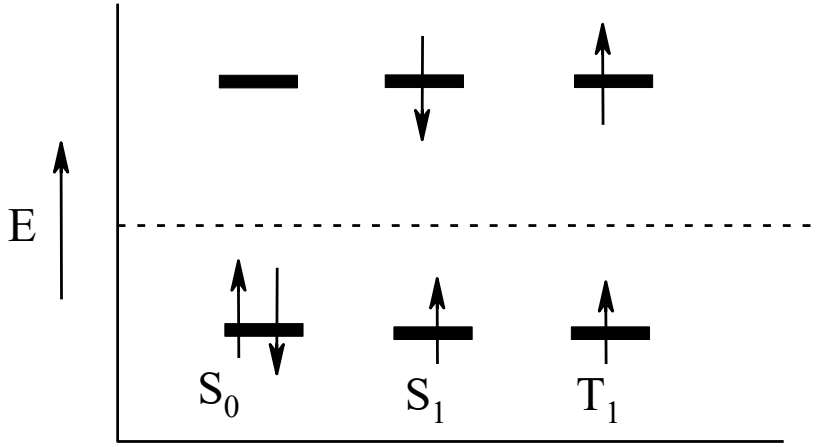


Relative energies of σ, π and n MOs



Absorption maxima for few molecules and functional groups

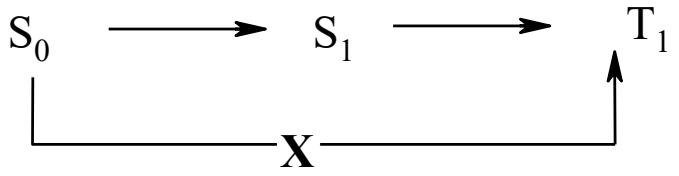
Molecule	Transition	λ_{max} (nm)	E (Kcal/mol)
Iodobutane	n-σ*	224	127.7
Ethylene	π–π*	165	173.3
Ethyne	π–π*	173	165.3
Acetone	π–π*	150	190.7
	n-σ*	188	152.1
	n-π*	279	102.5
Butadiene	π–π*	217	131.8
Acrolein	π–π*	210	136.2
	n-π*	315	90.8
Functional group			
RCH = CHR		165	173.3
		193	148.2
Alkyne		173	165.3
Ketones		188	152.1
		279	102.5
Aldehydes		290	98.6
Carboxylic acids		<205	<137.5



Antibonding (SOMO)

Bonding

Excited states



S_0 : Ground state (spin paired, Pauli exclusion principle)

S_1: Excited singlet state

T_1: Excited triplet state (spin inversion)

 # T_1 is more stable than S_1 (parallel spin, lesser inter-electronic repulsion)