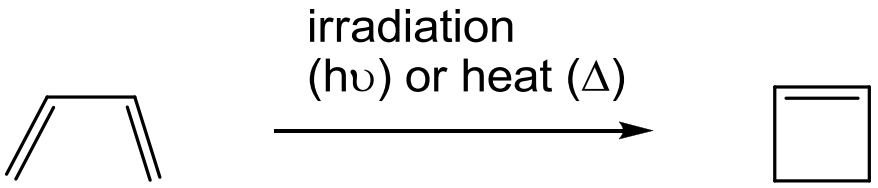
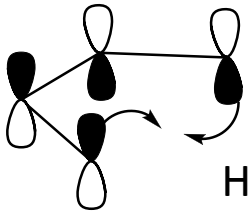
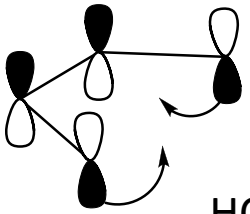
Pericyclic Reaction: Selectivity and Reactivity

Electrocyclic Reactions: Selectivity and reactivity

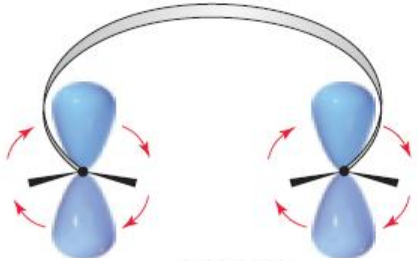




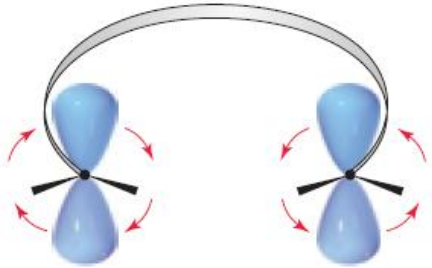
Conrotation



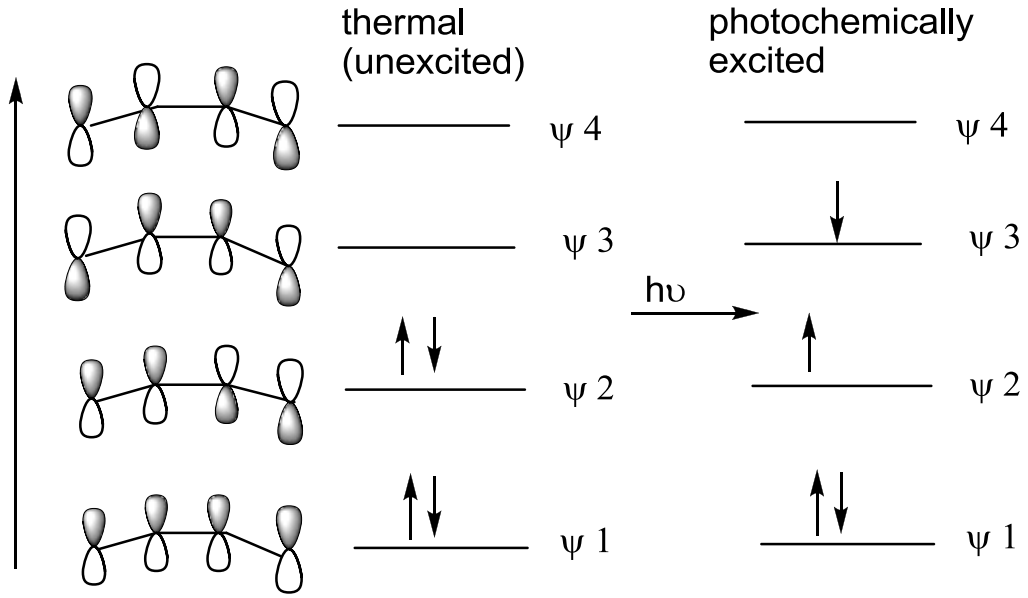
Disrotation



rotation in the same direction



rotation in the opposite direction

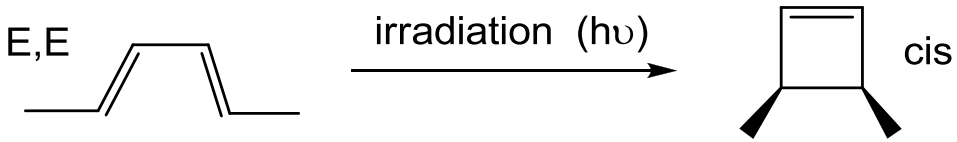


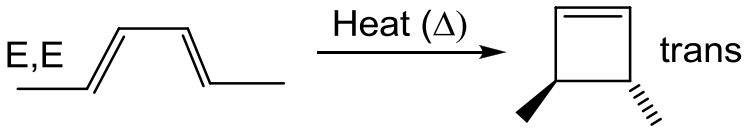
HOMO is considered to explain the reactivity and selectivity of electrocyclic reaction

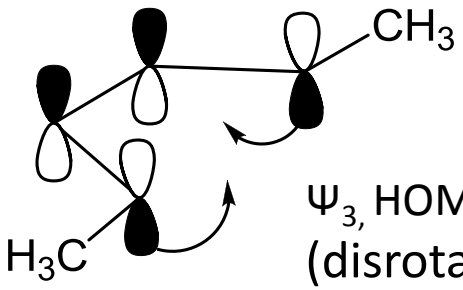
4π electrocyclization:

Thermally : conrotation
Photochemically: disrotation

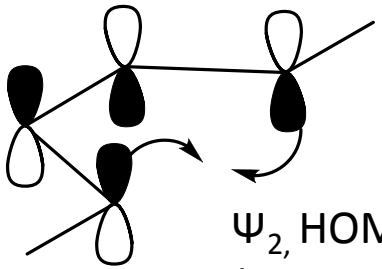
Electrocyclic Reactions: Selectivity and Reactivity



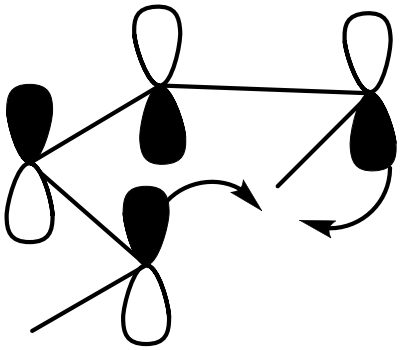


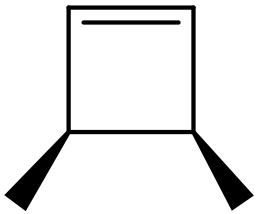


Ψ_3, HOMO (hv)
(disrotation)



Ψ_2, HOMO
(conrotation)

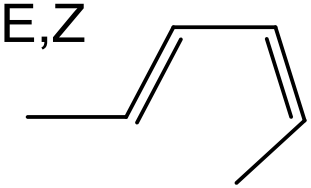


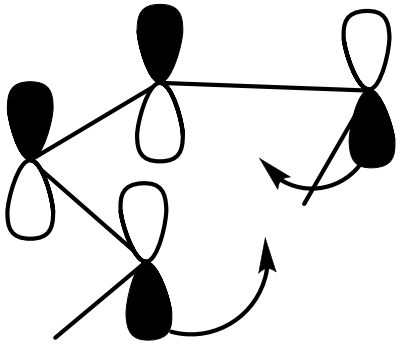


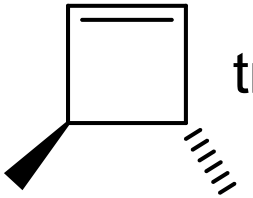
cis

Heat (Δ)

E,Z



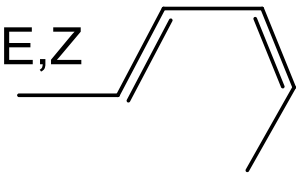




trans

irradiation (hυ)

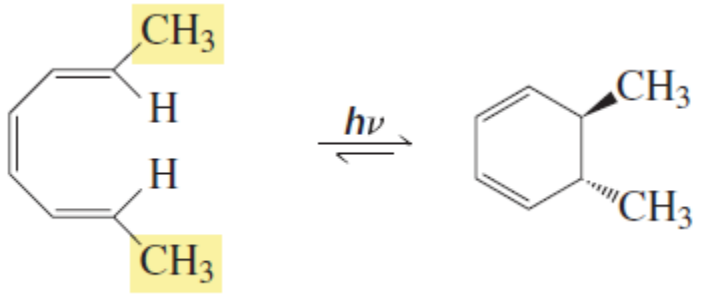
E,Z



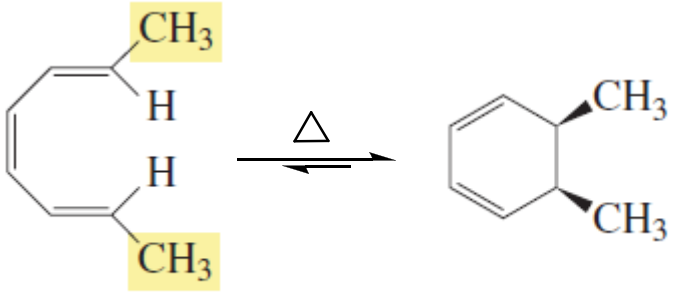
4π electrocyclization:

Thermally : conrotation and Photochemically: disrotation

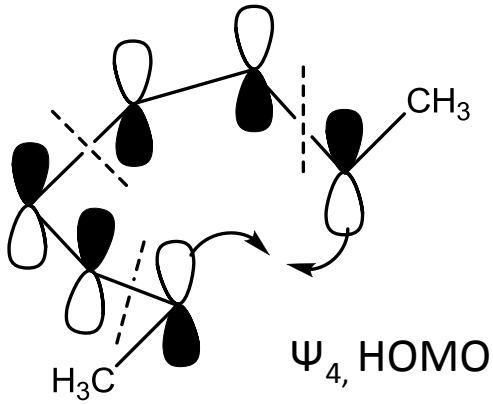
Electrocyclic Reactions: Selectivity and Reactivity



(2*E*,4*Z*,6*E*)-octatriene

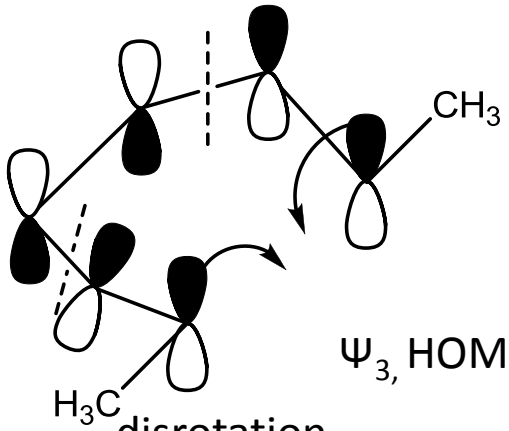


(2*E*,4*Z*,6*E*)-octatriene



Ψ_4, HOMO (hv)

conrotation

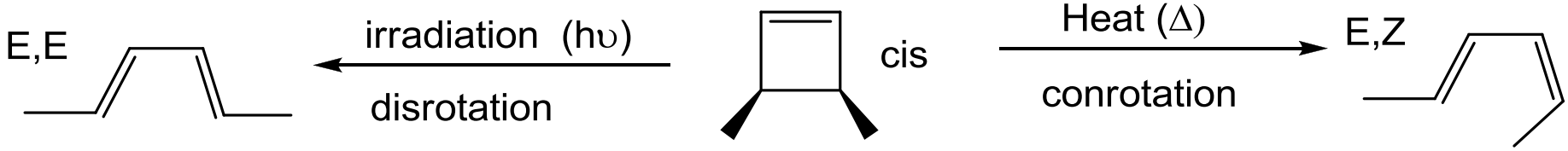


Ψ_3, HOMO

disrotation

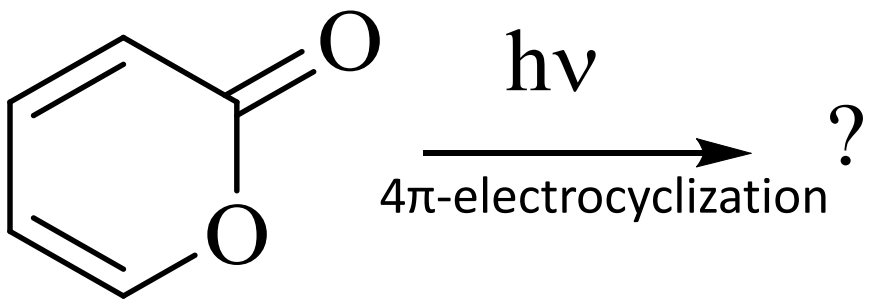
6π electrocyclization:

Thermally : disrotation and Photochemically: conrotation



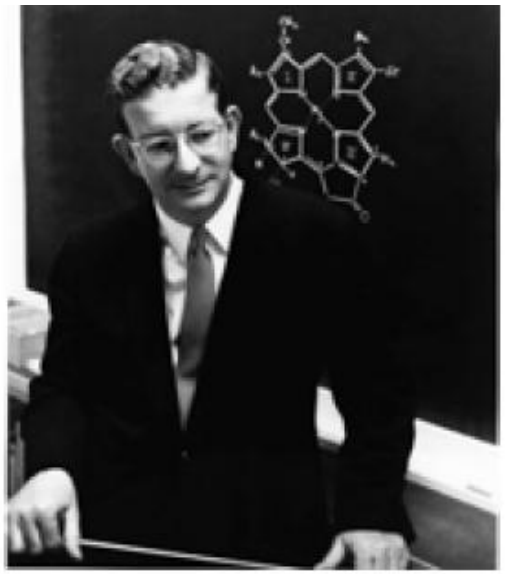
Electrocyclic Reactions: Selectivity and Reactivity

Write the product for the following reaction with proper relative stereo chemistry



A summary of the Woodward-Hoffmann rules

	Thermal	Photochem.	Thermal	Photochem.
	4n+2	4n	4n	4n+2
Electrocyclic	Disrotation	Disrotation	Conrotation	Conrotation
Cycloaddition	allowed	allowed	forbidden	forbidden



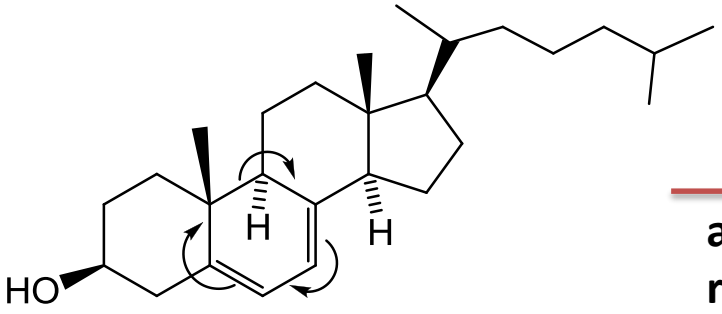
Robert B. Woodward (1917–1979)

Roald Hoffmann *(1937-)*

Kenichi Fukui (1918–1998)

Shared the 1981 Nobel Prize *in chemistry for the conservation of orbital Symmetry theory and the frontier orbital theory*

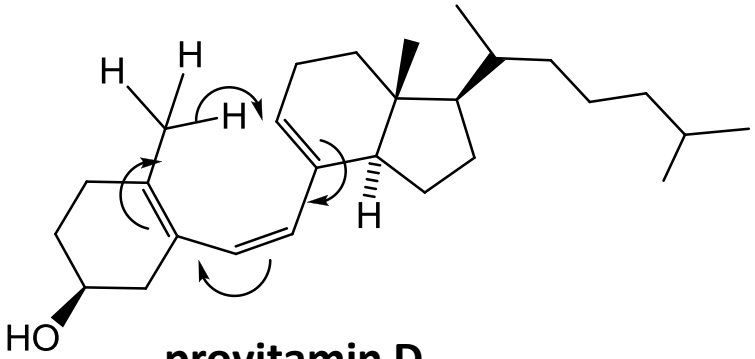
Pericyclic Reaction: Biological Importance



7-dehydrocholesterol
(Steroid found in skin)

hν

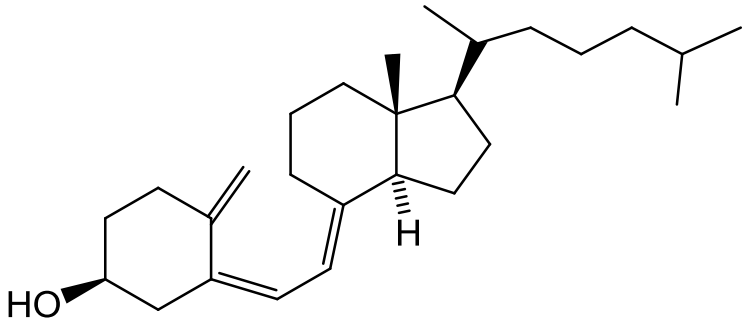
an electrocyclic reaction



provitamin D_3

a [1,7] sigmatropic rearrangement

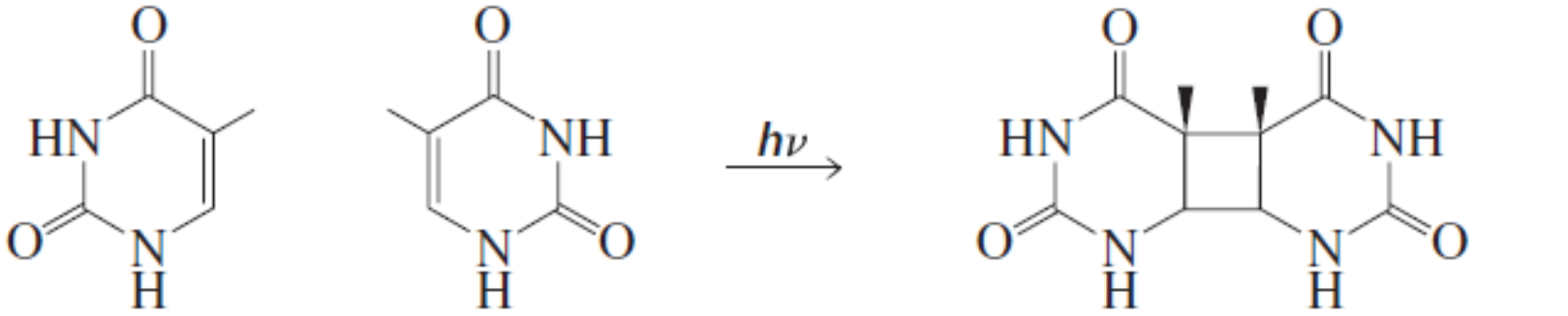
Why light is required?



vitamin D_3

Pericyclic Reaction: Biological Importance

Exposure to ultraviolet light causes skin cancer



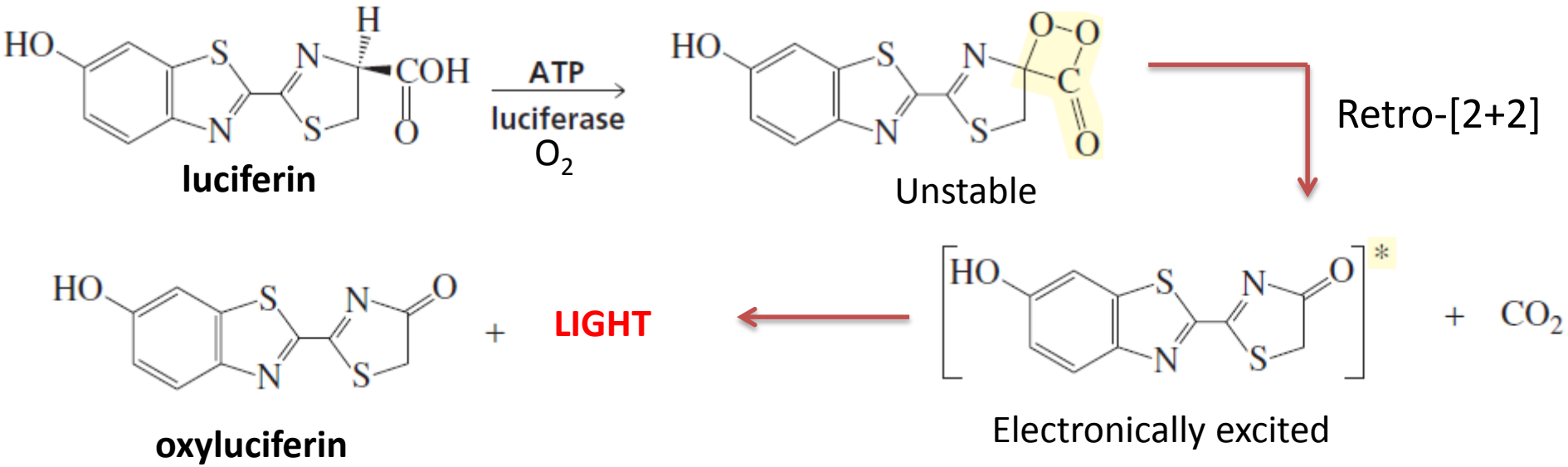
two adjacent thymine residues on DNA

mutation-causing thymine dimer

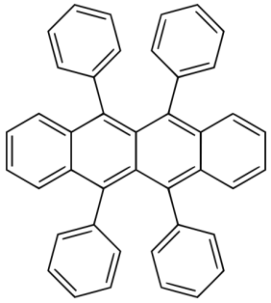
DNA photolyase: The enzymes that repair damaged DNA

Pericyclic Reaction: Biological Importance

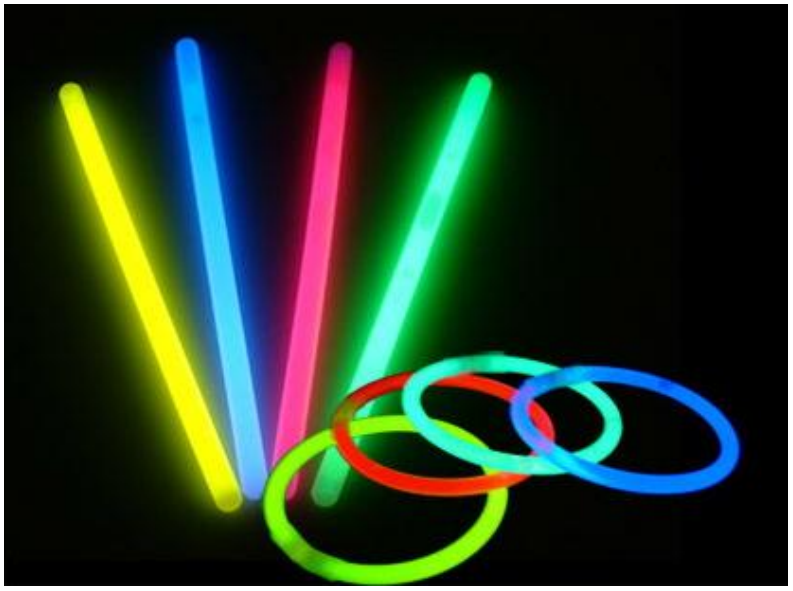
A firefly

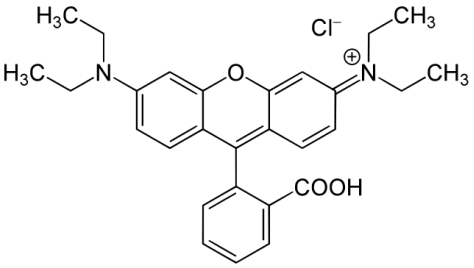


Pericyclic Reaction: Glow Stick

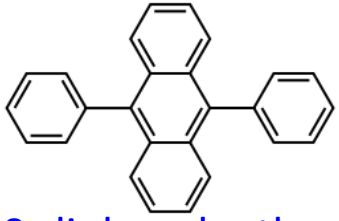


[Rubrene](#)
yields yellow light

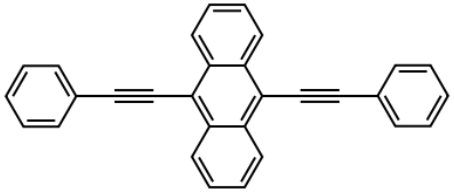




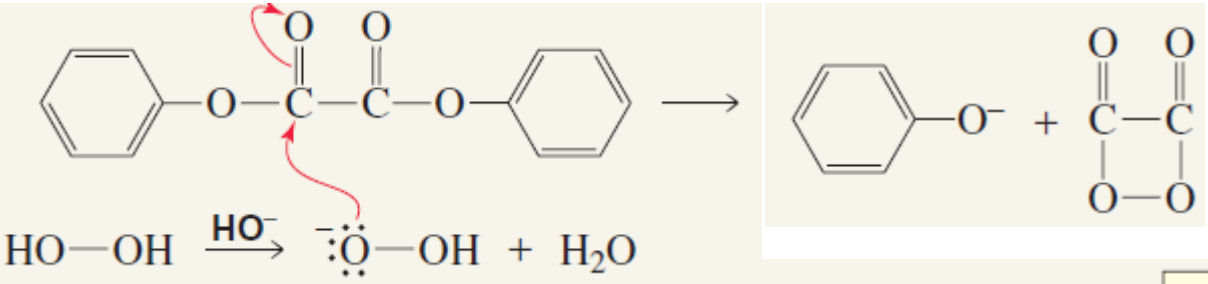
[Rhodamine B](#)
yields red light

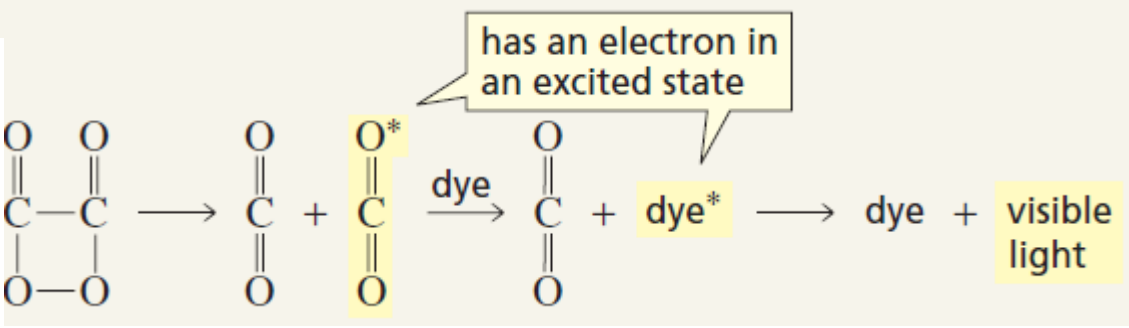


[9,10-diphenylanthracene](#)
yields blue light



[9,10-bis(phenylethynyl) anthracene](#)
yields green light





Looking forward

Mid Sem Examination
on
Topics Discussed So Far