Photochemistry

The branch of chemistry which deals with the study of chemical reaction initiated by light.

Energy of photon

The photon is **quantized energy**: **light quantum**

$$\varepsilon = h\gamma = h\frac{C}{\lambda} = hC\,\nu$$

Where h is the Plank constant, C the velocity of light in vacuum, λ the wave-length of the light, and ν the wave number.

- **Light is absorbed by the molecules in quantized units known as photons (or quanta).**

- **Avogadro's number of photons (6×10^{23}) is known as Einstein.**

- **An Einstein of light represents a different amount of energy depending on the wavelength of light.**

Interaction between light and media

absorption

transmission

Reflection

Scattering

refraction
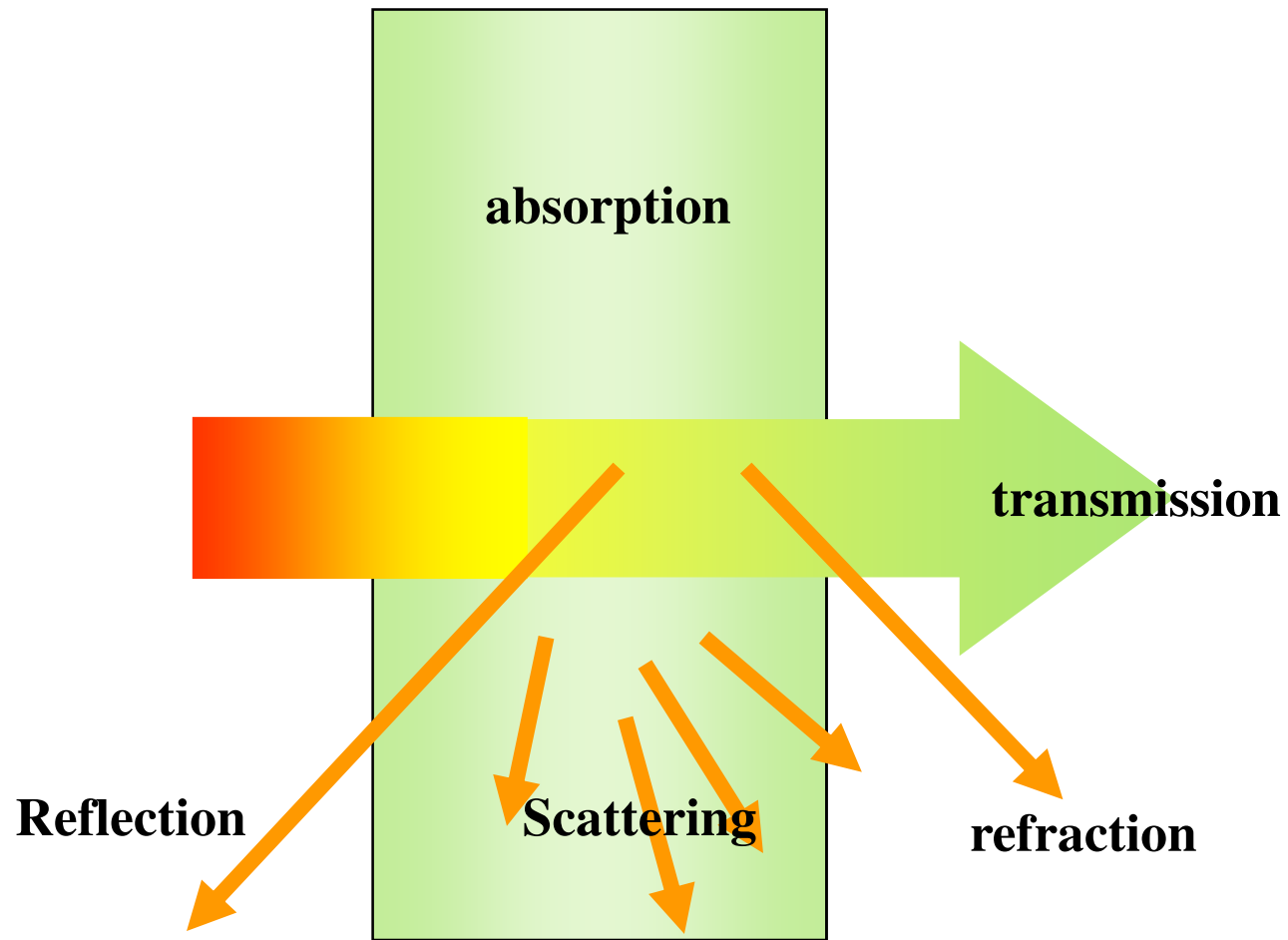
$$\text{Quantum Yield} = \frac{\text{Number of molecule undergoing a particular process}}{\text{Number of photons absorbed}}$$

Number of molecules undergoing a particular process is a measure of chemical yield.

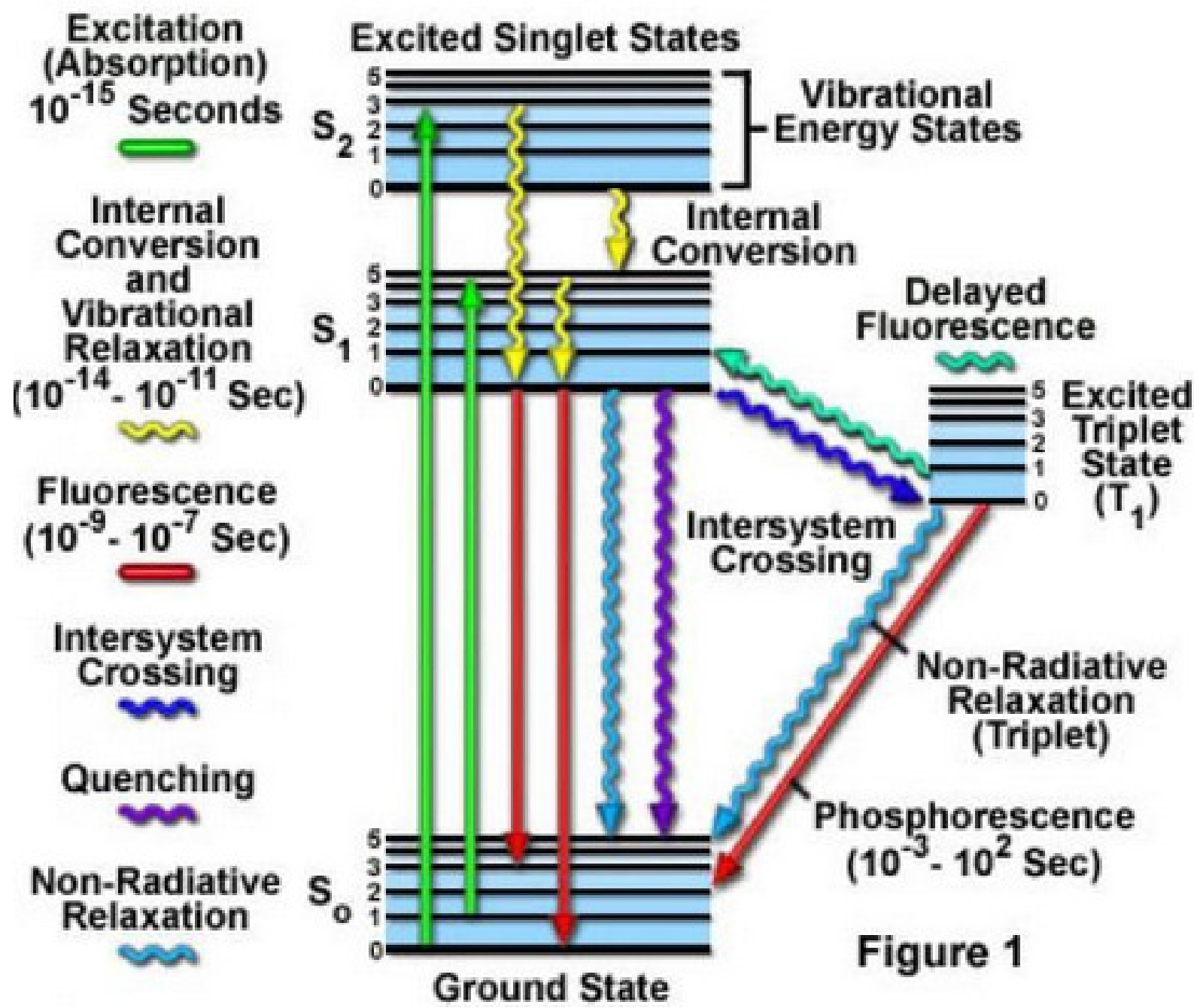Number of photons absorbed by the system is determined by an instrument called Actinometer.

Photochemical Processes:

•The first step in a photochemical process is excitation of molecule.

•Either return to the ground state or leads to chemical reaction.

•Reaction takes place depending on the potential intramolecular

or intermolecular interactions.

•This will be determined by the energy relations between molecules
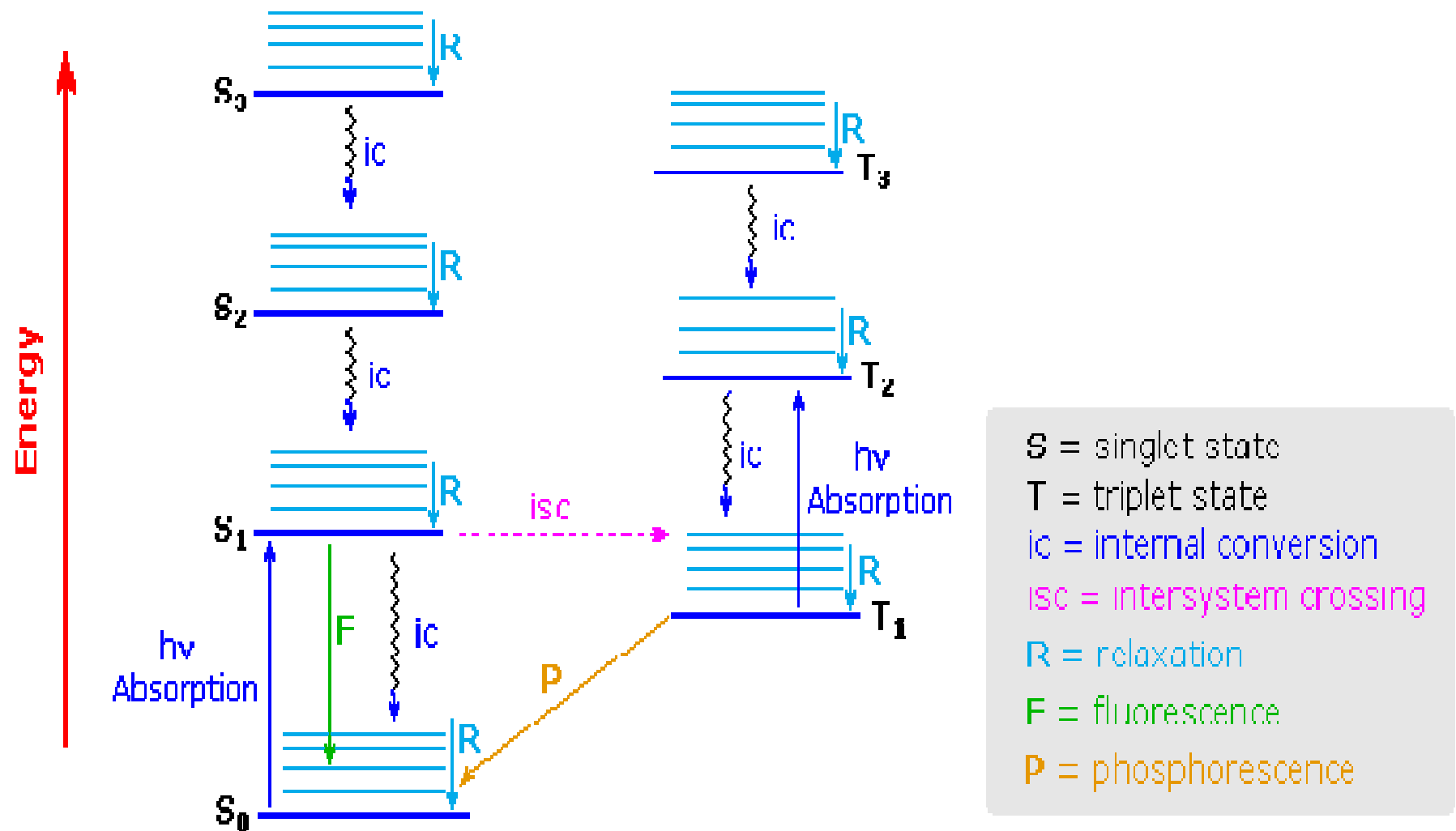
and by quantum mechanical rules.
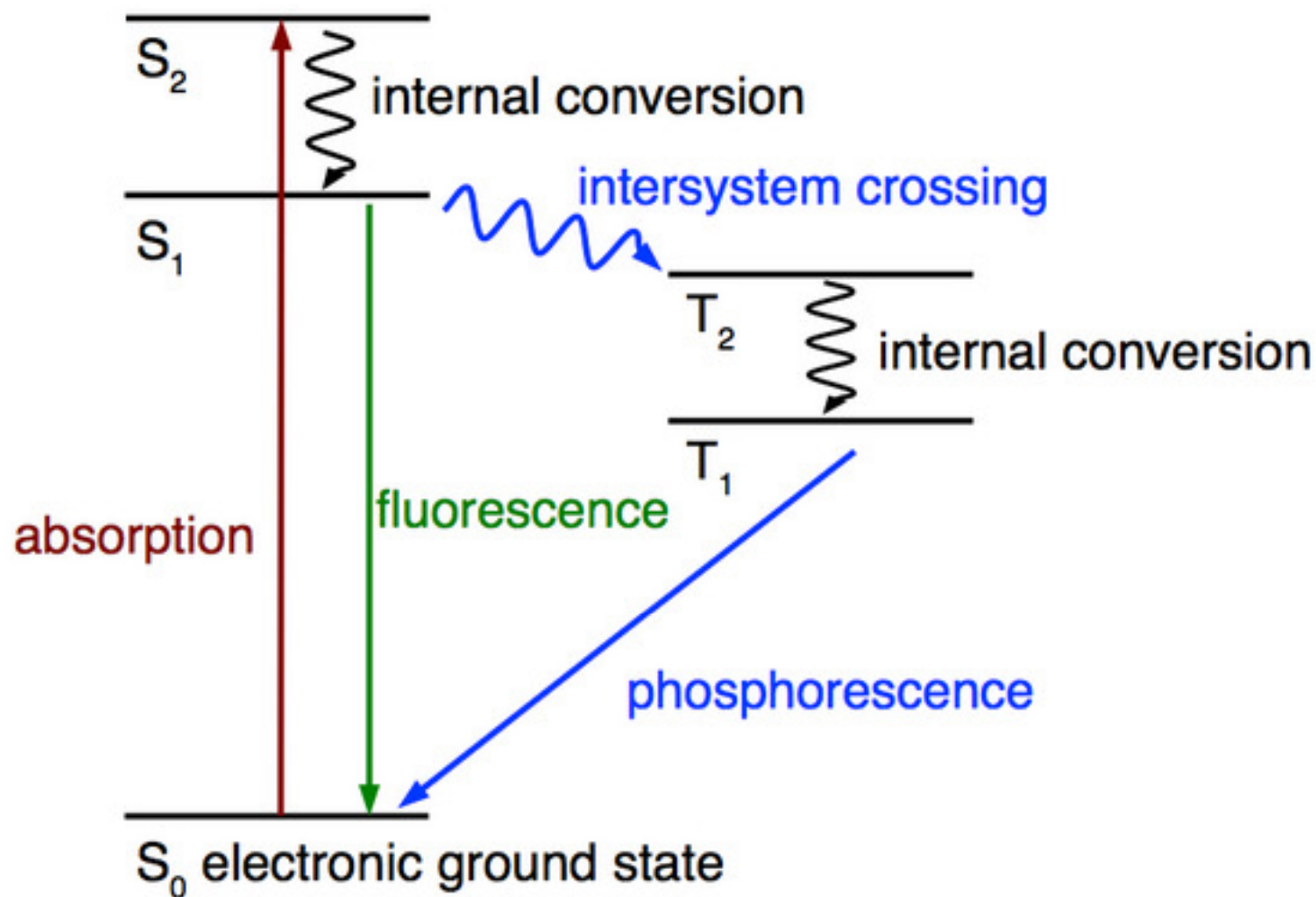
Internal Conversion: Decay of an excited state to another state of the same multiplicity (Singlet to singlet or triplet to triplet) is called internal conversion
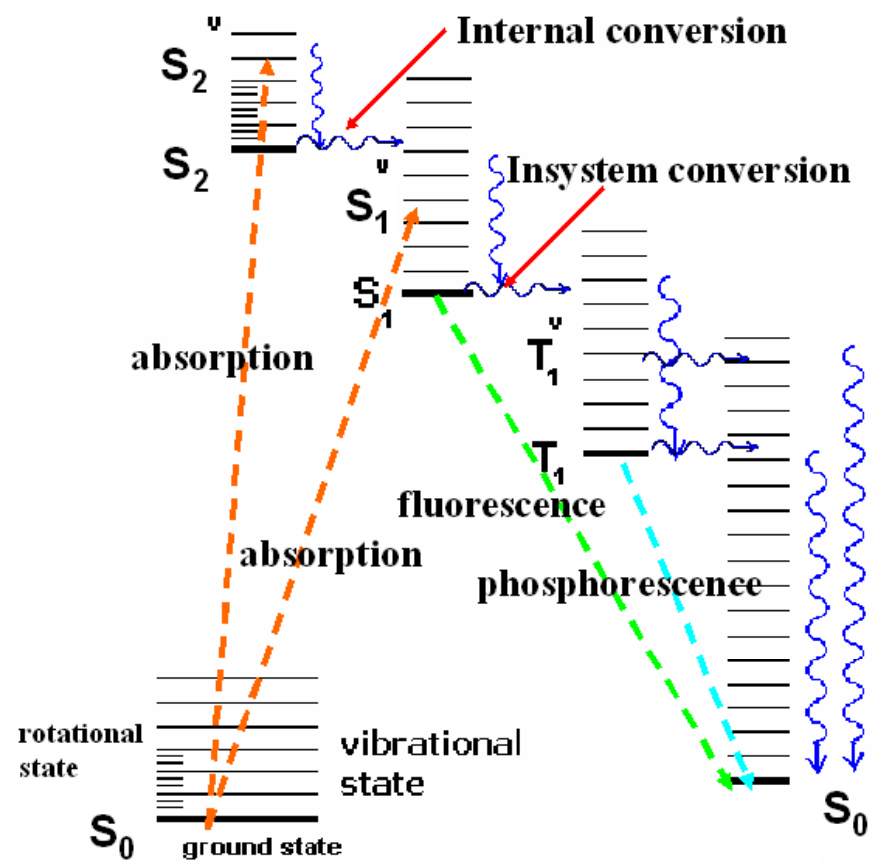
Jablonski Energy Diagram

Excited Singlet States
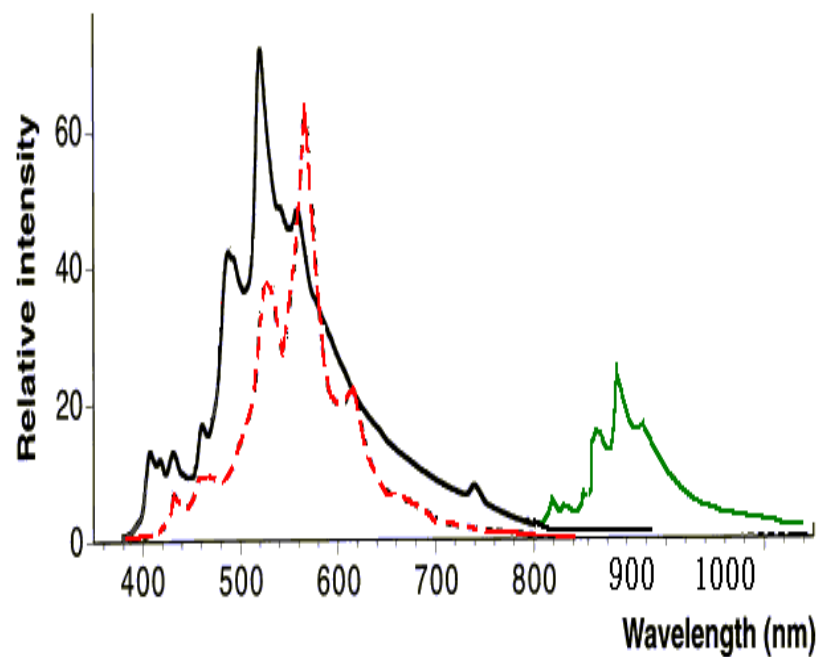
Excitation (Absorption) 10^{-15} Seconds

Internal Conversion and Vibrational Relaxation (10^{-14} - 10^{-11} Sec)

Fluorescence (10^{-9} - 10^{-7} Sec)

Intersystem Crossing

Quenching

Non-Radiative Relaxation

S_2

Vibrational Energy States

Internal Conversion

S_1

Delayed Fluorescence

Intersystem Crossing

Excited Triplet State (T_1)

Non-Radiative Relaxation (Triplet)

Phosphorescence (10^{-3} - 10^2 Sec)

S_0

Ground State

Figure 1

A Jablonski Diagram

S_3 R
S_2 R
S_1 R
S_0 R

ic
ic
ic

hv Absorption

F

isc

P

T_3 R
T_2 R
T_1 R

ic
ic

hv Absorption

S = singlet state
T = triplet state
ic = internal conversion
isc = intersystem crossing
R = relaxation
F = fluorescence
P = phosphorescence

Energy

Process	Transition	Timescale (sec)
Light Absorption (Excitation)	$S_0 \rightarrow S_n$	ca. 10^{-15} (instantaneous)
Internal Conversion	$S_n \rightarrow S_1$	10^{-14} to 10^{-11}
Vibrational Relaxation	$S_n^* \rightarrow S_n$	10^{-12} to 10^{-10}
Intersystem Crossing	$S_1 \rightarrow T_1$	10^{-11} to 10^{-6}
Fluorescence	$S_1 \rightarrow S_0$	10^{-9} to 10^{-6}
Phosphorescence	$T_1 \rightarrow S_0$	10^{-3} to 100
Non-Radiative Decay	$S_1 \rightarrow S_0$ $T_1 \rightarrow S_0$	10^{-7} to 10^{-5} 10^{-3} to 100

Internal conversion

Insystem conversion

S_2

S_2

S_1

S_1

T_1

T_1

S_0

absorption

absorption

fluorescence

phosphorescence

rotational state

vibrational state

ground state

Radiation-less decay

Jablonsky diagram

Frank Condon Principle:

The photo excitation process is very rapid (10^{-15} s), it is faster than a molecular vibration. Thus the molecule will initially have exactly the same inter-atomic distance in the excited state as it had in its original state.
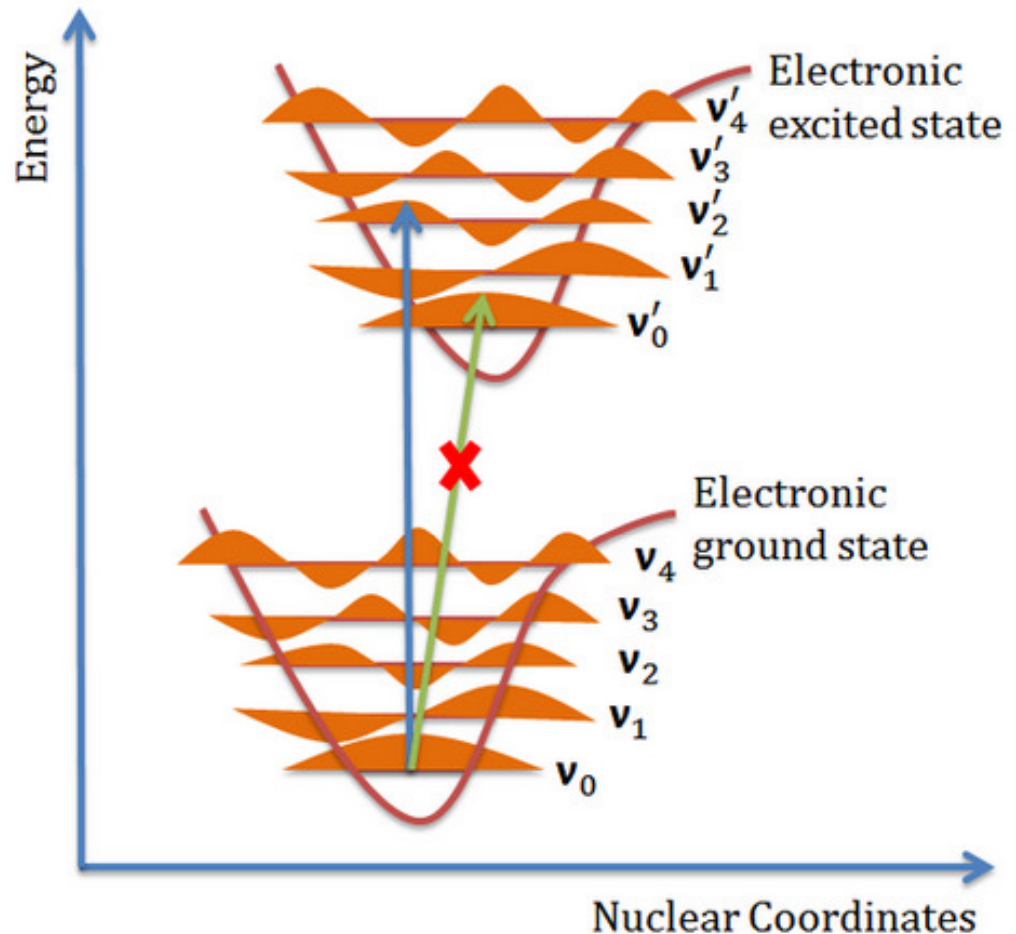
Fig. 2 Franck-Condon energy diagram

Energy Transfer and Photosensitization

A molecule may be promoted to an electronically excited state by an indirect process, i.e.; by transfer of energy from another molecule already in an excited state.

The common indirect excitation method is **Photosensitization-** the process whereby a photo excite state molecules transfer its energy in exciting another molecules.

Photosensitizers: It is an photo excited molecules which absorb light at a different wavelength from that of the molecule it will subsequently excite.

It should have an energy level higher and there should be spin conservation.

Energy Transfer

Most common mechanism of Energy transfer is triplet-triplet mechanism involves a collision or electron exc

$$Sens \xrightarrow{h\nu} {}^1Sens \longrightarrow {}^3Sens$$

$${}^3Sens \left(\uparrow\uparrow\right) + A\left(\uparrow\downarrow\right) \longrightarrow Sens\left(\uparrow\downarrow\right) + {}^3A\left(\uparrow\uparrow\right)$$

Spin Exchange

$$(C_6H_5)_2C=O \xrightarrow{h\nu} (C_6H_5)_2=O^{*1} \longrightarrow (C_6H_5)_2C=O^{*3}$$

$$(C_6H_5)_2C=O^{*3} + \text{[naphthalene]} \xrightarrow{\text{Energy transfer}} (C_6H_5)_2C=O + \text{[naphthalene]}^{*3}$$
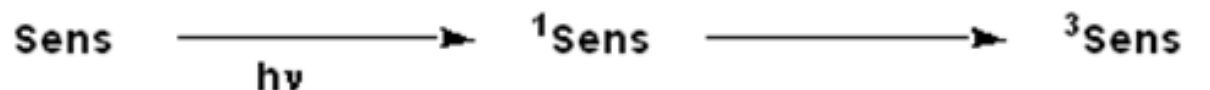
$$\longrightarrow \text{[naphthalene]} + \quad h\nu$$

(*Phosphorescence*)
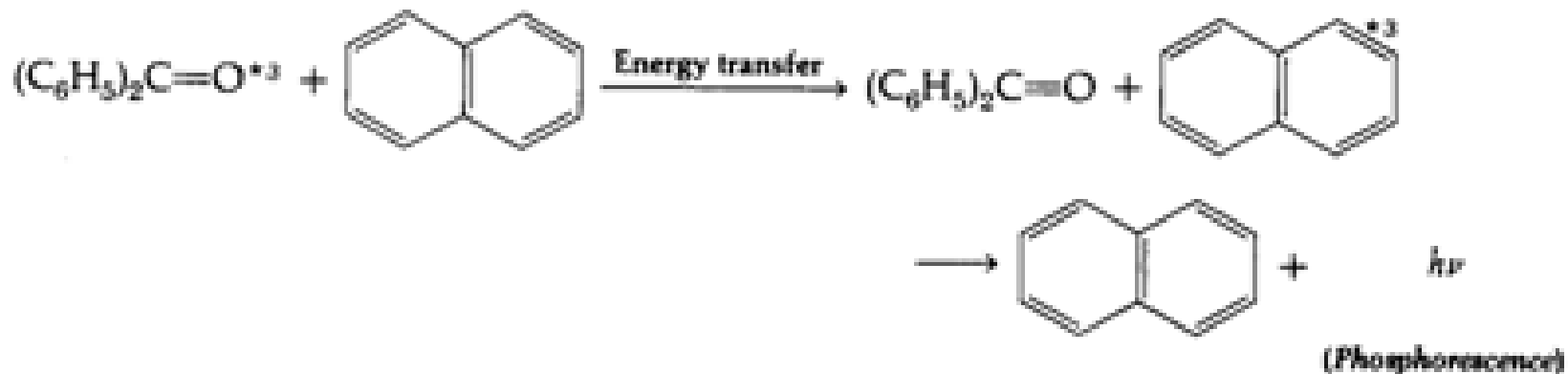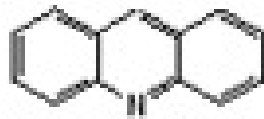
Some Sensitizers

Acridine
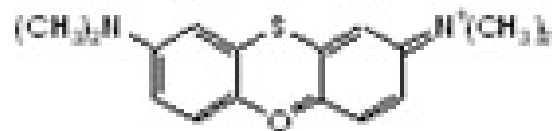
Methylene Blue
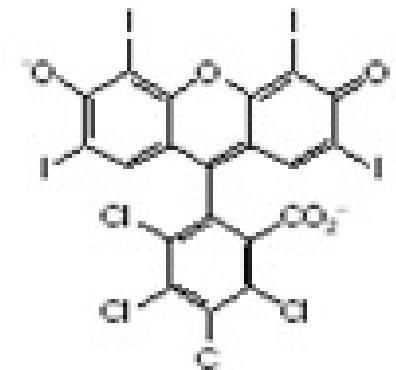
Rose Bengal
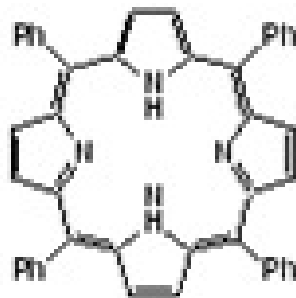
Tetraphenylporphine
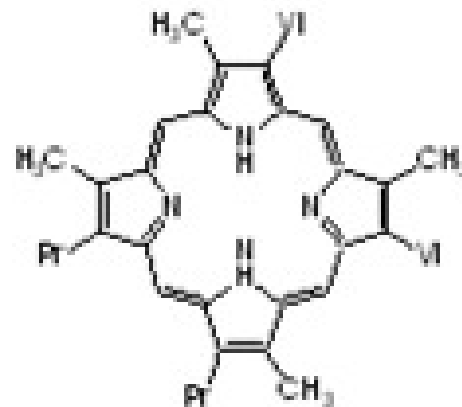
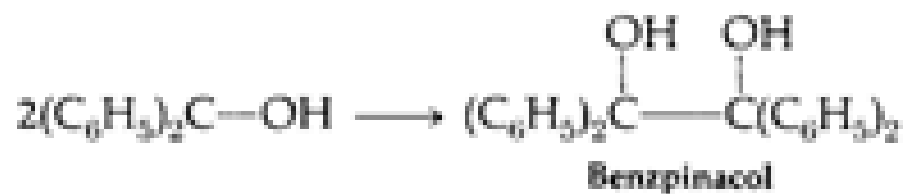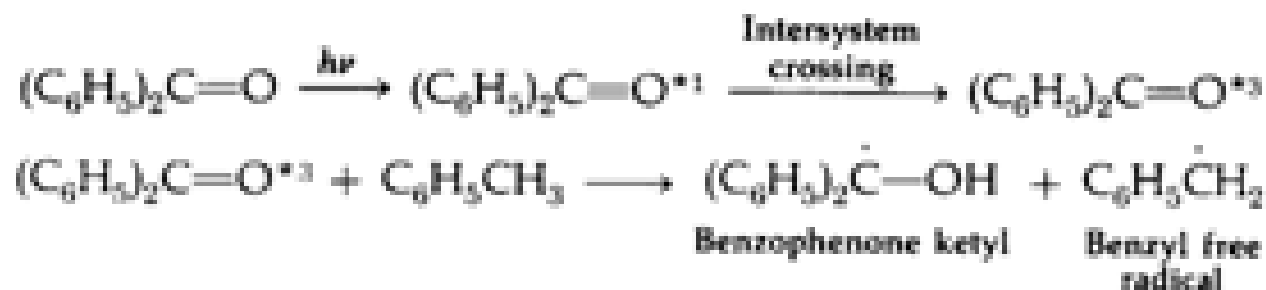**A Protoporphyrin**

A Phthalocyanine

20
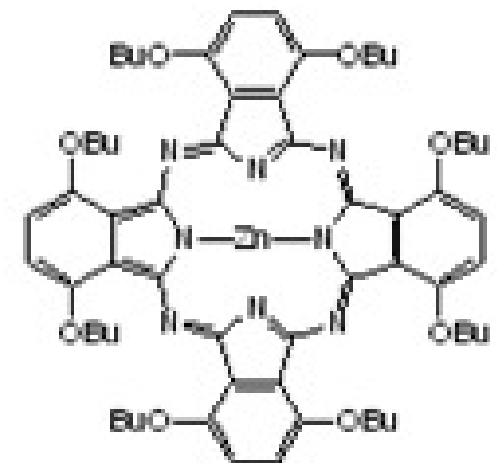
Criteria of an ideal sensitizer

- It must be excited by the irradiation to be used, small singlet triplet splitting. High ISC yield.

- It must be present in sufficient concentration to absorb more strongly than the other reactants under the condition.

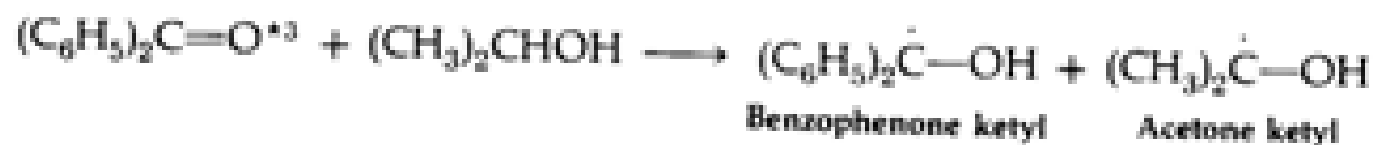- It must be able to transfer energy to the desired reactant, low chemical reactivity in Triplet state.

Photochemical Reactions

Photolysis: Cleavage of bond as s result of photo activation, and intramolecular rearrangement are typical photoreaction.

A. PHOTO REDUCTION

$$(C_6H_5)_2C=O \xrightarrow{h\nu} (C_6H_5)_2C=O^{*1} \xrightarrow[\text{crossing}]{\text{Intersystem}} (C_6H_5)_2C=O^{*3}$$

$$(C_6H_5)_2C=O^{*3} + C_6H_5CH_3 \longrightarrow (C_6H_5)_2\dot{C}-OH + C_6H_5\dot{C}H_2$$

Benzophenone ketyl   Benzyl free radical

$$2(C_6H_5)_2\dot{C}-OH \longrightarrow (C_6H_5)_2\overset{\overset{OH}{|}}{C}-\overset{\overset{OH}{|}}{C}(C_6H_5)_2$$

Benzpinacol

$$2C_6H_5\dot{C}H_2 \longrightarrow C_6H_5CH_2CH_2C_6H_5$$

Bibenzyl

$$(C_6H_5)_2\dot{C}-OH + C_6H_5\dot{C}H_2 \longrightarrow (C_6H_5)_2\overset{\overset{OH}{|}}{C}CH_2C_6H_5$$

Benzyldiphenyl carbinol

$(C_6H_5)_2C=O \xrightarrow{h\nu} \longrightarrow (C_6H_5)_2C=O^{*3}$

$(C_6H_5)_2C=O^{*3} + (CH_3)_2CHOH \longrightarrow (C_6H_5)_2\dot{C}-OH + (CH_3)_2\dot{C}-OH$

Benzophenone ketyl　　　Acetone ketyl

$(C_6H_5)_2C=O + (CH_3)_2\dot{C}-OH \longrightarrow (C_6H_5)_2\dot{C}-OH + (CH_3)_2C=O$

Acetone

$$2(C_6H_5)_2\dot{C}-OH \longrightarrow (C_6H_5)_2\overset{\overset{\displaystyle OH}{|}}{C}-\overset{\overset{\displaystyle OH}{|}}{C}(C_6H_5)_2$$

Suggest an explanation for the fact that the benzyl free radical dimerizes in the photoreduction of benzophenone with toluene whereas the 2-hydroxy-2-propyl radical formed in the presence of 2-propanol gives up a hydrogen atom to benzophenone.

Suggest a reaction sequence for the photoreduction of benzophenone in the presence of diphenyl methanol. What maximum quantum yield would be expected for the disappearance of benzophenone and for the formation of benzpinacol in this reaction?

Unsymmetrical ketones tend to under go dissociation so as to give the more stable of the two possible free radicals

$$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3 \xrightarrow{h\nu} CH_3\overset{O}{\overset{\|}{C}}\cdot + \cdot CH_2CH_3$$

$$CH_3\overset{O}{\overset{\|}{C}}C(CH_3)_3 \xrightarrow{h\nu} CH_3\overset{O}{\overset{\|}{C}}\cdot + \cdot C(CH_3)_3$$

Irradiation of 2,2,4,4-tetramethyl-3-pentanone (di-*tert*-butyl ketone) in a solution of carbon tetrachloride produces 2,2-dimethylpropanal (pivaldehyde), chloroform, 2-methylpropene, 2-chloro-2-methylpropane, and carbon monoxide. Suggest a pathway to each of these products.

Photopinacolization or Photoreduction

benzpinacol
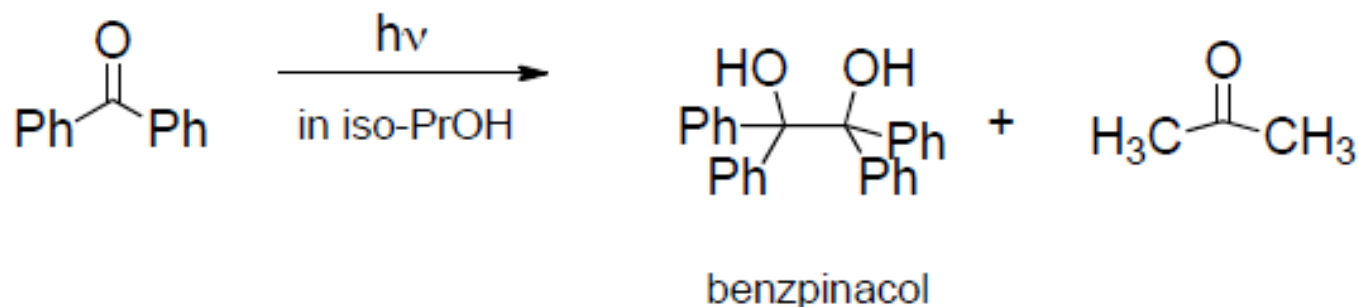
1. Photoreduction can be quenched by triplet quenchers, such as oxygen.

2. If hydrogen donor S-H is replaced by S-D, a primary kinetic isotope is obesrved: a decreased rate of reduction relative to non-productive decay to the ground state.

3. In 2-propanol, the quantum yield for photolytic conversion of $Ph_2C=O$ to benzpinacol is 2.0.

PHOTOLYSIS

Norrish Type-I

Irradiation of molecules often leads to homolytic bond cleavage and produce free radical intermediates. Acetone undergo photolytic cleavage at the C-C bond a- to the cerbonyl group. This is known as Norrish type I cleavage (Ronald Norrish, Nobel laureate 1967)

Norrish type I cleavage
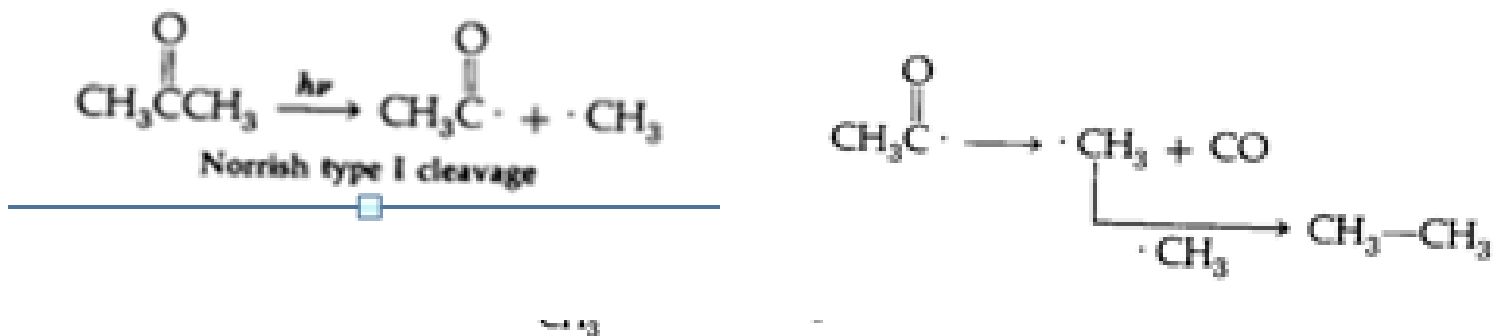
The reaction is quite general for acyclic and cyclic ketones.

Norrish Type I Photochemistry

α-cleavage:

$$R_1\!-\!\overset{\displaystyle O}{\underset{\displaystyle \|}{C}}\!-\!R_2 \quad \xrightarrow{\ h\nu\ } \quad R_1\!-\!\overset{\displaystyle \cdot}{C}\!=\!O \ + \ \cdot R_2$$
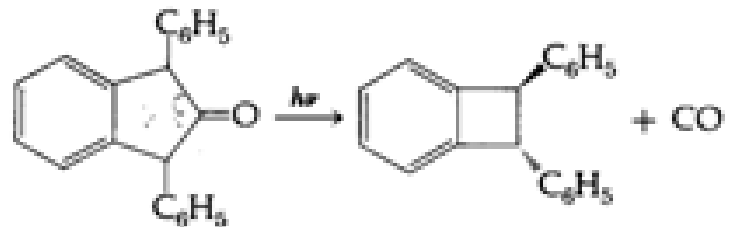
	rate constant (s^{-1})		rate constant (s^{-1})
Ph–CO–CH$_2$Ph	2×10^6	H$_3$C–CO–C(CH$_3$)$_3$	$> 10^9$
Ph–CO–CH(CH$_3$)Ph	3×10^7	cyclopentanone	2×10^8
Ph–CO–C(CH$_3$)$_2$Ph	1×10^8	cyclohexanone	2×10^7
Ph–CO–C(CH$_3$)$_3$	1×10^7	2-methylcyclohexanone	2×10^8
		2,2-dimethyl cyclohexenone	$\sim\!2 \times 10^9$

Norrish Type I Photochemistry

Primary Process (α-cleavage):

$$RH_2C-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle R_2}{|}}{C}HCH_2R_1 \quad \xrightarrow{h\nu} \quad RH_2C-\overset{\displaystyle \cdot}{C}=O \quad + \quad \cdot\underset{\underset{\displaystyle R_2}{|}}{C}HCH_2R_1$$

Secondary Process:

$$RH_2C-\overset{\displaystyle \cdot}{C}=O$$

decarbonylation → $\cdot CH_2R + CO$

H - abstraction (with $\cdot \underset{\underset{\displaystyle R_2}{|}}{C}HCH_2R_1$) → $\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle R}{|}}{C}}=C=O \quad + \quad R_1H_2C-CH_2R_1$

H - abstraction (with $\cdot \underset{\underset{\displaystyle R_2}{|}}{C}HCH_2R_1$) → $RH_2C-\underset{\underset{\displaystyle H}{|}}{C}=O \qquad R_2HC=CHR_1$

Norrish Type I Photochemistry

Ph—C(=O)—CH2—Ph, Ph $\xrightarrow[{}^3(n,\pi^*)]{hv}$ Ph⌒⌒Ph + Ph⌒CH(Ph)Ph + Ph2CH—CHPh2

25% 50% 25%

Ph—C(=O)—CH2—Ph, Ph $\xrightarrow[{}^3(n,\pi^*)]{hv}$ Ph—C(=O)•↑   •CH(Ph)Ph↑   radical pair iside solvent cage cavity

↓ diffusion out of 'solvent cage'

free radicals   Ph—C(=O)•   •CH(Ph)Ph

- CO ↓ fast

Ph—CH2•

2 x ↓

Ph⌒⌒Ph

Ph⌒CH(Ph)Ph

2 x ↓

Ph2CH—CHPh2
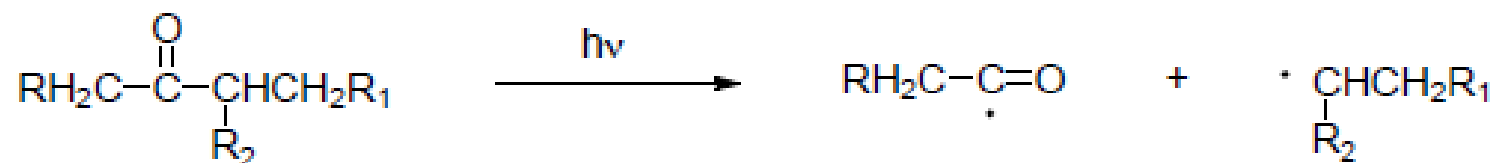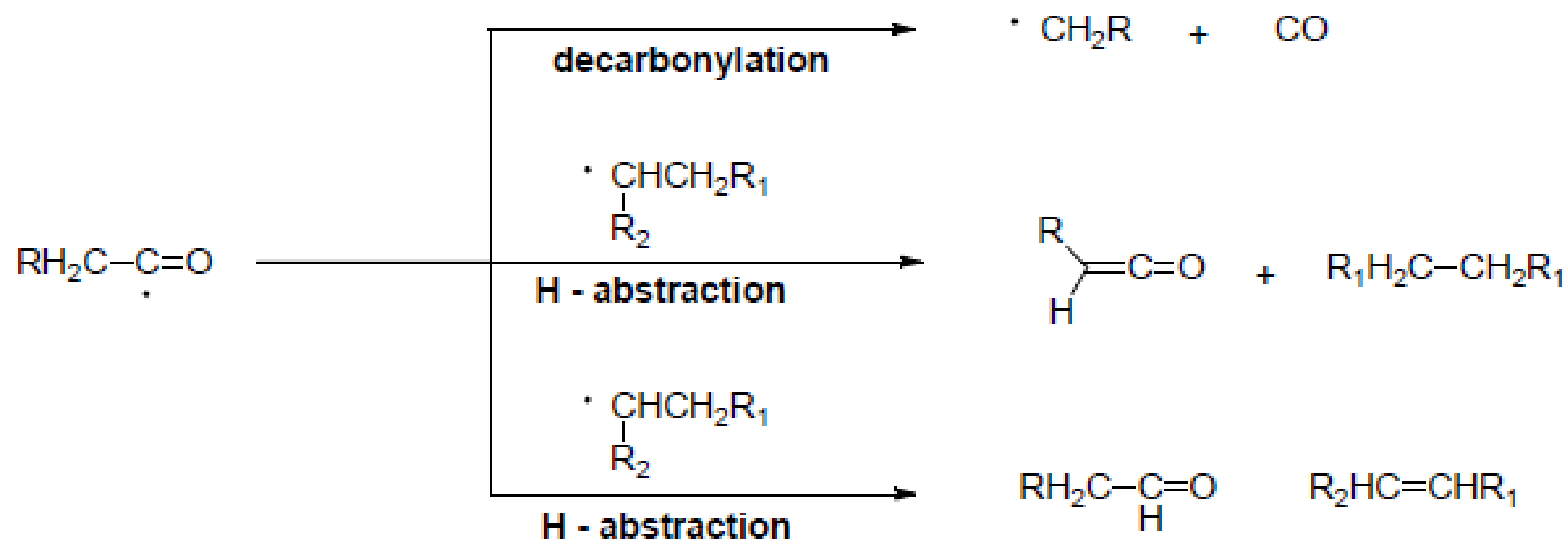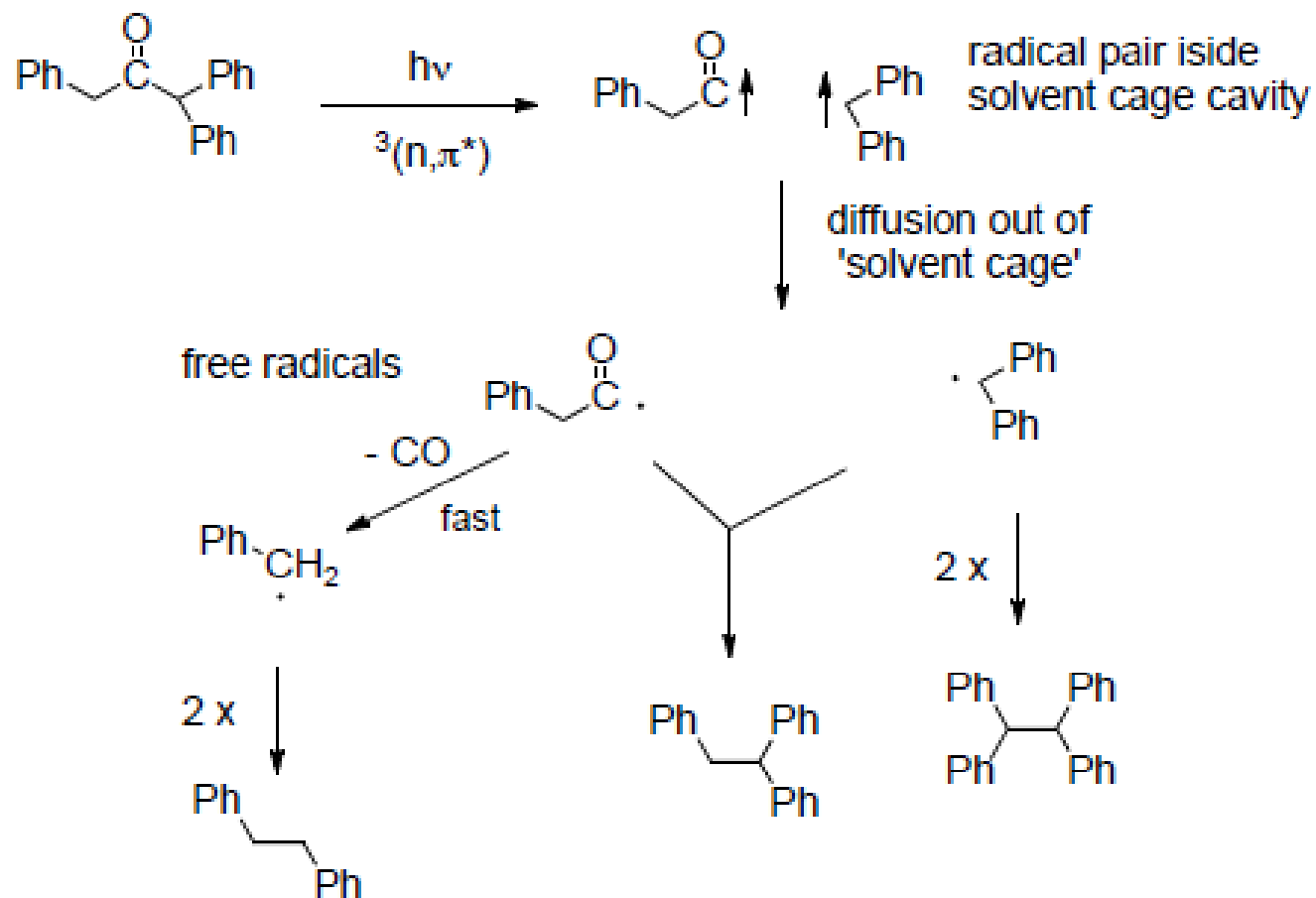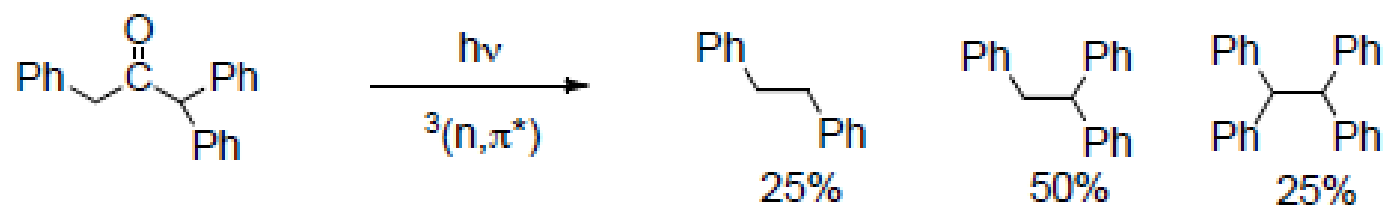
Norrish Type I photochemistry in cyclobutanones

hv
in MeOH

H₃CO, O

H

68%   +   11%   +   13%

13%
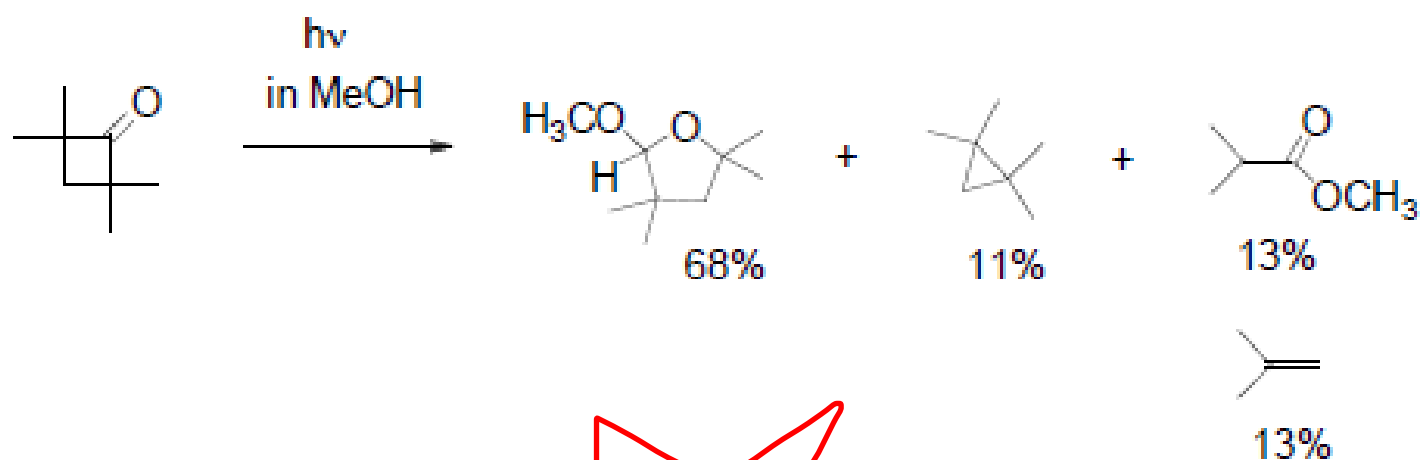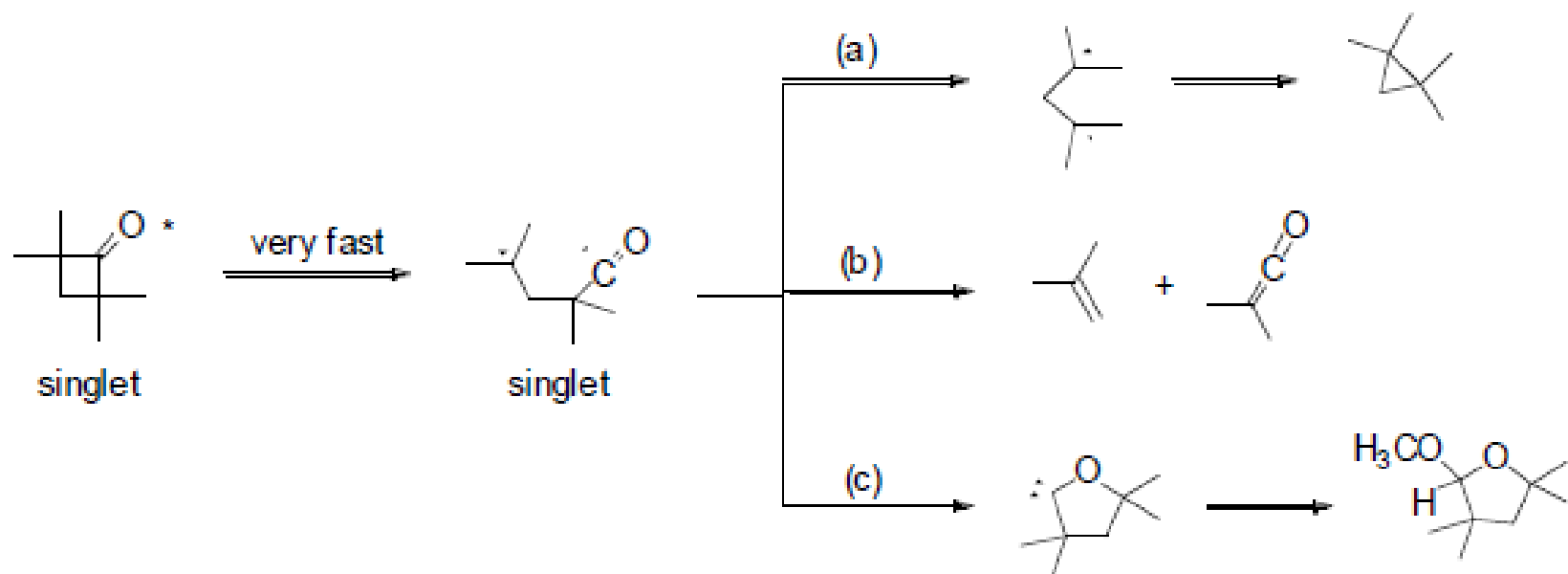
(a)   Decarbonylation
(b)   β-cleavage   (common fragmentation of 1,4-biradicals)
(c)   oxacarbene formation

1. α-cleavage (primary process) from S_1 ($^1(n,\pi^*)$); faster than ISC due to relieve of ring strain and stability of diradical

Paternò-Büchi Reaction

Hetero [2+2]-cycloaddition between a carbonyl group and an alkene

hν → oxetane

from S_1 $^1(n, \pi^*)$ or T_1 $^3(n, \pi^*)$

excited
state

$Ph \quad Ph$ + $Me \quad Me$ → hν

90% + 10%
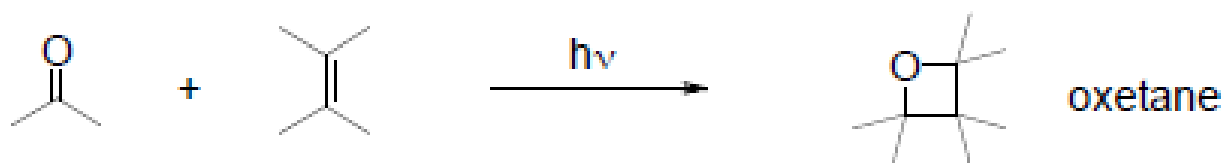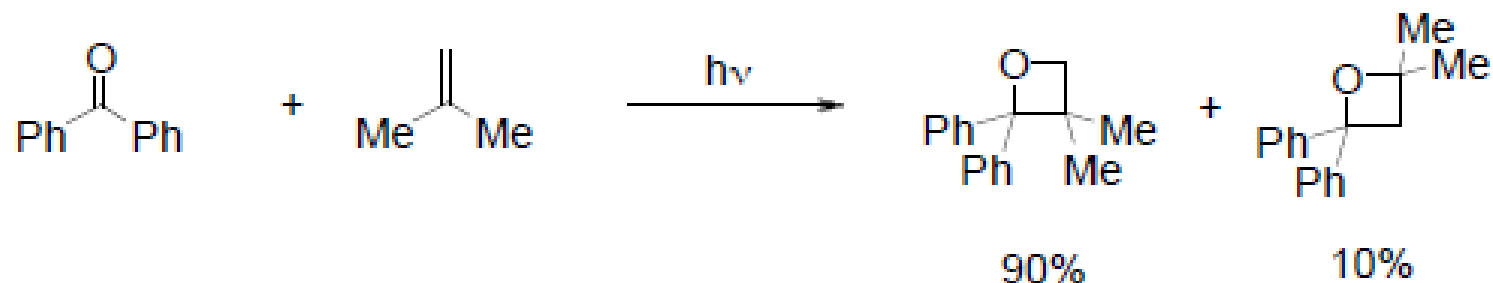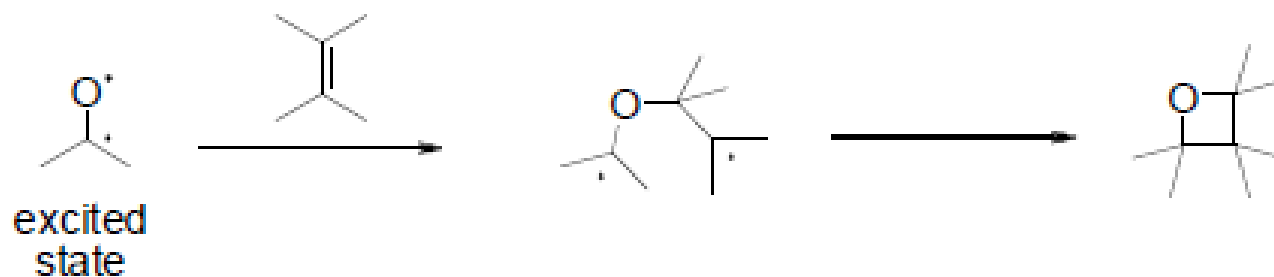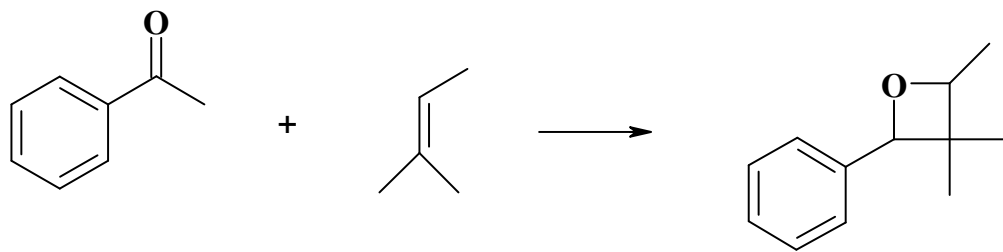
Paterno and Chieffi (1909), Buchi in 1954 mechanistic analysis
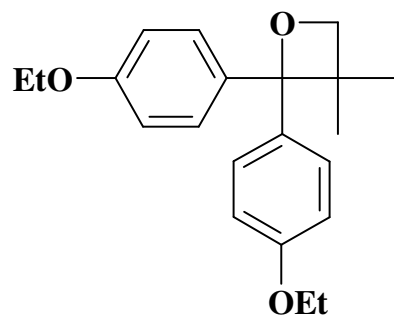
Insecticidal activity
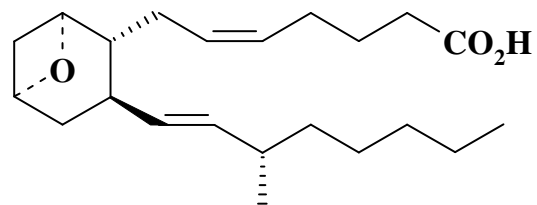
Thromboxane A$_2$
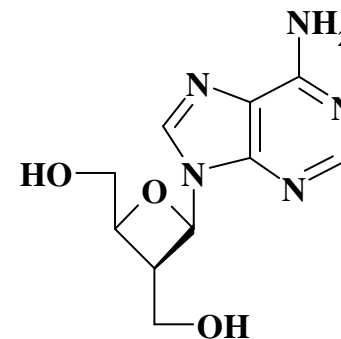
Oxetanocine
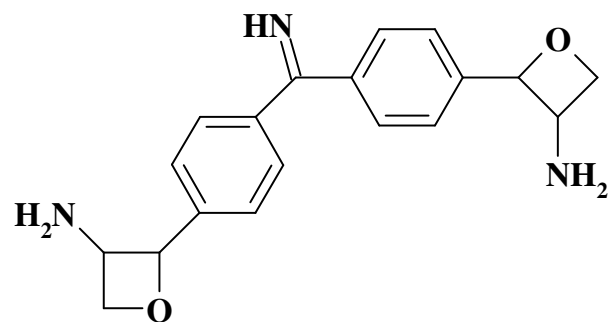
Bradyoxetin
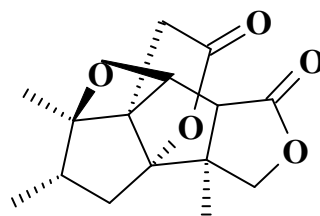
Merrilactone A
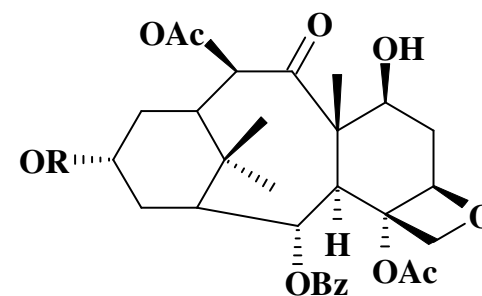
Palitaxel

Reaction mechanism

$[PhCHO]\ S_1$ $\xrightarrow{\ ISC\ }$ $[PhCHO]\ T_1$

$(n-\pi^*)$

$K_{isc\ aromatic} \gg K_{isc\ aliphatic}$ $(\gg 10^{10}/s)$

responsible

electrophile   +   nucleophile   →   **Biradical intermediate**   +

Major   Minor
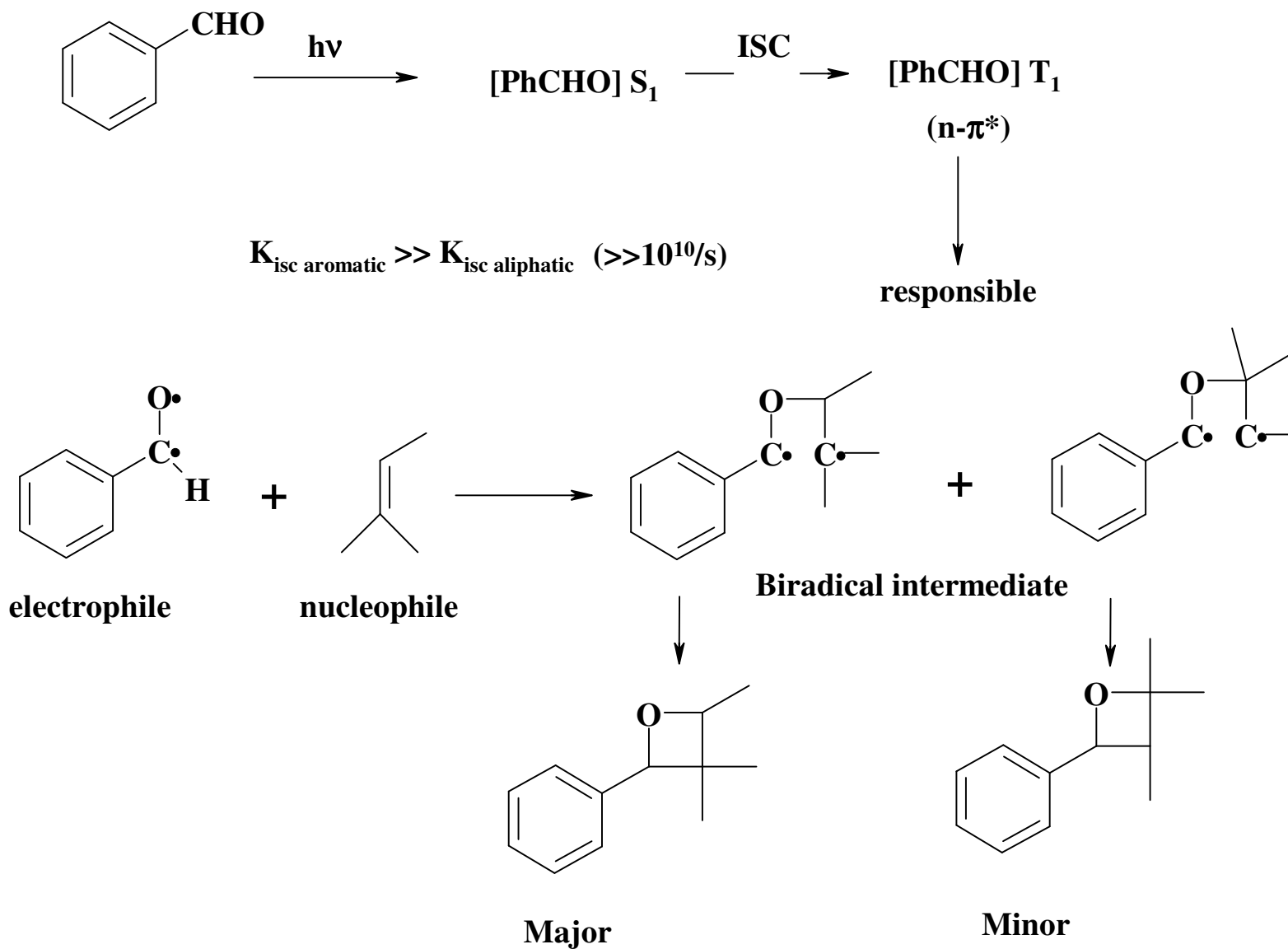
Intermediacy of biradical

1   1.6

lifetime = 1.6 ns
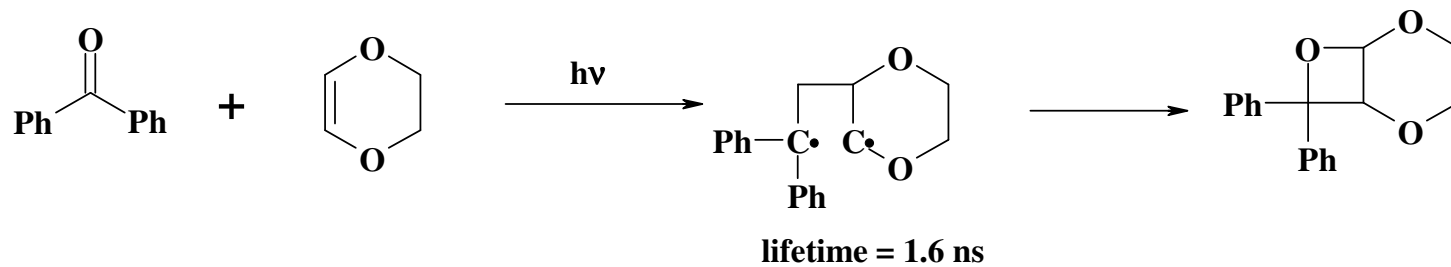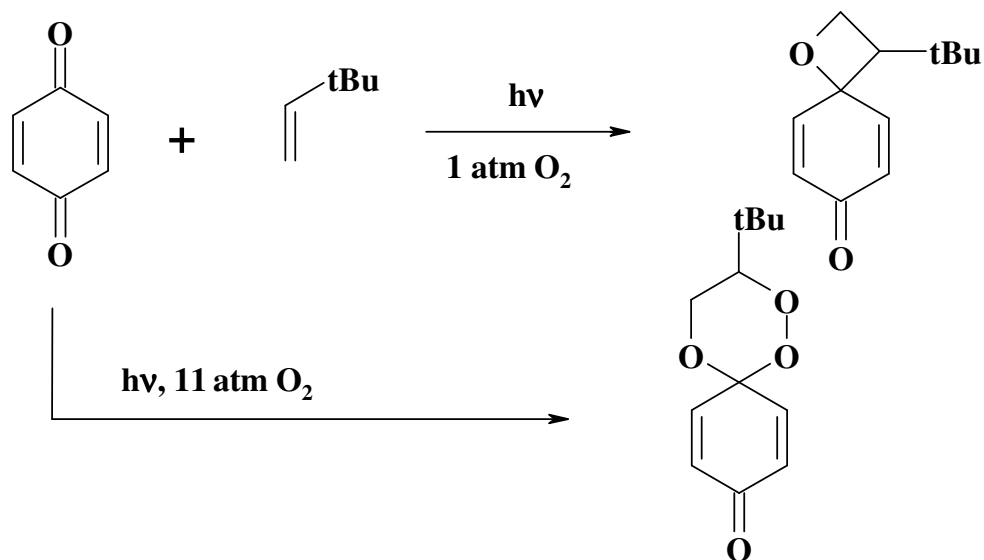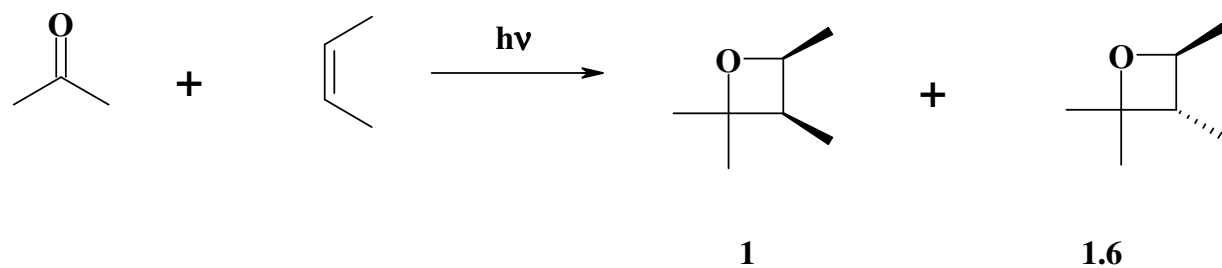
Paternò-Büchi Reaction
Limitations

Triplet energy transfer to alkene observed preferentially, if the E_T of alkene is lower than E_T of carbonyl group. In the example below, some of the singlet excited state gives the oxetane product. Some inter system crosses to the triplet excited state and transfers its triplet energy to cis-dicyanoethylene. The latter isomerizes.
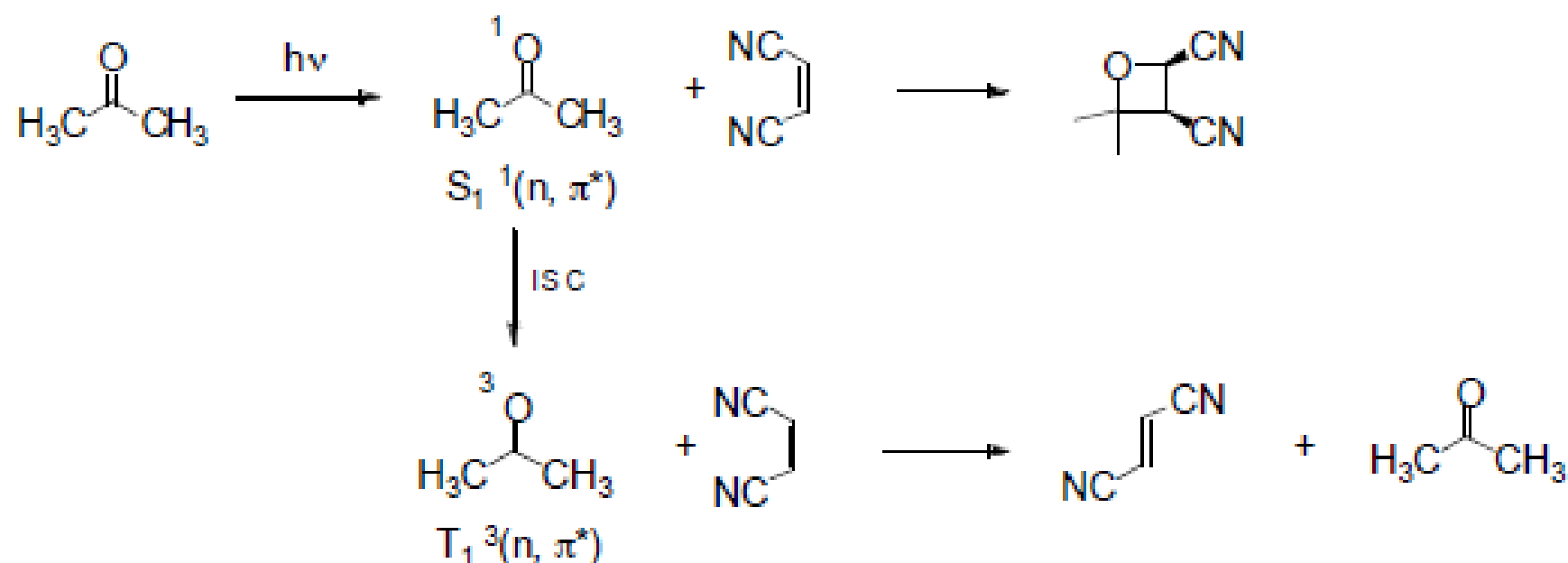
Norrish Type –II reaction

Another photolysis reaction of ketones is γ to elimination known as the Norrish type II cleavage.

- Takes place with ketone bearing γ- hydrogen.
- Abstraction of a γ- hydrogen in a primary photochemical step.
- Formation of a six-membered cyclic transition state.
- Secondary reaction of diradical results in cleavage of an alkene and a new ketone.

Norrish Type II Photochemistry

Intramolecular H-abstractions of photochemically excited carbonyl compounds
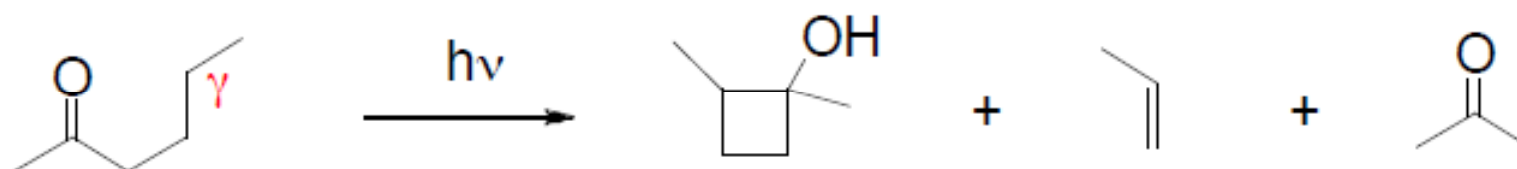
1) Norrish Type I photochemistry slow, e.g. if α-cleavage leads to relatively unstable radical (Ph, CH_3, prim. R·)
2) γ-H available in carbonyl compound.

Norrish Type II Photochemistry
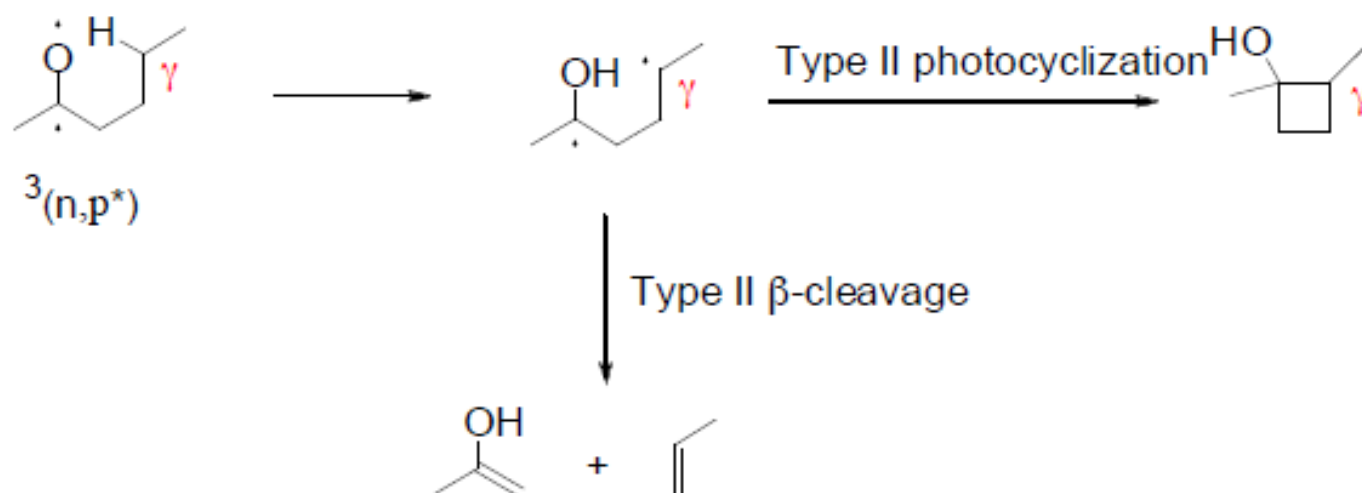
1) H-abstraction rate increases with increasing radical stability:

$$H\text{-}CH_2R \; < \; H\text{-}CHR_2 \; < H\text{-}CR_3$$

2) Reaction exclusively from (n, π^*) excited states.

3) Ratio of photocyclization/β-cleavage depends of the spin-state
$S_1 (n, \pi^*)$ => more cleavage
$T_1(n, \pi^*)$ => more cyclization

Norrish Type II Photochemistry

3) H-abstraction requires coplanarity of the p-orbital at O and the β-bond
   (planar transition state)

β-bond

hν
S_1 (n,π*)

$$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_3 \xrightarrow{h\nu} \quad CH_3\overset{\cdot O}{\overset{}{C}}\cdots\overset{H}{\overset{}{CH-CH_3}} \longrightarrow$$

(cyclic structure with CH_2, CH_2)

$$CH_3\overset{OH}{\overset{}{C}}-CH_2-CH_2-\overset{\cdot}{C}HCH_3 \longrightarrow CH_3\overset{OH}{\overset{}{C}}=CH_2 + CH_2=CHCH_3$$

$$\downarrow$$

$$CH_3\overset{O}{\overset{\|}{C}}CH_3$$

Esters possessing a γ-hydrogen atom in their carboxylic acid portion or a β-hydrogen atom in their alcohol portion undergo Norrish type II cleavage also.

$$RO\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3 \xrightarrow{h\nu} RO\overset{O}{\overset{\|}{C}}CH_3 + CH_2=CH_2$$

$$R\overset{O}{\overset{\|}{C}}OCH_2CH_3 \xrightarrow{h\nu} R\overset{O}{\overset{\|}{C}}OH + CH_2=CH_2$$

PROBLEM 27-7

Gas phase irradiation of 2-pentanone produces acetone and ethylene in about 90% yield along with 10% of 1-methylcyclobutanol. Account for the formation of those three photochemical products.

PROBLEM 27-8

Suggest a mechanism for the photochemical cleavage of:

a Methyl butyrate

b Ethyl acetate

$$[\overset{..}{\overset{-}{C}}H_2-\overset{+}{N}\equiv N: \longleftrightarrow CH_2=\overset{+}{N}=\overset{..}{\overset{-}{N}}:] \xrightarrow{h\nu} :CH_2 + N_2$$

Diazomethane   Methylene

$$CH_2N_2 + \quad \underset{CH_3}{\overset{H}{}}C=C\underset{CH_3}{\overset{H}{}} \xrightarrow[-N_2]{h\nu}$$

$$:CH_2^{*1} + \quad \underset{CH_3}{\overset{H}{}}C=C\underset{CH_3}{\overset{H}{}} \longrightarrow \quad H-\underset{CH_2}{\overset{CH_3 \quad CH_3}{C-C}}-H \longrightarrow \textit{cis}\text{-1,2-Dimethylcyclopropane}$$

$$\downarrow\uparrow :CH_2^{*1} \xrightarrow[\text{deactivation}]{\text{Collisional}} \uparrow \cdot \overset{\uparrow}{C}H_2^{*3}$$

Spin inversion

Ring closure

Benzyne

$+ 2CO_2$

$+ CO_2$

1,3-Cyclobutadiene

C. Cycloaddition

Photochemical cycloaddition of alkenes to form four-membered rings has been used in many synthesis sequences. For example, a key step in one of the syntheses of grandisol, a sex-attractant pheromone (Sec. 23-5) emitted by male boll weevils, was the acetophenone-sensitized formation of the requisite cyclobutane.

Grandisol
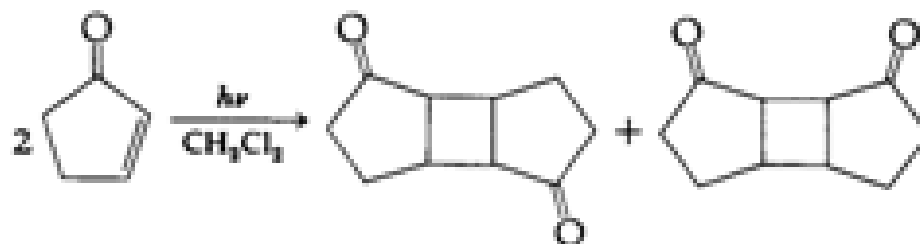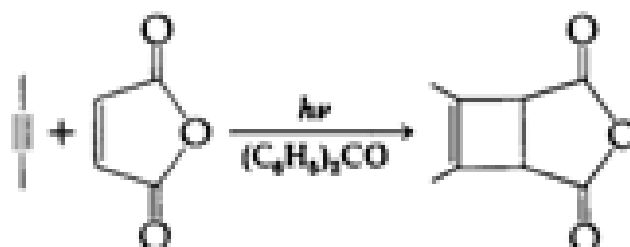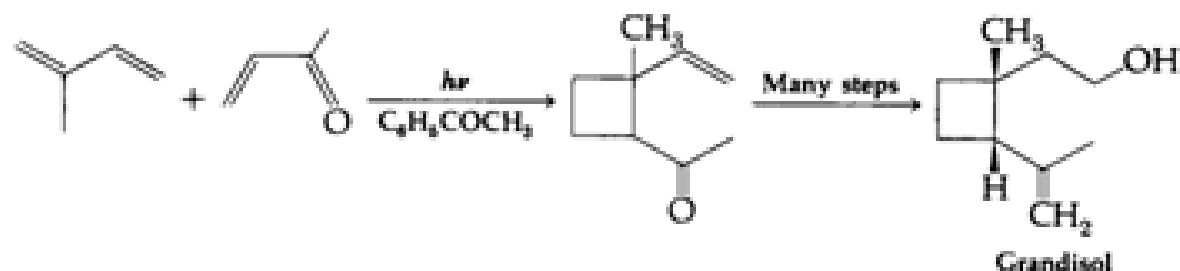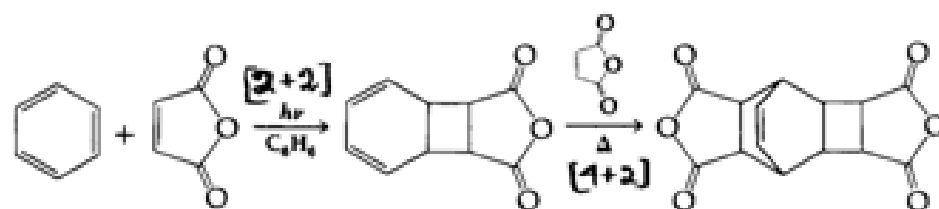
D. Isomerization and Rearrangement

Geometrical isomerization is a typical photoreaction of many olefinic compounds. The reaction is promoted by direct irradiation of the substrate as well as by photosensitized energy transfer. In some simple alkenes the E isomer absorbs energy more effectively (it has a larger molar absorptivity ϵ; Appendix) and at a slightly different wavelength than does the Z isomer. It is therefore sometimes possible to at least partially convert an E isomer to its thermodynamically less stable Z form—a technique known as optical pumping.

E-Butenedioic acid
(Fumaric acid)

Z-Butenedioic acid
(Maleic acid)

E-Azobenzene

Z-Azobenzene
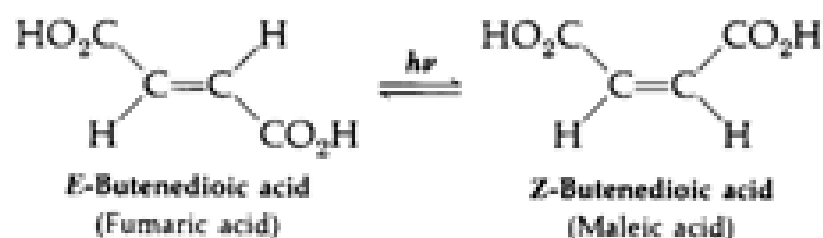
Geometrical Isomerism
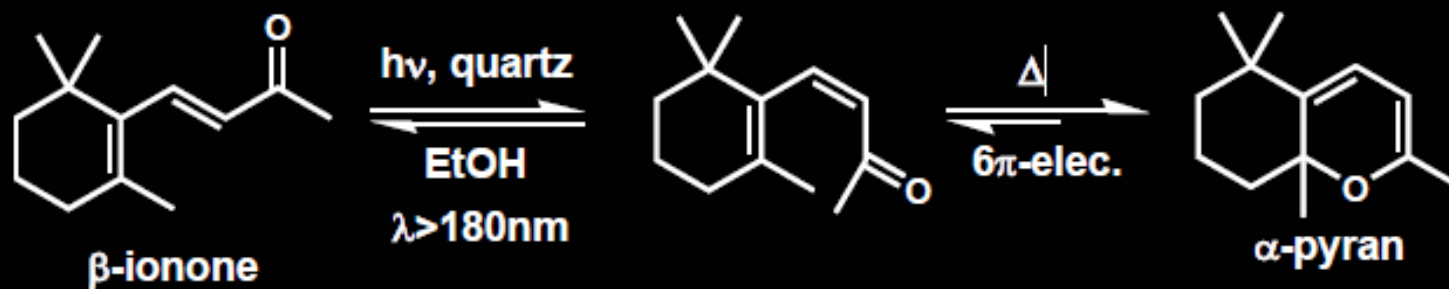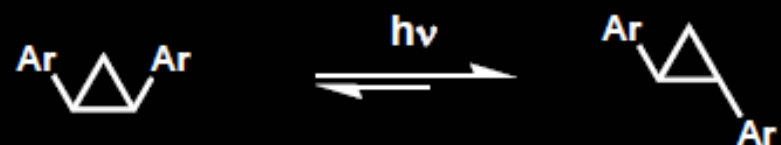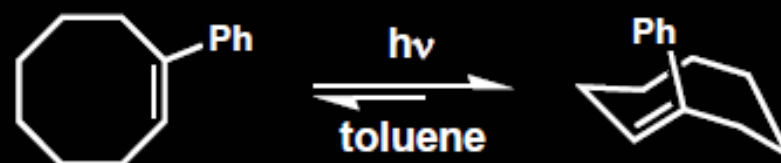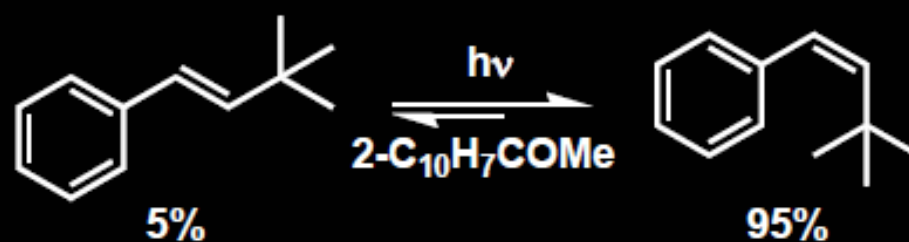
Geometrical Isomerism
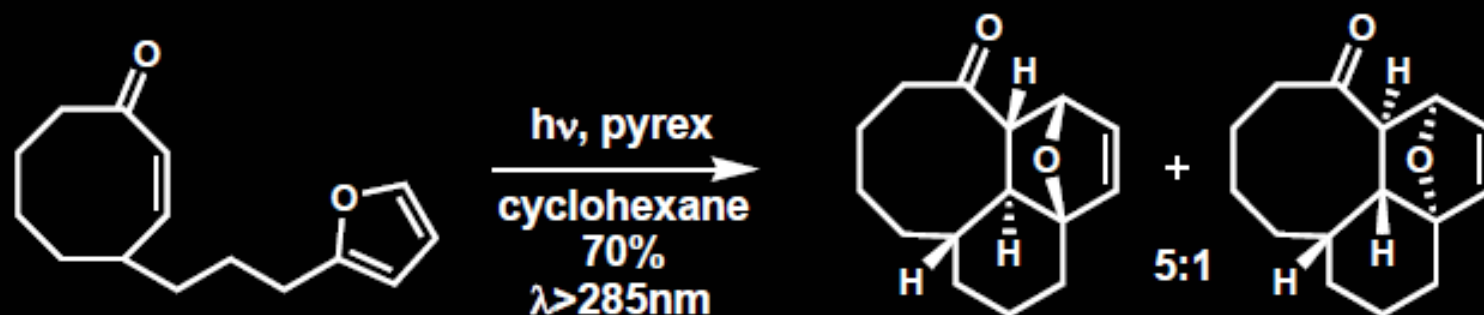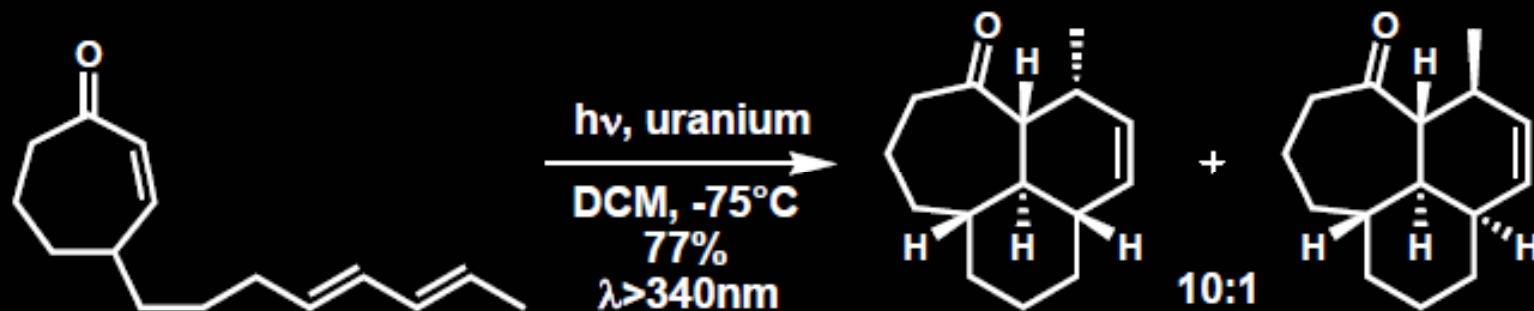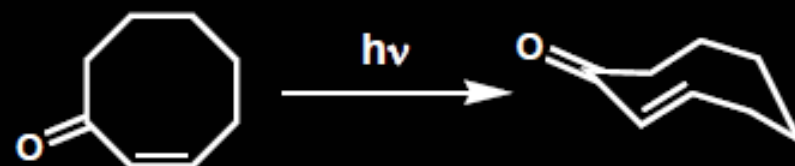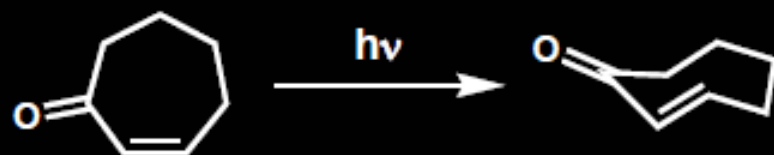
Photochemical Reactions

Photoisomerization

Ground State

Excited State
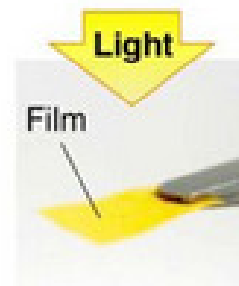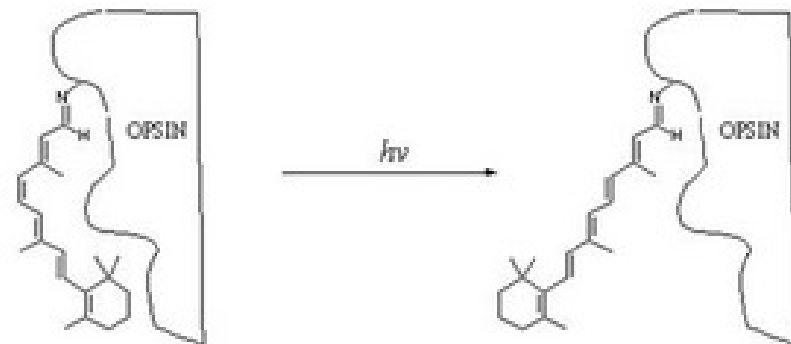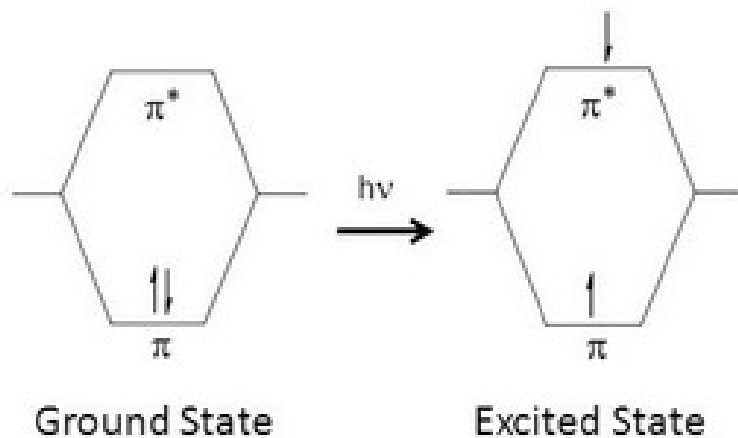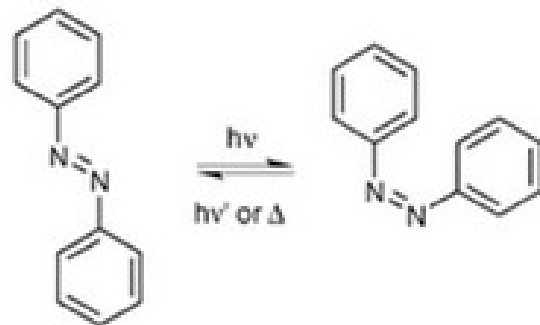
Light
Film

UV light
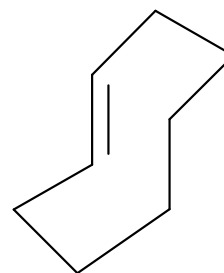10 sec

Visible light
8 sec

Light

trans form

UV light

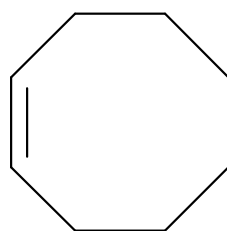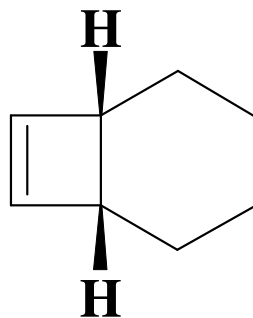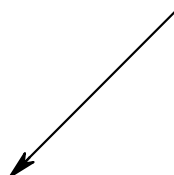Visible light

cis form
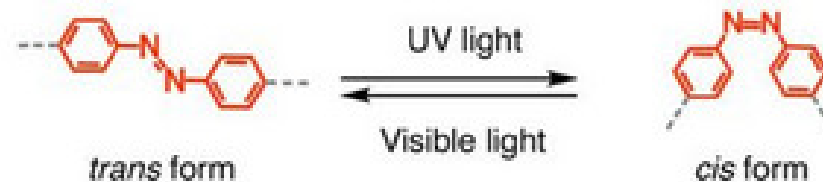
Cis-Trans isomerization of alkenes

Chemistry of vision

11-cis retinal → (Cys-NH$_2$, Opsin) → **Rhodopsin** → (hν) →

Bathorhodopsin (contains all trans retinal) → (−H$^+$) → **Metarhodopsin II**

(H$_3$O$^+$, Opsin) → **all trans retinal** → (retinal isomerase) → **11-cis retinal**