PHOTOCHEMISTRY

لطلاب الفرقة الثالثة كيمياء خاص- كلية العلوم
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Photochemistry: Definition and Examples

- A branch of chemistry deals with the chemical processes that are caused by the absorption of light.

- The study of the chemical and physical behaviours that may occur under the influence of light.

Examples:
- ❑ Photosynthesis
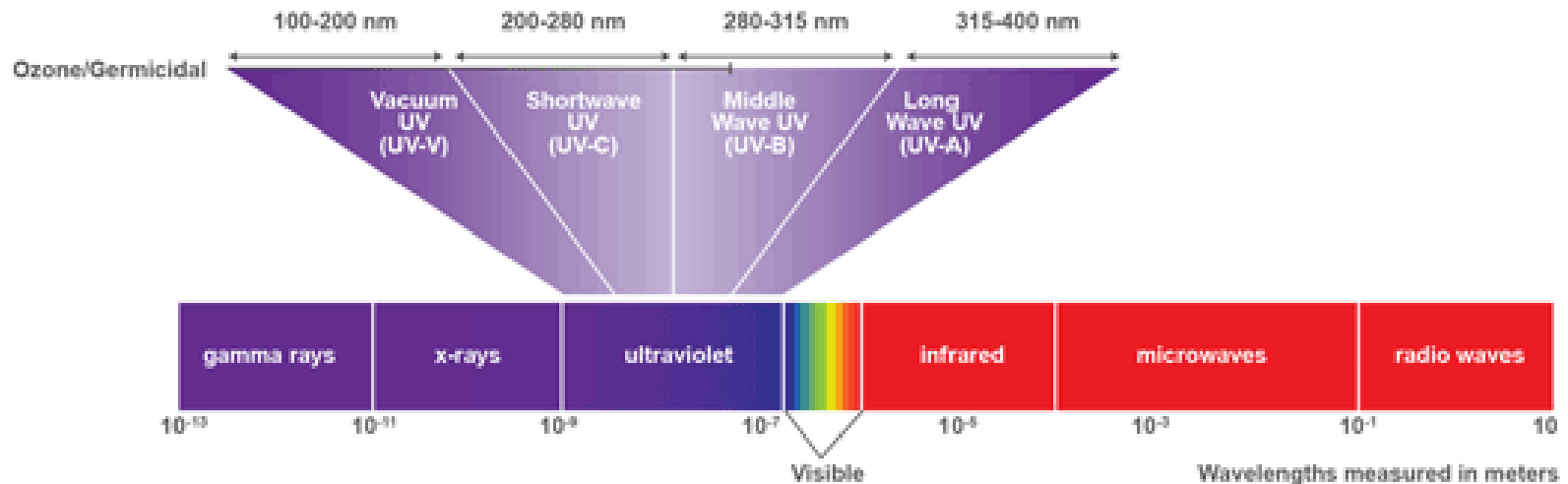- ❑ Ozone formation
- ❑ Solar cells

Fundamental Laws of Photochemistry

- **First Law (Grotthus-Draper Law)**: light must be absorbed by a compound in order for a photochemical process to take place and the progress of photochemical reaction is proportional to the quantity of light absorbed.

- **Second Law (Stark-Einstein Law)**: for each photon of light absorbed by a chemical system, only one molecule is activated for subsequent reaction.

Number of molecules activated = Number of photons absorbed

Energy of the Photon

$$E = h\nu = \frac{hc}{\lambda}$$

| 100-200 nm | 200-280 nm | 280-315 nm | 315-400 nm |

Ozone/Germicidal

Vacuum UV (UV-V) Shortwave UV (UV-C) Middle Wave UV (UV-B) Long Wave UV (UV-A)

gamma rays   x-rays   ultraviolet   infrared   microwaves   radio waves

10^{-13} 10^{-11} 10^{-9} 10^{-7} 10^{-5} 10^{-3} 10^{-1} 10

Visible

Wavelengths measured in meters

Photon Energy Vs Bond Energy

<u>Energies</u>

100 kcal/mol = 4.3 eV = 286 nm (near UV)

286 kcal/mol = 12.4 eV = 100 nm (far UV)

Typical Bond Energies

   C-H = 110 kcal/mol

   C-C = 80

   C=C = 150

   C=O = 170

UV light 100 - 400 nm wavelength, so this is sufficient energy to break bonds –knock electrons out of bonding orbitals (electronic excitation).

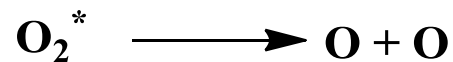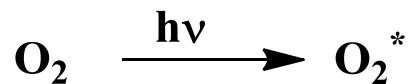# Photochemical Processes

Primary photochemical process

$$M \xrightarrow{h\nu} M^*$$

- $M + light$ (Luminescence)
- $\xrightarrow{+\,C}$ $M + C^*$ (Energy transfer)
- $M^+ + e$ (Photoionisation)
- $A^{\bullet} + B^{\bullet}$ (Photodissociation)
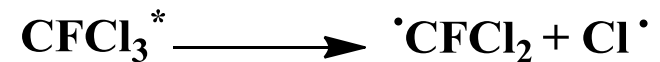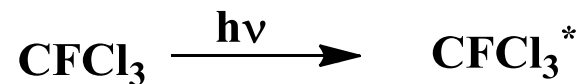- N (Photoisomerisation-Rearrangment)
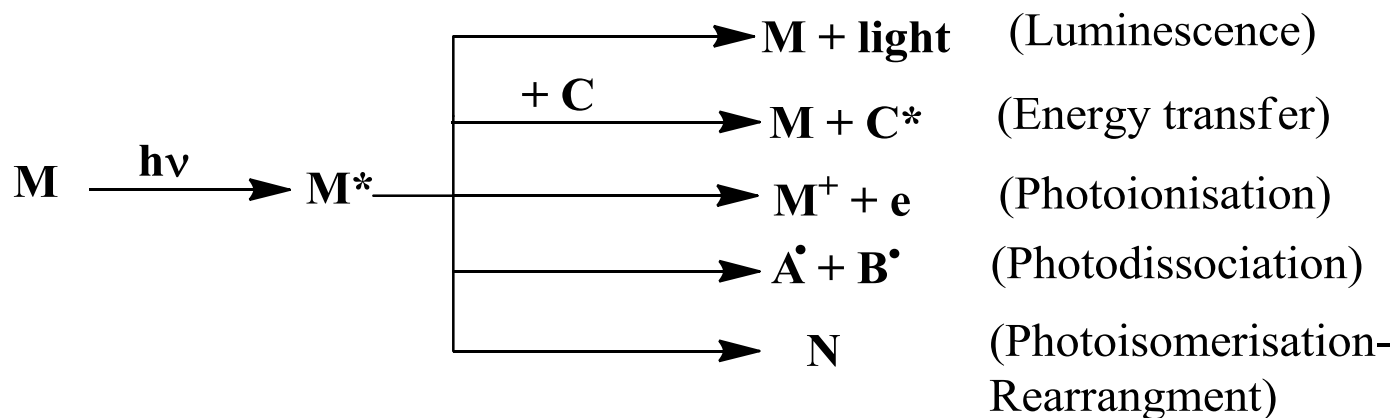
Secondary photochemical process

Secondary process occurs after primary process – it is based on the general knowledge of the chemical reaction.

Examples:

Ozone Formation

$$O_2 \xrightarrow{h\nu} O_2^*$$

$$O_2^* \longrightarrow O + O$$

$$O + O_2 \longrightarrow O_3$$

Ozone Depletion

$$CFCl_3 \xrightarrow{h\nu} CFCl_3^*$$

$$CFCl_3^* \longrightarrow {}^{\bullet}CFCl_2 + Cl^{\bullet}$$

$$Cl^{\bullet} + O_3 \longrightarrow ClO + O_2$$

$$ClO + O_3 \longrightarrow Cl^{\bullet} + 2O_2$$
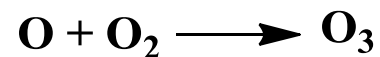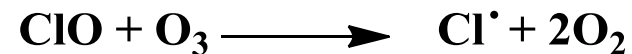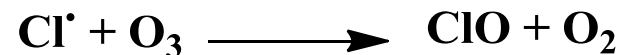
Advantages and Disadvantages

Advantages:

- Overcome large kinetic barriers in a short amount of time
- Produce immense molecular complexity in a single step
- Form thermodynamically disfavored products
- Allows reactivity that would otherwise be inaccessible by almost any other synthetic method
- The reagent (light) is cheap, easily accessible, and renewable

Disadvantages:

- Reactivity is often unpredictable
- Selectivity and conversion are sometimes low

- Organic photochemistry means the interaction of light with organic material.

$$R \xrightarrow{h\nu} P$$

Ground state reactant → Ground state product

How is (R) transformed to (P)?

$$R \xrightarrow{h\nu} R^* \longrightarrow I \longrightarrow P$$

Ground state reactant → Excited stae reactant → Short lived intermediate → Ground state product
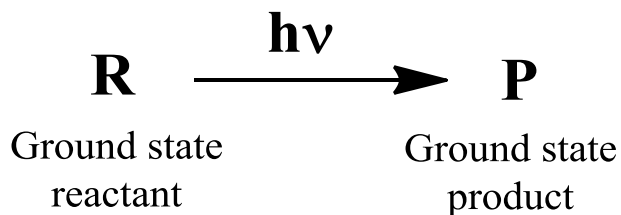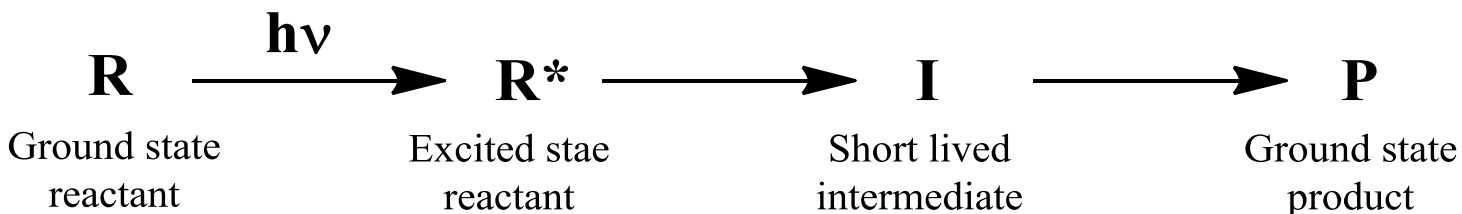
- We will take formaldehyde as a simple model.....what are the possible transitions which formaldehyde can do?

(π) bonding electrons

(n) non-bonding electrons

(σ) bonding electrons

Energy

σ^*

π^*

$h\nu$

n

π

σ
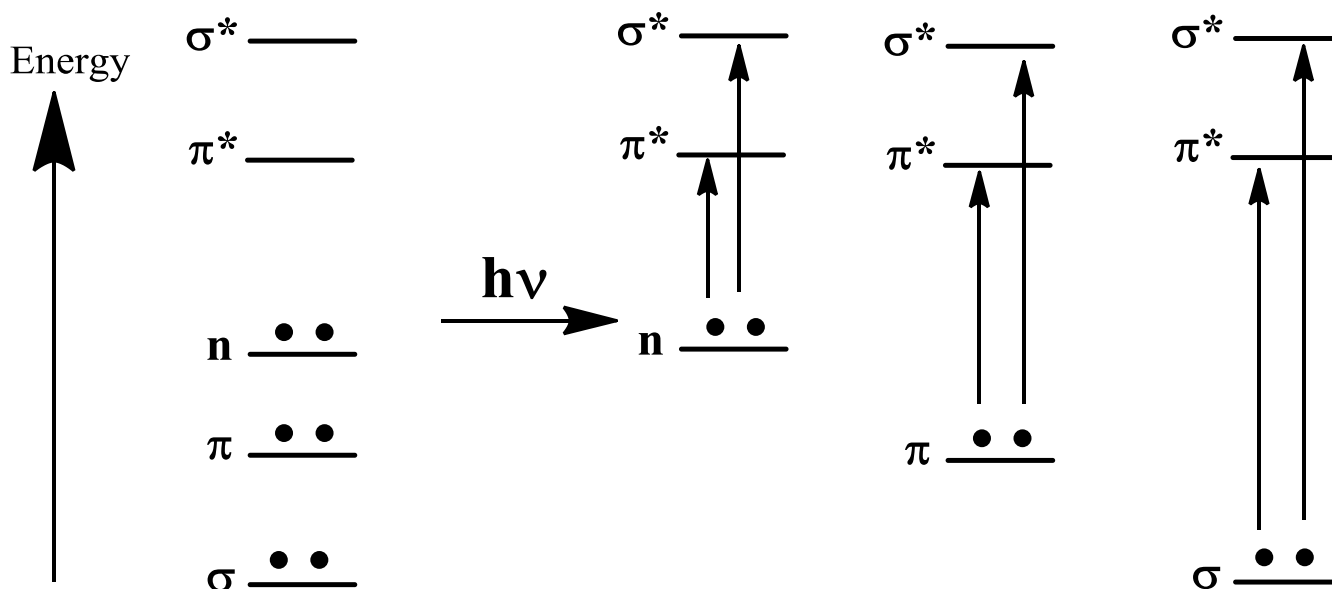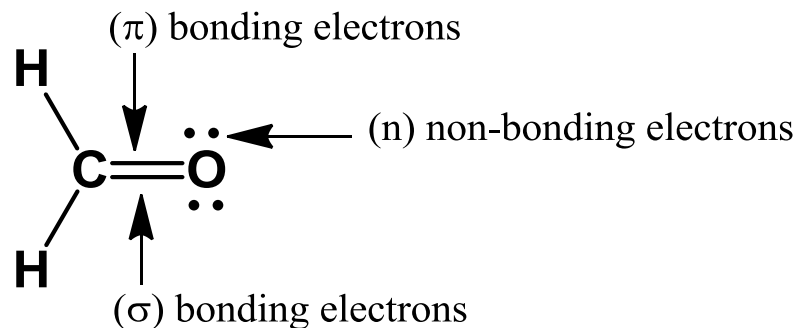
- The applied energy.....which transition is possible?

- The spin of the excited electron

Energy
σ*
π*

hν
Energy enough only
for n-π* excitation

n
π
σ

Clarify the spin

Or

Singlet transition state
(antiparallel spin)

Triplet transition state
(parallel spin)
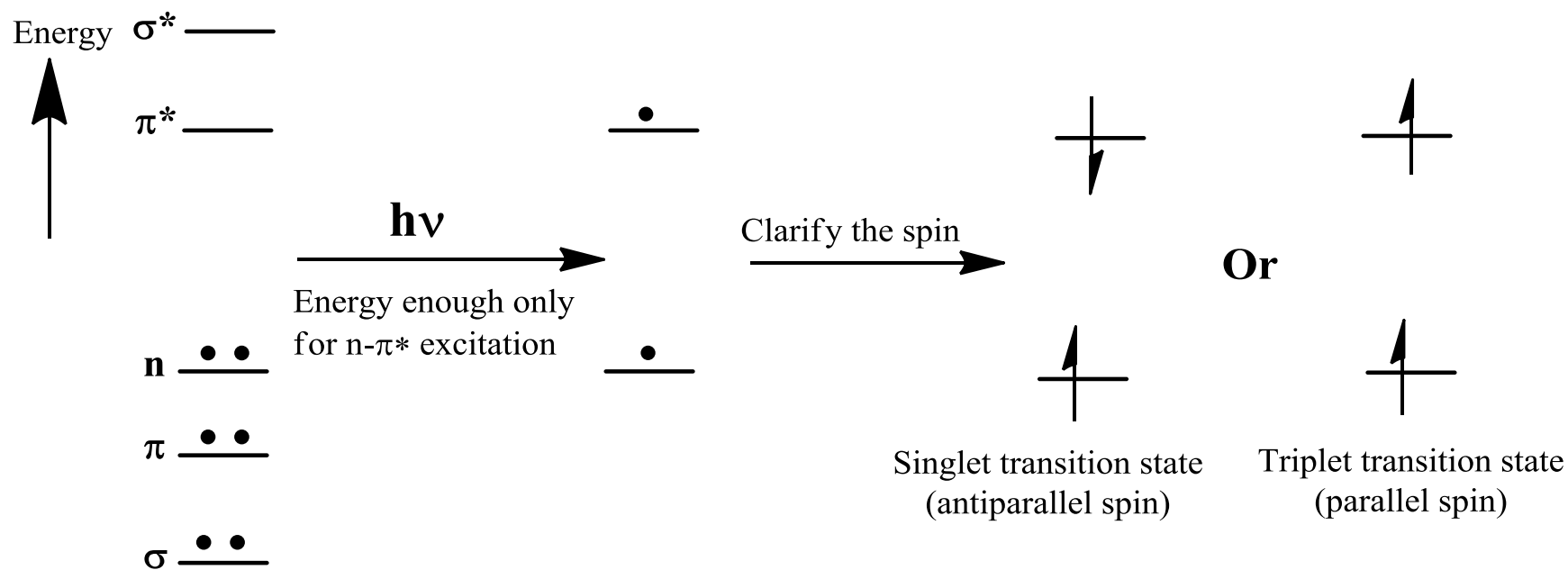
The state of the spin of electrons can be specified by its spin multiplicity (2S + 1, (S) is the total spin).

Hund's Rule

❑ For a given electron configuration, the term/state with maximum multiplicity has the lowest energy

❑ A greater total spin state usually makes the resulting atom more stable

Energy

π^* ——

hν →

S_1

T_1

n

S_0
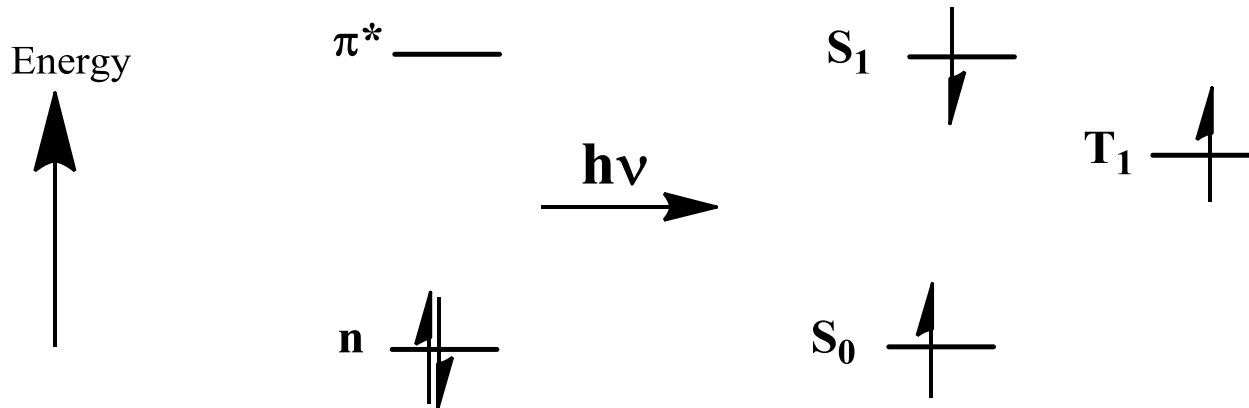
S_1 = Energy of the singlet excited state
T_1 = Energy of the triplet excited state

❑ It is a diagram illustrates the electronic states of a molecule and the transition between them.

What are the possible/fastest transitions in (e.g. n-π*) orbitals?

$S_1 \rightarrow S_0 + h\nu_1$ (**Fluorescence**) $10^{-8} - 10^{-6}$ sec

$S_1 \rightarrow S_0 + \Delta_1$ (**Internal Conversion**) $10^{-9} - 10^{-7}$ sec

$S_1 \rightarrow T_1 + \Delta_3$ (**Intersystem Crossing**) $10^{-11} - 10^{-8}$ sec

$T_1 \rightarrow S_0 + h\nu_2$ (**Phosphorescence**) $10^{-3} - 100$ sec

$T_1 \rightarrow S_0 + \Delta_2$ (**Intersystem Crossing**) $10^{-8} - 10^{-3}$ sec
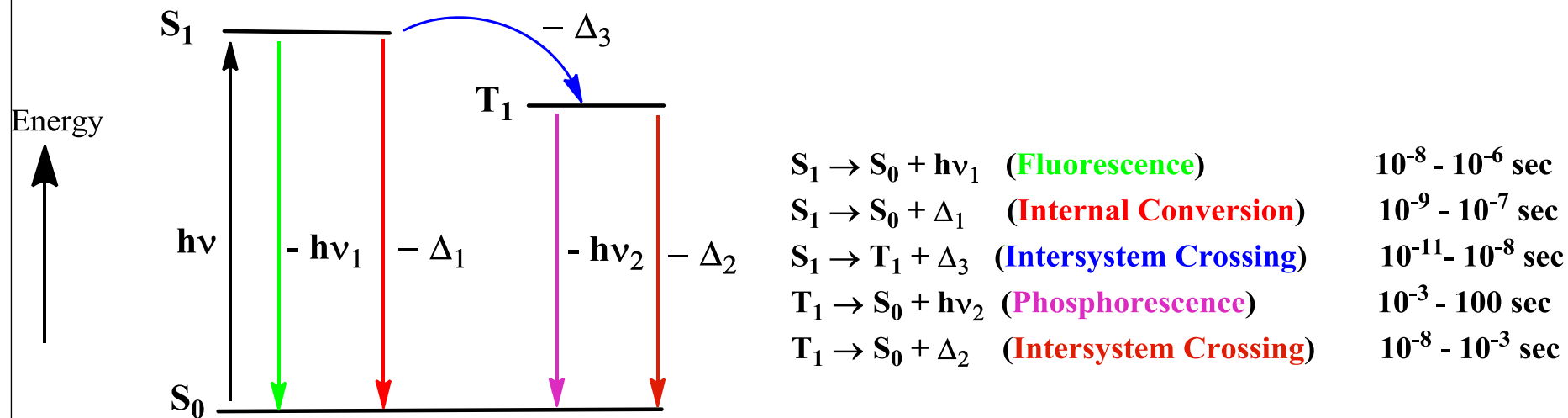
K_F vs K_P & K_{IC} vs K_F & K_{ISC} vs K_P & K_{ISC} vs K_{IC}

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*Diagram with two excited states (S_1 and T_1) and without vibrational levels is demonstrated for simplicity.

Fluorescence is the emission of <u>light</u> by a substance that has absorbed light or other <u>electromagnetic radiation</u>.

- Excitation: $S_0 + h\nu_{ex} \rightarrow S_1$
- Fluorescence (emission): $S_1 \rightarrow S_0 + h\nu_{em} + heat$

Phosphorescence is a type of <u>photoluminescence</u> related to <u>fluorescence</u>. Unlike fluorescence, a phosphorescent material does not immediately re-emit the radiation it absorbs.

Kasha's Rule

❑ The rule states that photon emission (fluorescence or phosphorescence) occurs only from the lowest excited state of a given multiplicity. ($h\nu \neq h\nu_1 \neq h\nu_2$)
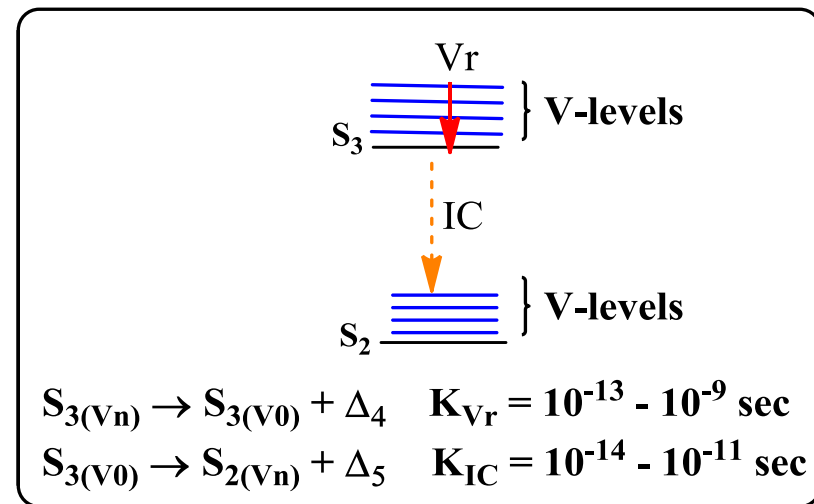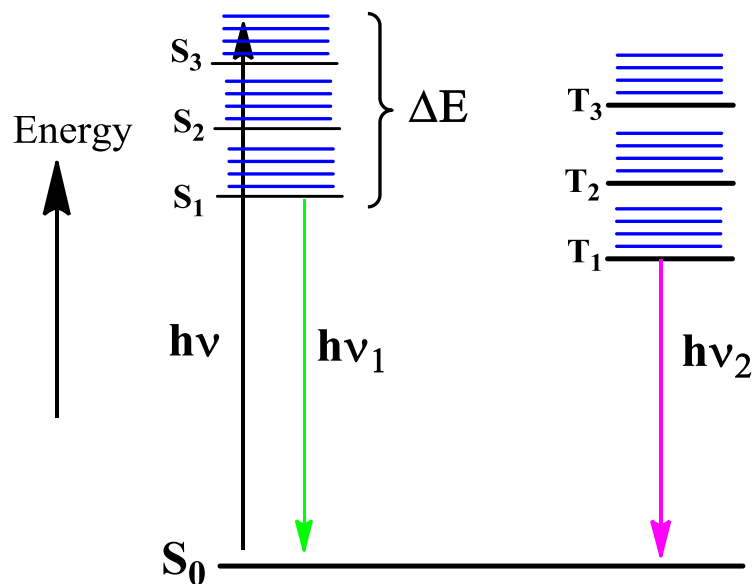
➤ In general the excited states energy difference is so small.
➤ Great overlapping will lead to quicker transitions
➤ $K_{Vr} + K_{IC} > K_F$

$$R \xrightarrow{h\nu} R^* \longrightarrow I \longrightarrow P$$

Ground state reactant   Excited stae reactant   Short lived intermediate   Ground state product
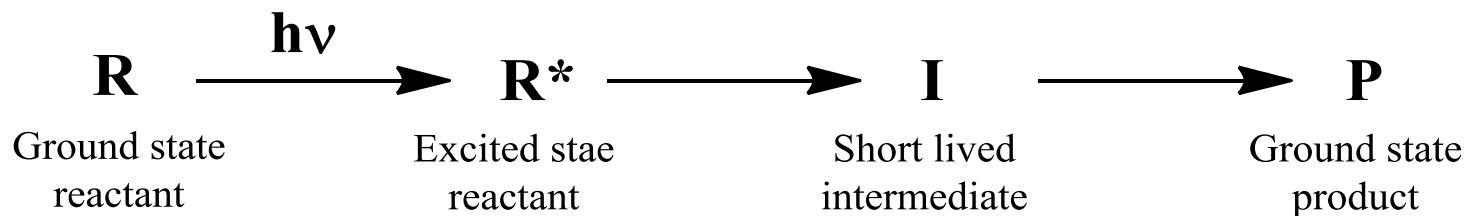
According to the previous discussion the R* can be existed in two states (singlet then triplet) through ISC process.

$$R \xrightarrow{h\nu} R_{(S)}^* \xrightarrow{ISC} R_{(T)}^* \longrightarrow I \longrightarrow P$$
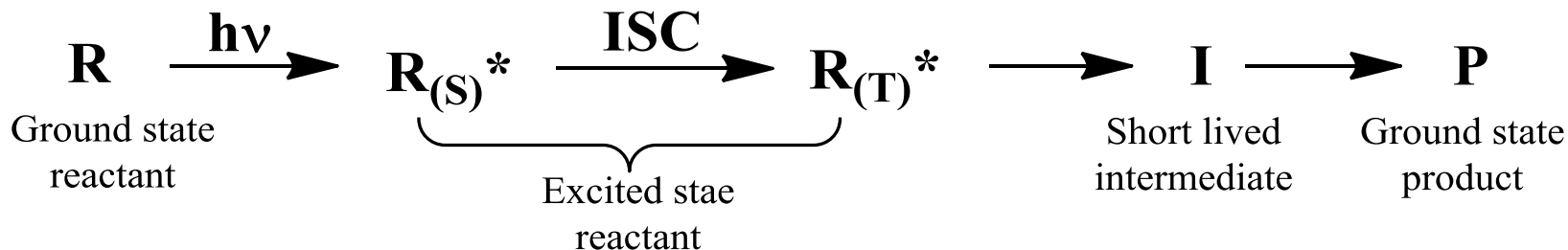
Ground state reactant   Excited stae reactant   Short lived intermediate   Ground state product

The ISC depends upon the energy gap between S_1 and T_1 excited states

Energy

S_1 ——

T_1 —— $\Big\} \Delta E_1$

S_0 ——

S_1 ——

T_1 —— $\Big\} \Delta E_2$

S_0 ——
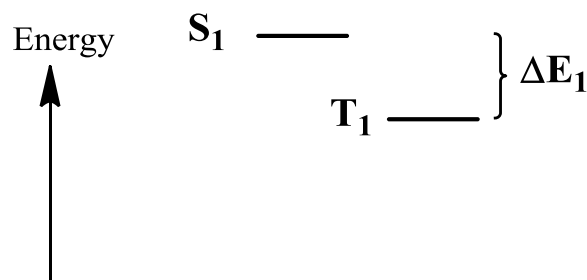
n-π* transition

Ketone: S_1 - $T_1 \approx 5$ kcal/mol
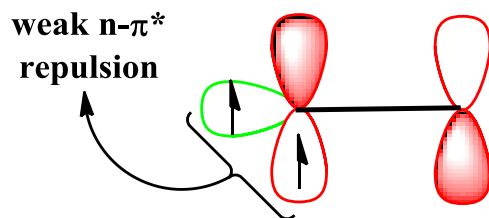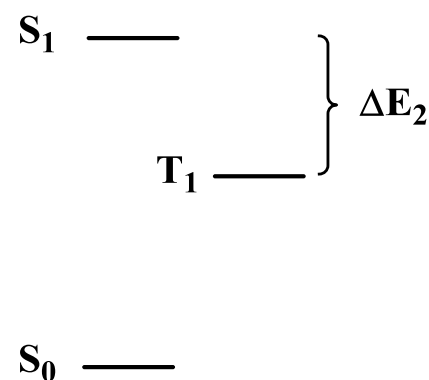
π- π* transition

Ar-hydrocarbon: S_1 - $T_1 = 30$ kcal/mol

weak n-π* repulsion

strong π-π* repulsion

the triplet state in n-π* transition
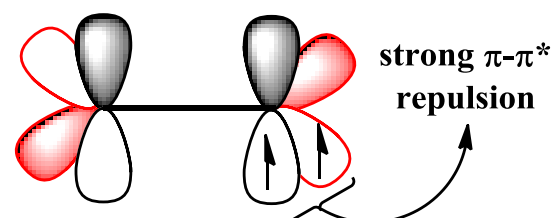
the triplet state in π-π* transition

The photochemistry can take place from triplet or singlet states or from both depending on the energy level for S_1 and T_1.

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➢The excited state reactant R* can undergo some sort of chemical reactions to give the intermediate (I).

➢The properties of the intermediate (I) help its transformation directly to the product (P).

➢The spin of the intermediate (I) is exactly the same as the excited state reactant (R*)...... **Be careful**

$$\textbf{R}_{\textbf{(S)}}\textbf{*} \longrightarrow \textbf{I}_{\textbf{(S)}}$$

$$\textbf{R}_{\textbf{(T)}}\textbf{*} \longrightarrow \textbf{I}_{\textbf{(T)}} \longrightarrow \textbf{I}_{\textbf{(S)}}$$
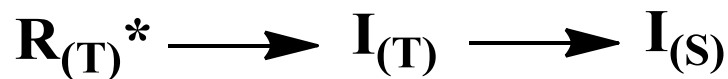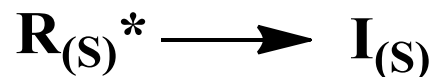
$R_{(T)}*$ species does not have time for the electron to flip around to give $I_{(S)}$ but instead affords the intermediate $I_{(T)}$ which changes its spin to give $I_{(S)}$

Once you get the intermediate (I), there are two possible things you should remember:

    i.   The conversion of (I) to (P) can be through a single step or multi-steps process

    ii.   The conversion of (I) to (P) produces, in general, different products

Summarizing the general equation of photochemistry.
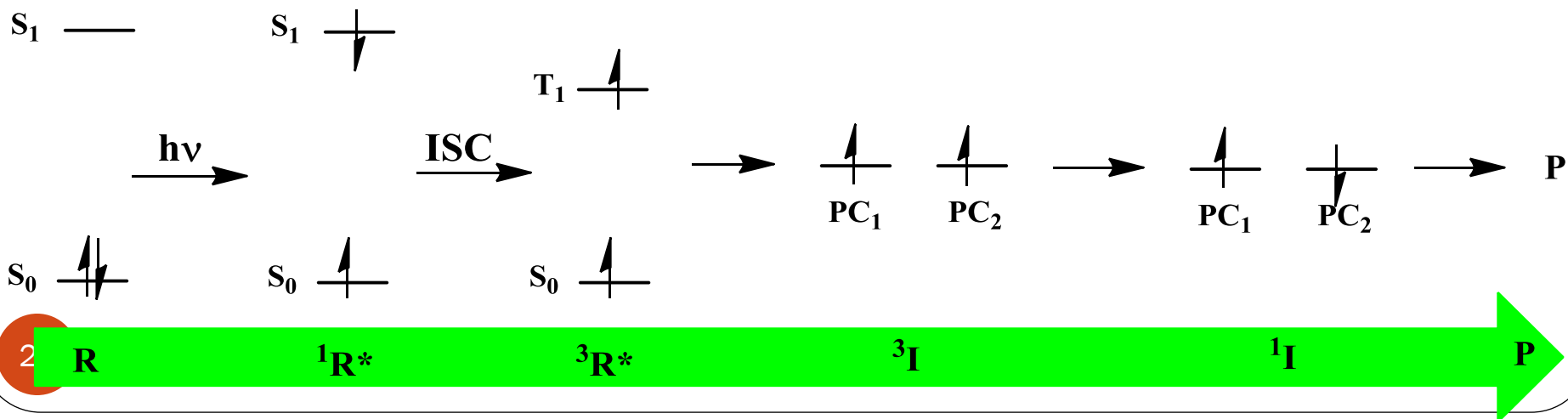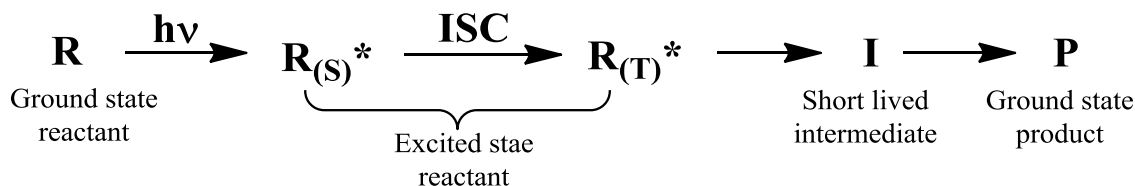
$$R \xrightarrow{h\nu} R_{(S)}^{*} \xrightarrow{ISC} R_{(T)}^{*} \longrightarrow I \longrightarrow P$$

Ground state reactant   Excited stae reactant   Short lived intermediate   Ground state product

S_1 S_1 T_1

$h\nu$ ISC PC_1 PC_2 PC_1 PC_2 P

S_0 S_0 S_0

R $^1R^*$ $^3R^*$ ^3I ^1I P

Plausible mechanism:

R
Ground state
reactant

R$_{(S)}$*

R$_{(T)}$*

I
Short lived
intermediate

P
Ground state
product

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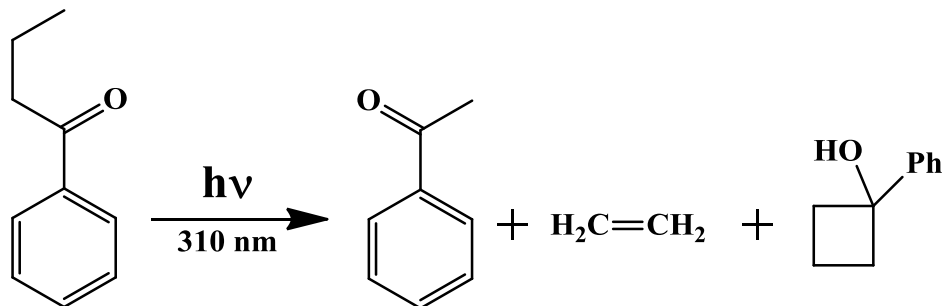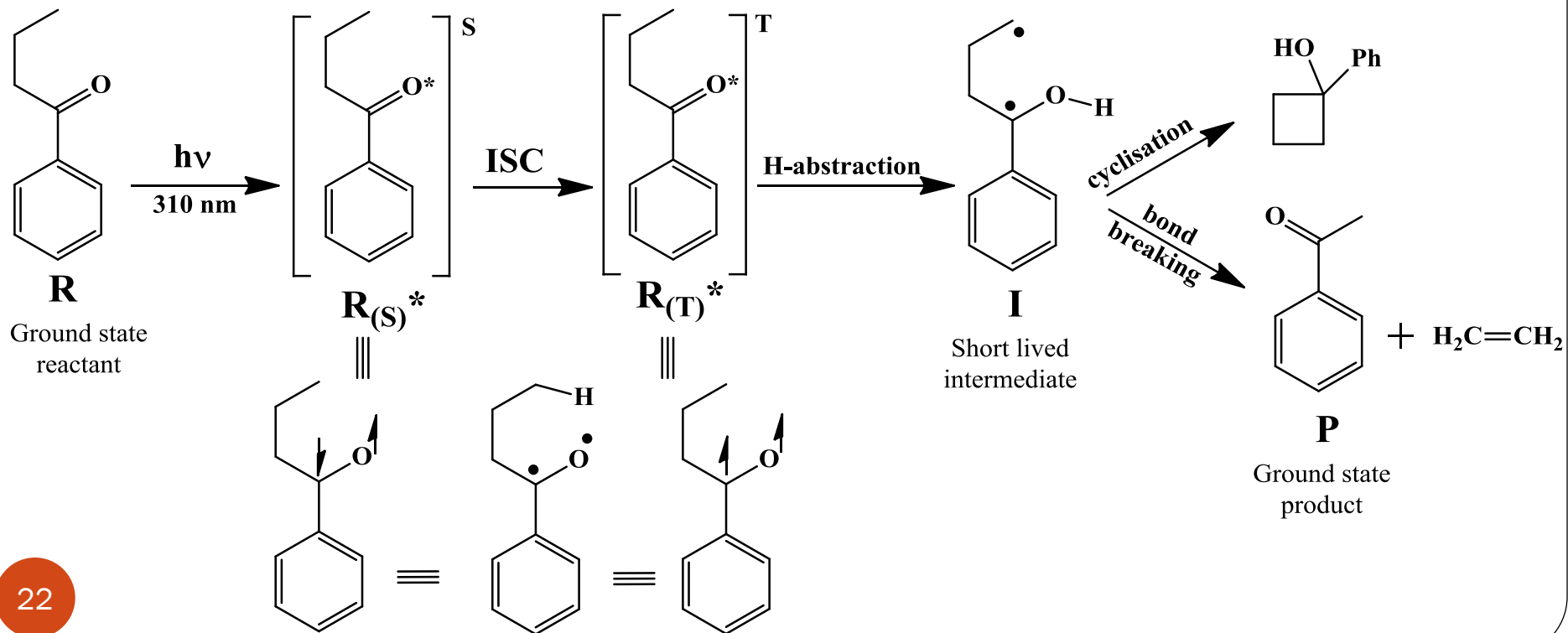
Quantum Yield

❑ measures the efficiency of a given photochemical process
❑ an important quantitative measurement of a photochemical process

Chemical Yield Vs Quantum Yield

➢ when we talk with respect to the reactant, it is a chemical yield but when we talk with respect to the photon, it is a quantum yield

$$\phi = \frac{\text{Number of product molecules formed}}{\text{Number of photons absorbed}}$$

▪ Quantum yield can be any number or a fraction of any number.
▪ Quantum yield equal to one is possible but rare
▪ Quantum yield greater than one means you have polymerization reaction

Why quantum yield is so important? or why $\phi = 1$ is so hard?

Further Reading

- Hybridization of C=O group
- Reactions of alkoxy radical
- Free radical, generation, stability,.......etc.

▪ We will deal with ketone system as an example for n-π* transition

▪ Shining the ketone system with UV light (310 nm) lets one electron from the nonbonding orbital to transfer to the π* orbital

Reactant   **Excited state**   **Alkoxy radical**
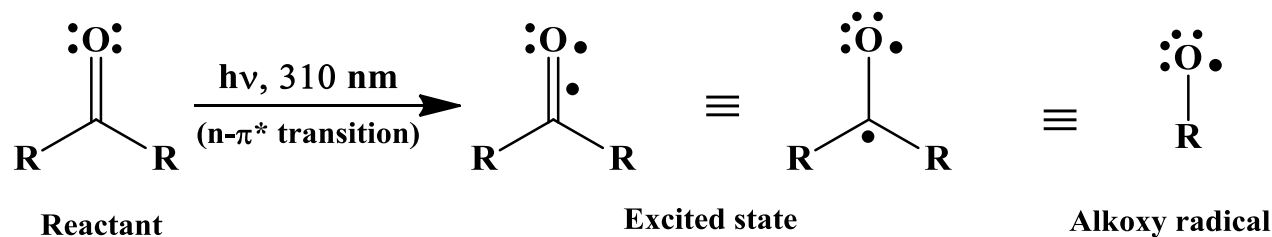
The possible chemistry of alkoxy radical
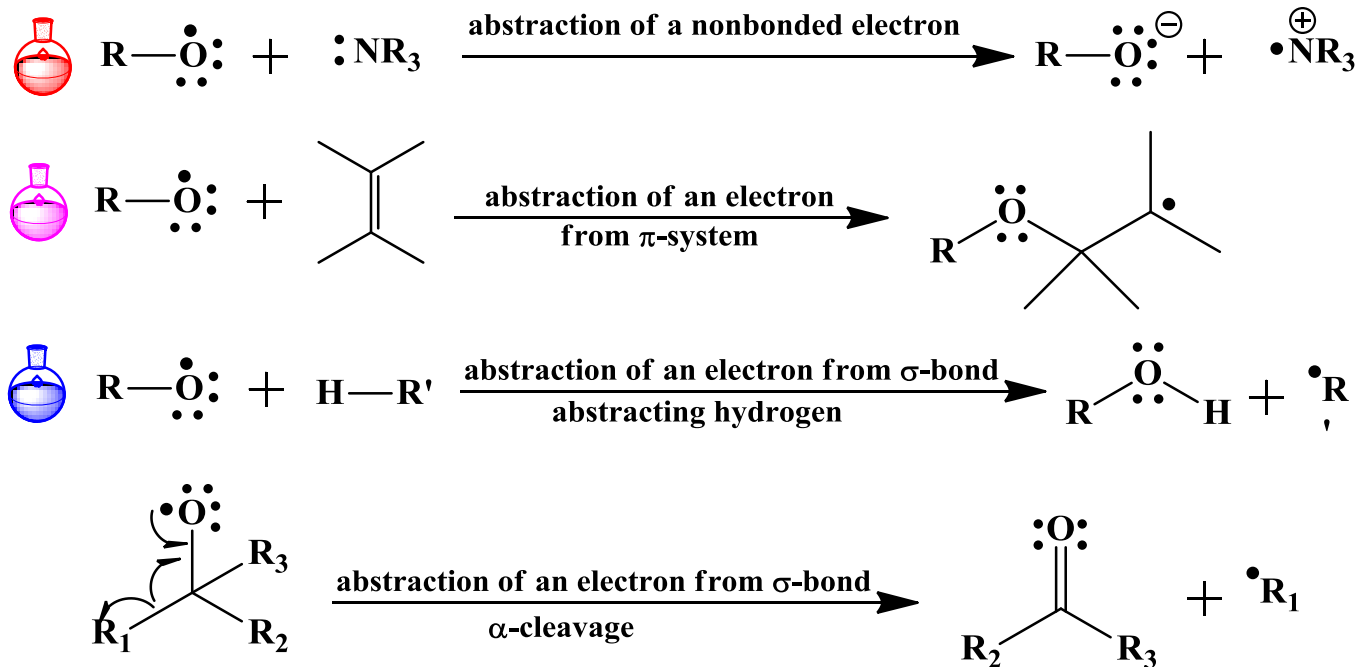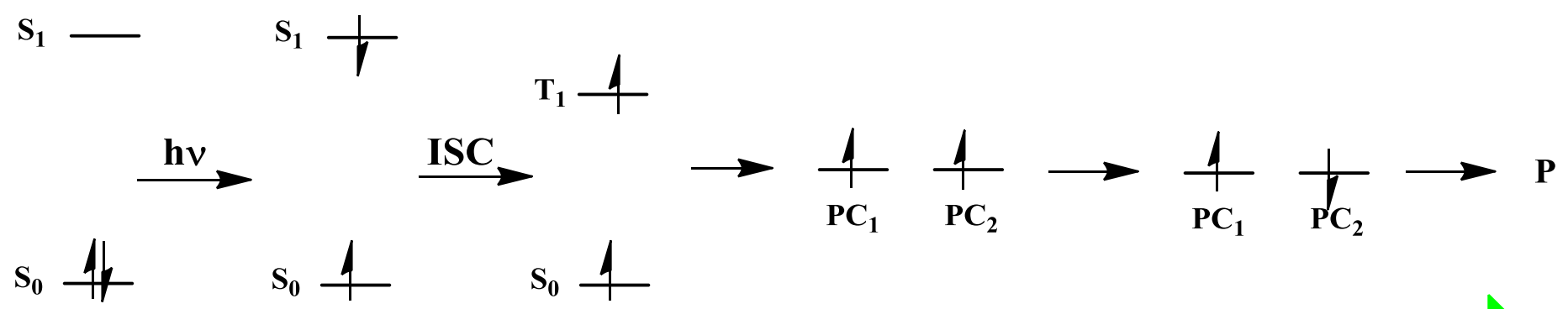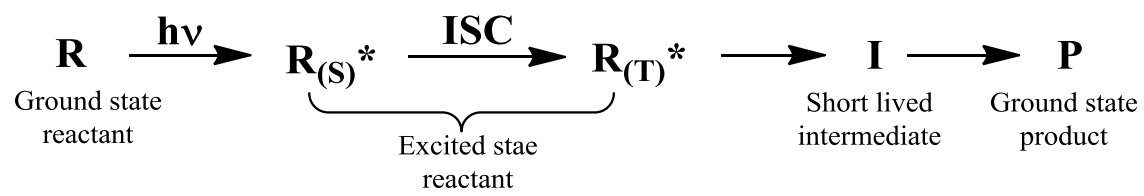
abstraction of a nonbonded electron

$R\!-\!\overset{..}{\underset{..}{O}}\!:$ + $:NR_3$ → $R\!-\!\overset{..}{\underset{..}{O}}\!:^{\ominus}$ + $^\bullet\overset{\oplus}{N}R_3$

abstraction of an electron from π-system

abstraction of an electron from σ-bond
abstracting hydrogen

$R\!-\!\overset{..}{\underset{..}{O}}\!:$ + $H\!-\!R'$ → $R\overset{..}{\underset{..}{O}}H$ + $^\bullet R'$

abstraction of an electron from σ-bond
α-cleavage

+ $^\bullet R_1$

Summarizing the general equation of photochemistry.

R $\xrightarrow{h\nu}$ $R_{(S)}*$ $\xrightarrow{ISC}$ $R_{(T)}*$ $\longrightarrow$ I $\longrightarrow$ P

Ground state reactant

Excited stae reactant

Short lived intermediate

Ground state product

S_1 —

S_1 ⤸

T_1 ↟

$h\nu$ →

ISC →

→ PC$_1$ PC$_2$ → PC$_1$ PC$_2$ → P

S_0 ⤵

S_0 ↟

S_0 ↟

R $^1R*$ $^3R*$ ^3I ^1I P

Primary Process:

Reactant

hv, 310 nm

(n-π* transition)

ISC

Excited states
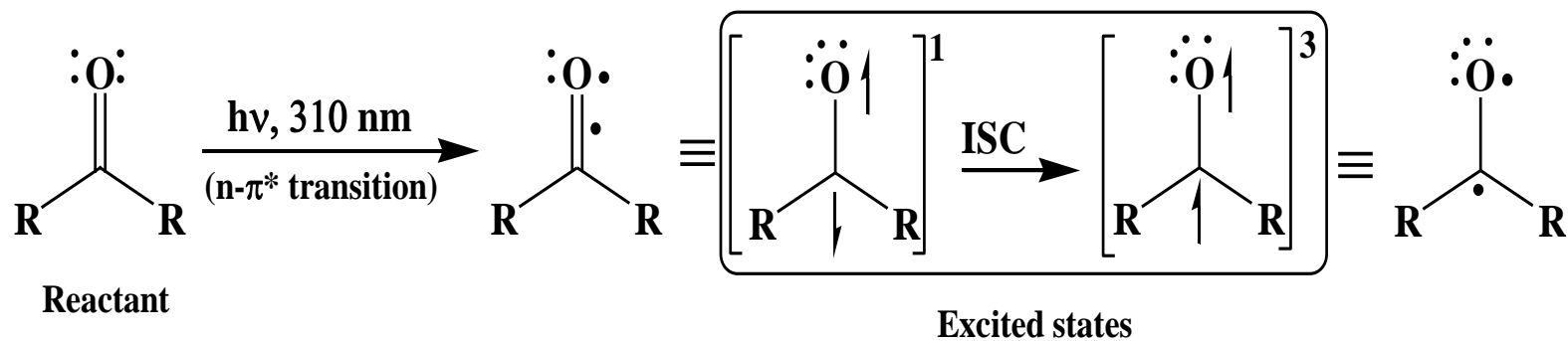
The oxygen atom of the excited carbonyl system has the same electronic configuration as the alkoxy radical so it will follow the same chemical behaviour.

Secondary Processes:
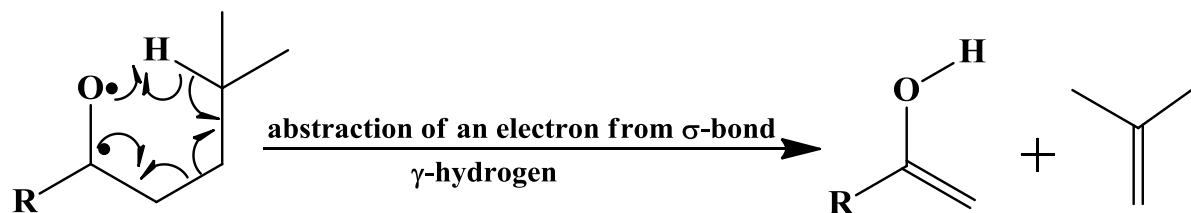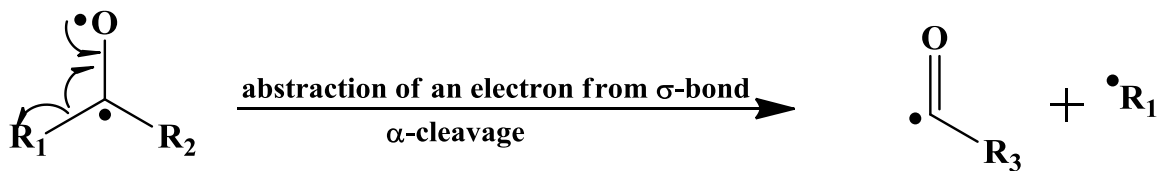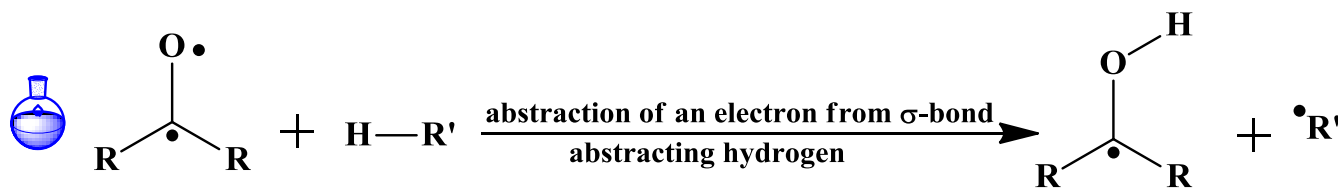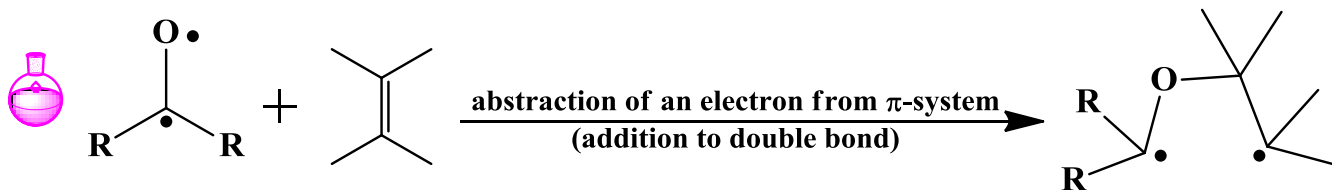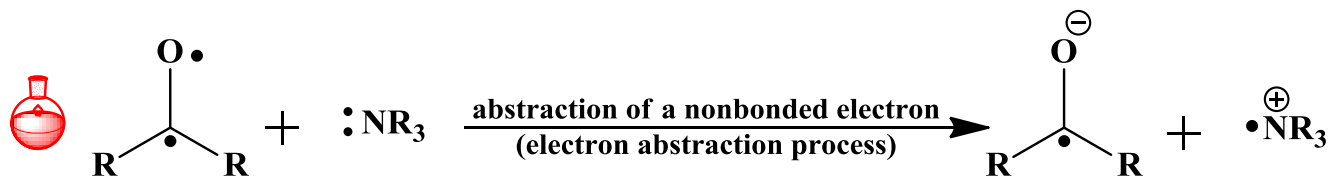
abstraction of a nonbonded electron
(electron abstraction process)

abstraction of an electron from π-system
(addition to double bond)

abstraction of an electron from σ-bond
abstracting hydrogen

abstraction of an electron from σ-bond
α-cleavage

abstraction of an electron from σ-bond
γ-hydrogen

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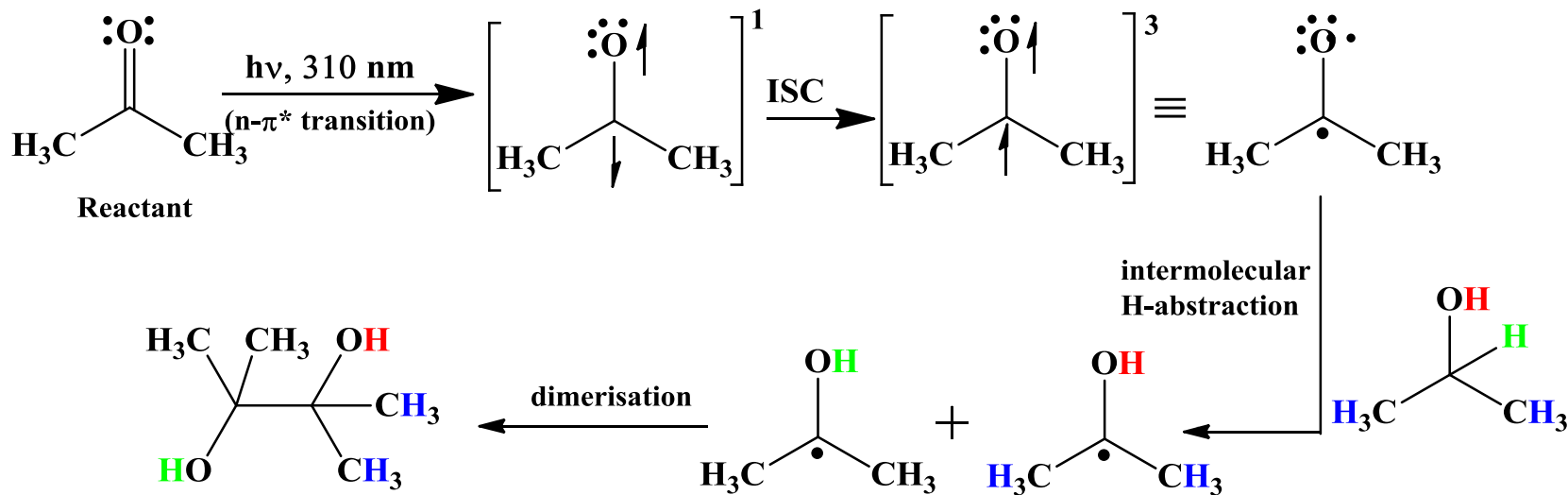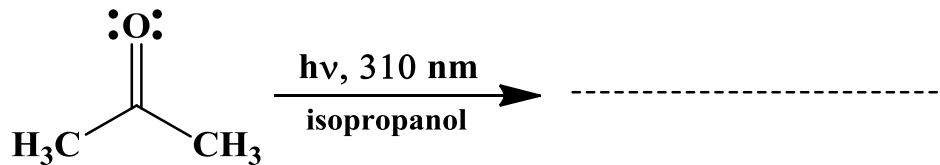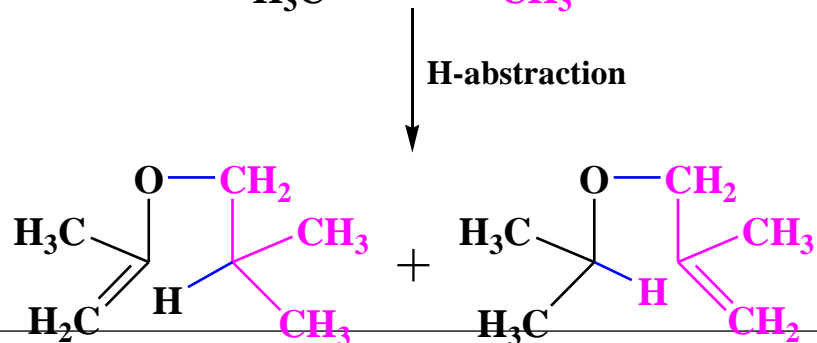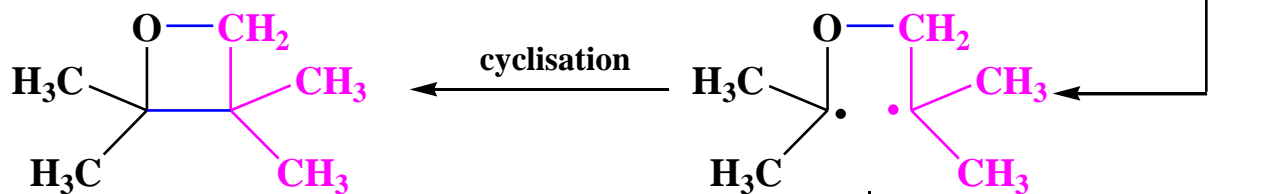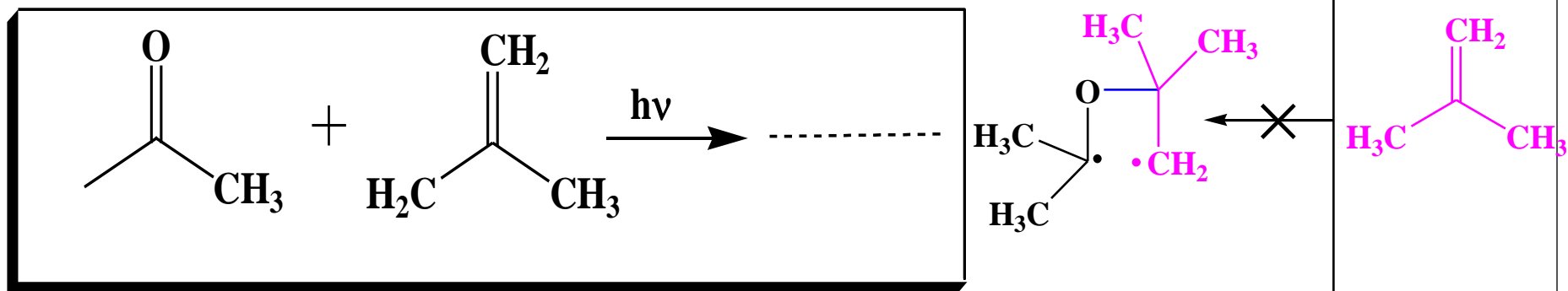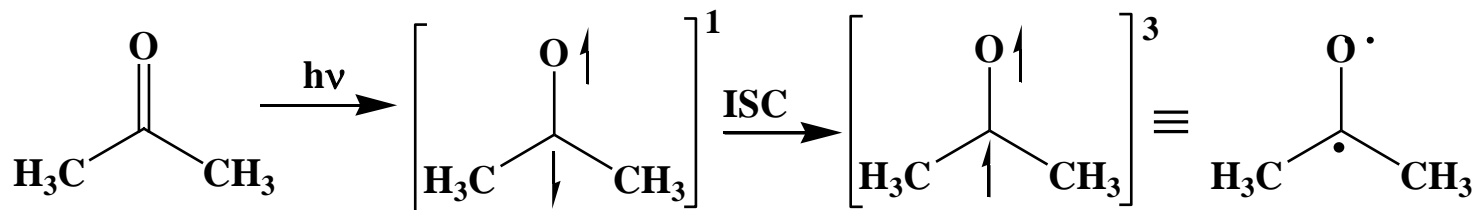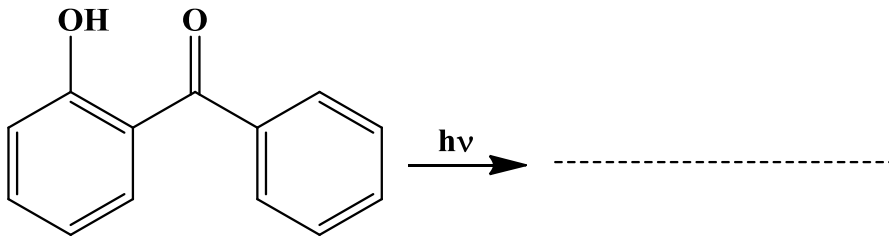
Photoenolisation:
- **Photostabilizer**
- **Sunscreen**
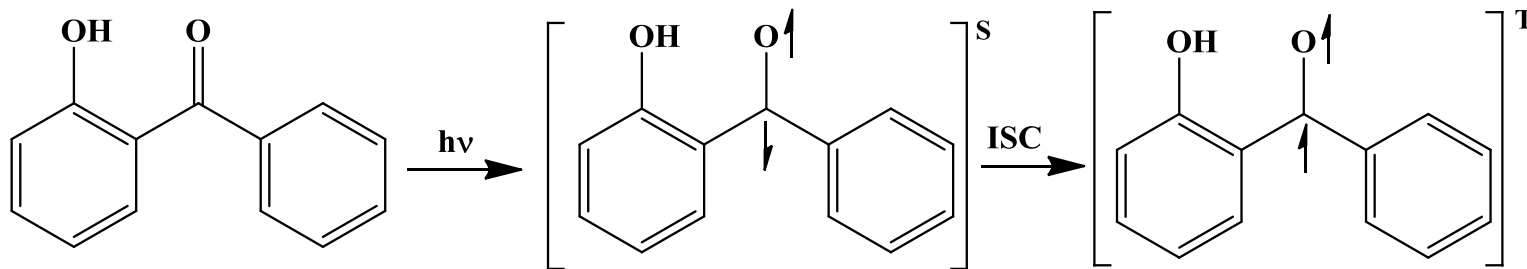
PHOTOENOLIZATION

ketone form
(stable)

Very fast step

enol form
(unstable)

intramolecular
H-abstraction

31

oxybenzone

salicylate ester

o-methylacetophenone

avobenzone
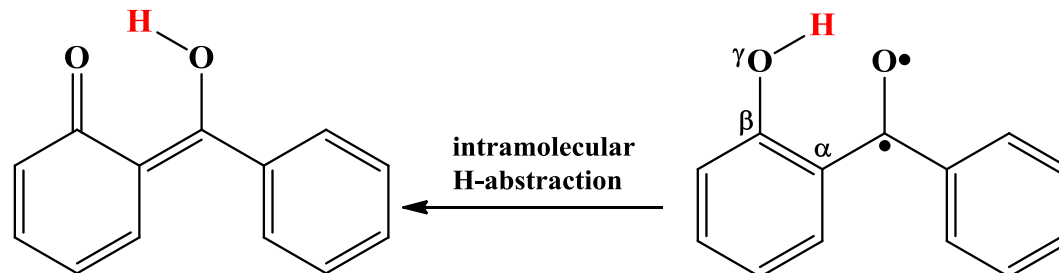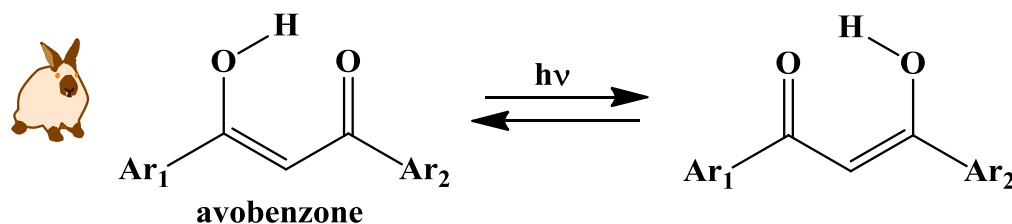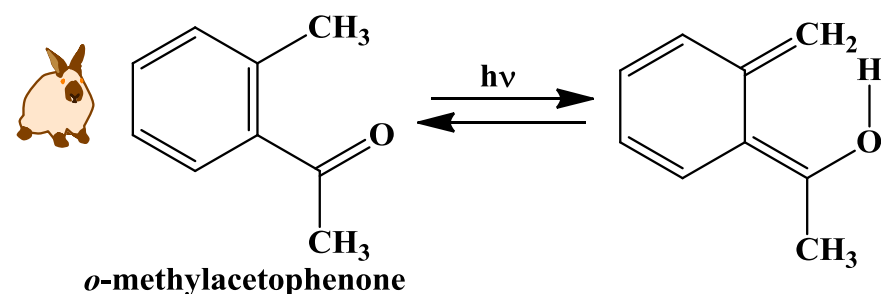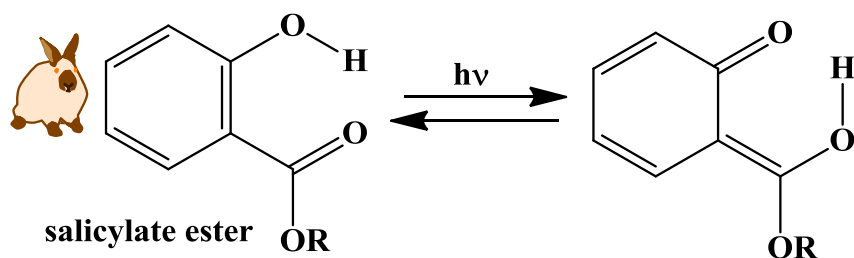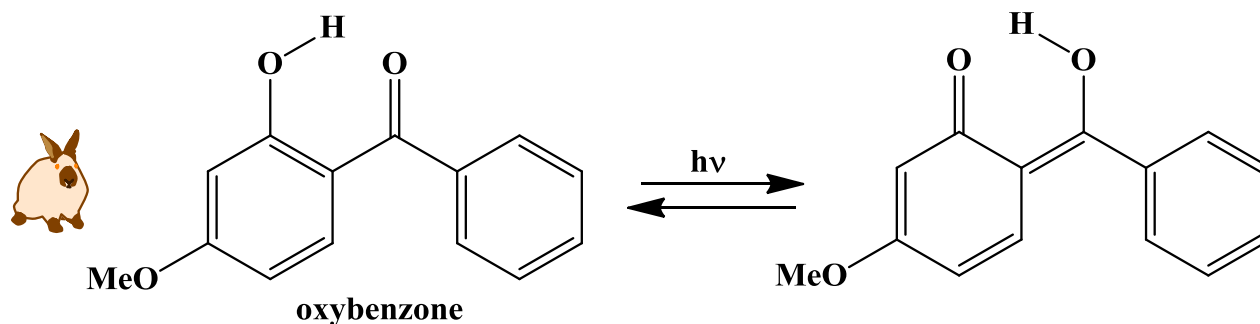
One requirement for photoenolisation to happen which is the presence of γ-hydrogen conjugated *via* an aromatic ring or double bond to the functional carbonyl group.

Norrish observed photodecarbonylation of ketones when exposed to UV light

Norrish type (I) reaction was observed in three different types of ketones:

    (i)   Saturated acyclic ketones

    (ii) Saturated cyclic ketones

    (iii) β-γ unsaturated ketones

Example (1)

Primary Process:
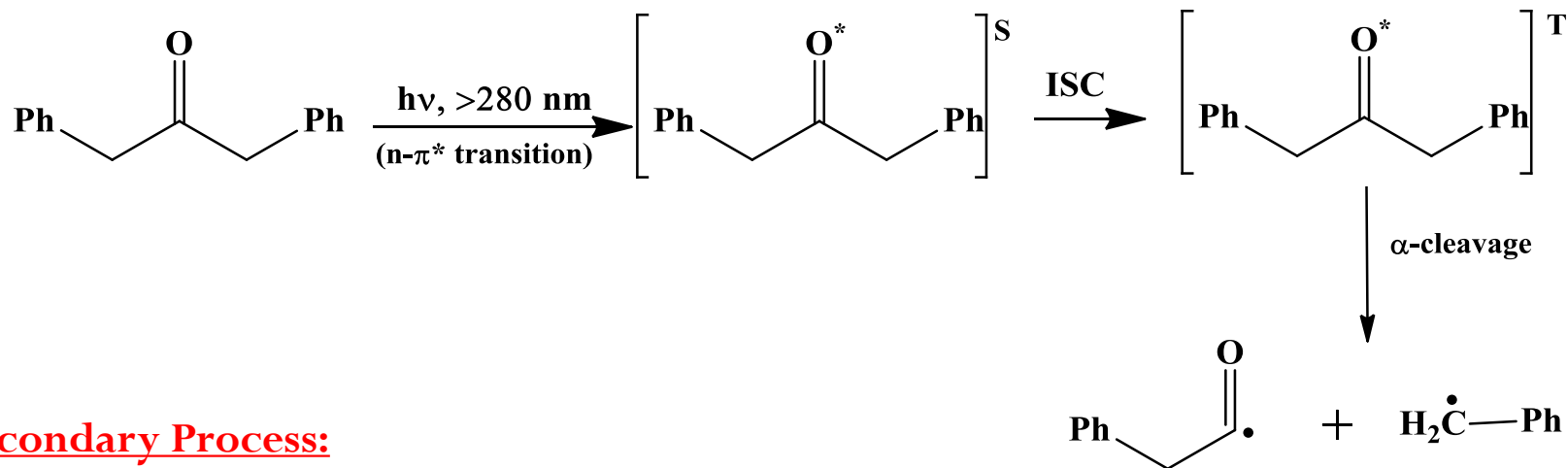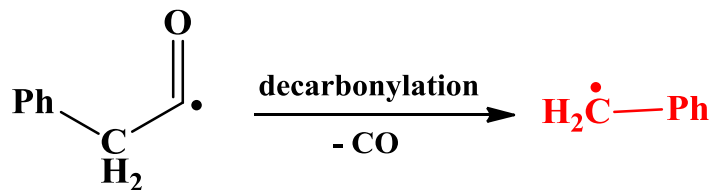
Secondary Process:

Example (2)

$$\text{Me-CO-C(Me)(Me)(Me)} \xrightarrow[\text{(n-π* transition)}]{\text{hv, >280 nm}} \text{---------------}$$

Example (3)

$$\text{Me-CH}_2\text{-CO-CH(CH}_2\text{Me)(Me)} \xrightarrow[\text{(n-π* transition)}]{\text{hv, >280 nm}} \text{---------------}$$
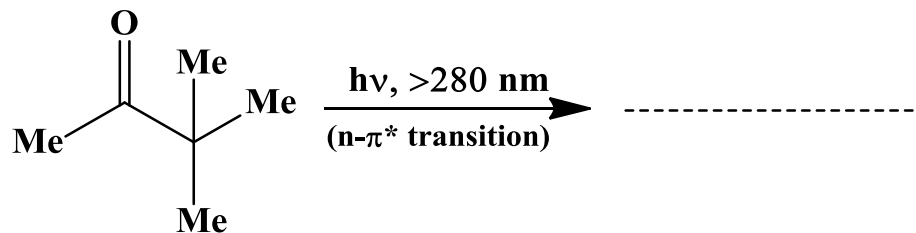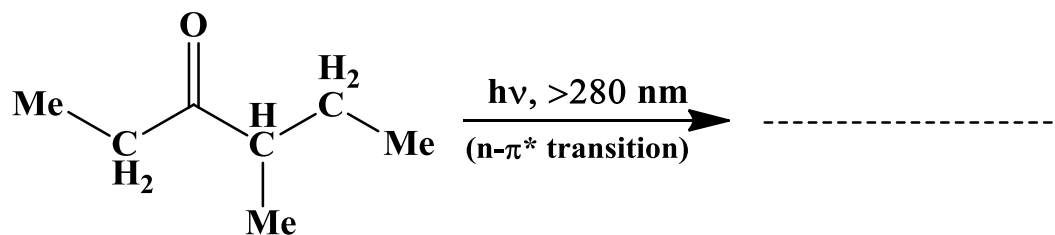
In case of saturated acyclic ketones, three sets of products are possible:

(a) Decarbonylation followed by radical recombination

(b) Intermolecular β-hydrogen abstraction to give adehyde and alkene

(c) Intermolecular β-hydrogen abstraction to give ketene and alkane

Example 1: Primary process

Secondary Process:

36

Example 2: Primary process

Secondary Process:

acyl/alkyl diradicals — Free rotation — acyl/alkyl diradicals

(1) Decarbonylation

(*cis*)-1,2- dimethyl + *trans*-alkene   (*trans*)-1,2- dimethyl + *cis*-alkene

(2) Intramolecular H-abstraction

unsaturated aldehyde + ketene   unsaturated aldehyde + ketene

(3) Radical recombination

(*cis*)-2,6-dimethyl   (*trans*)-2,6-dimethyl
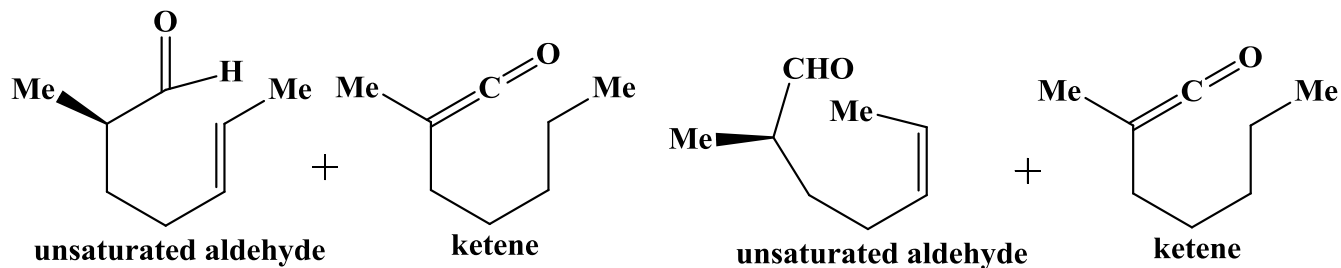
Example 3:

(1) Norrish Type (I) Reactions (α-Cleavage Reactions)
(ii) Saturated cyclic ketones ...... 5-membered systems

Example 1: Primary process

hν
(n-π* transition)

ISC

α-cleavage

S₁

T₁

acyl/alkyl diradicals

Secondary Process

acyl/alkyl diradicals

decarbonylation

1,4-diradical

recombination → cyclobutane

β-Cleavage → 2 alkene

recombination

intramolecular H-abstraction

unsaturated aldehyde + ketene

Example 2:

Example 3:

Example 1: Primary process

Secondary Process

Example 2:

Example (1).

Primary process:

Secondary process:

Major product

(traces)

Once you got β-γ unsaturated bond in the system, you should involve it into the reaction.

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Examples (2 and 3).

➤ The process is a source of energy transfer from the exited carbonyl group to the strained/weak C_α—C_β bond and as a result β-cleavage takes place.
➤ This type of reactions will take place from S_1 and/or T_1.

Example (1).

Primary Process:
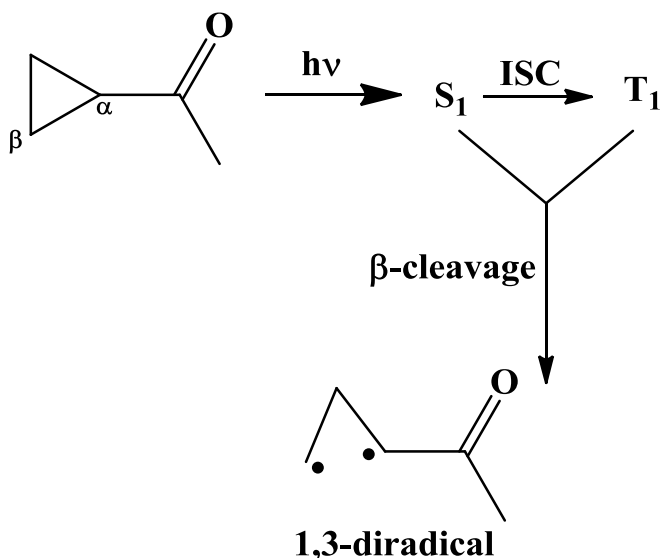
Secondary Process:

1,3-Diradical can undergo:
(i)   **1,2-hydrogen shift**
(ii) **1,2-group shift !!!!**
(iii) **1,2-bond migration**
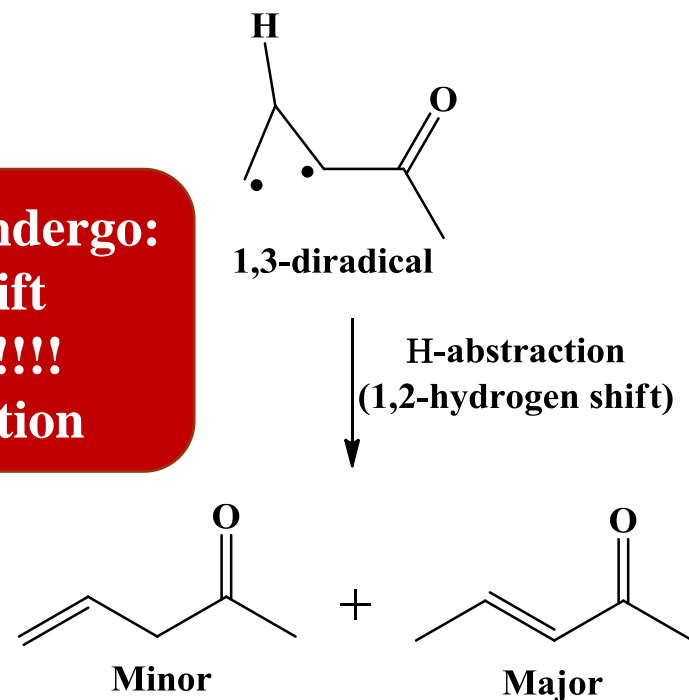
β-cleavage

1,3-diradical

1,3-diradical

H-abstraction
(1,2-hydrogen shift)

Minor

Major

46

Example (2).

Quizzes.

48
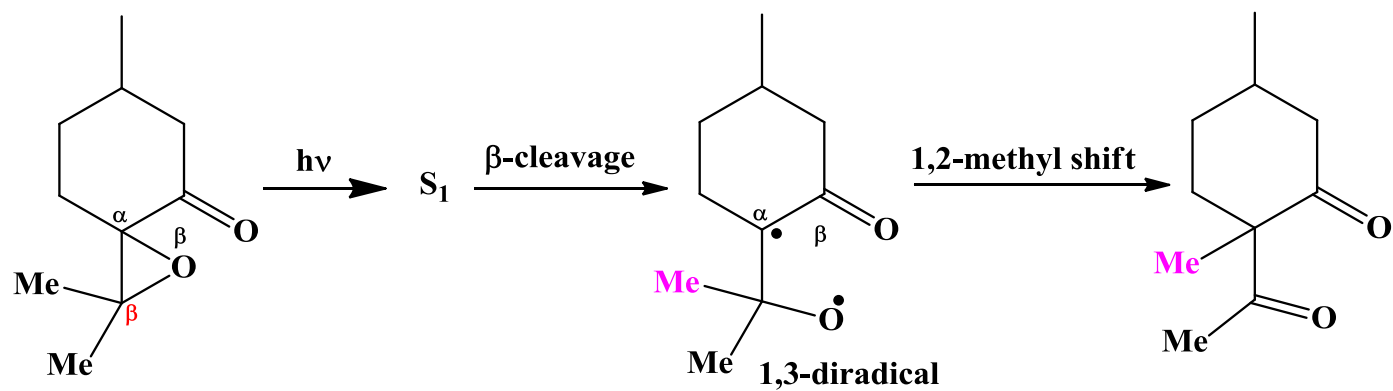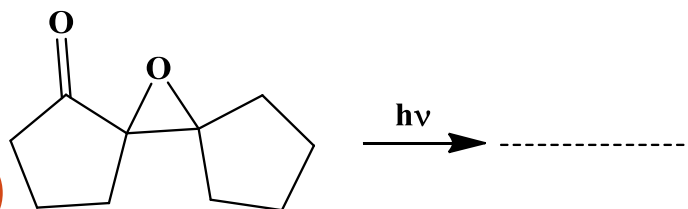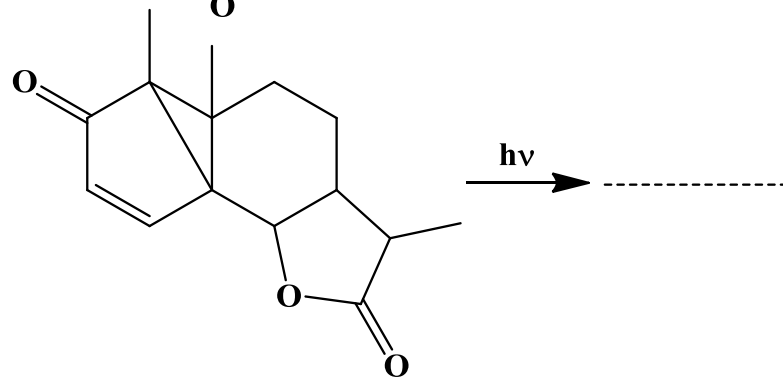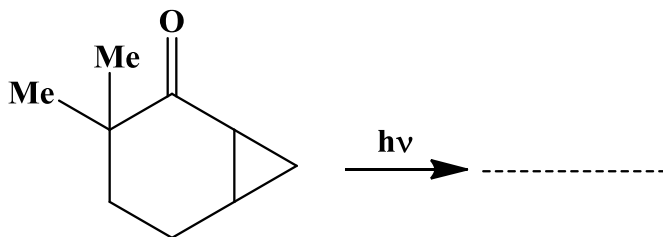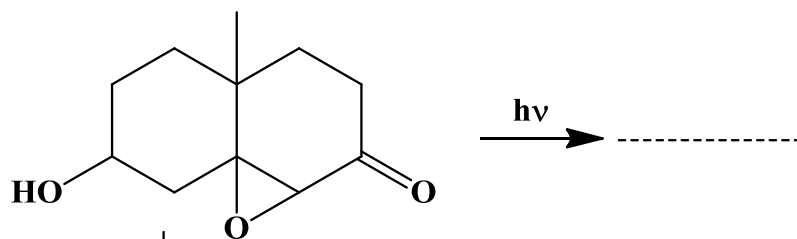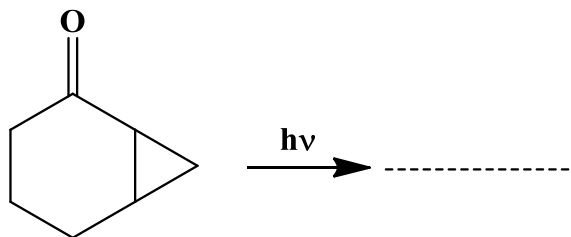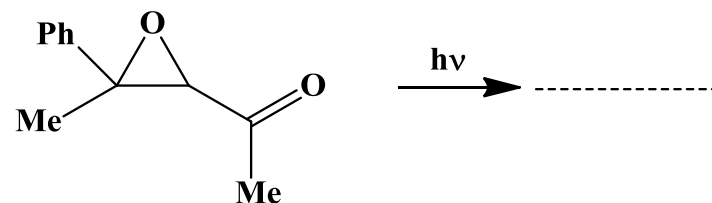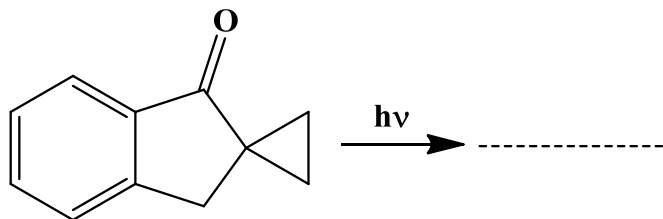
γ-Hydrogen abstraction

Primary Process:
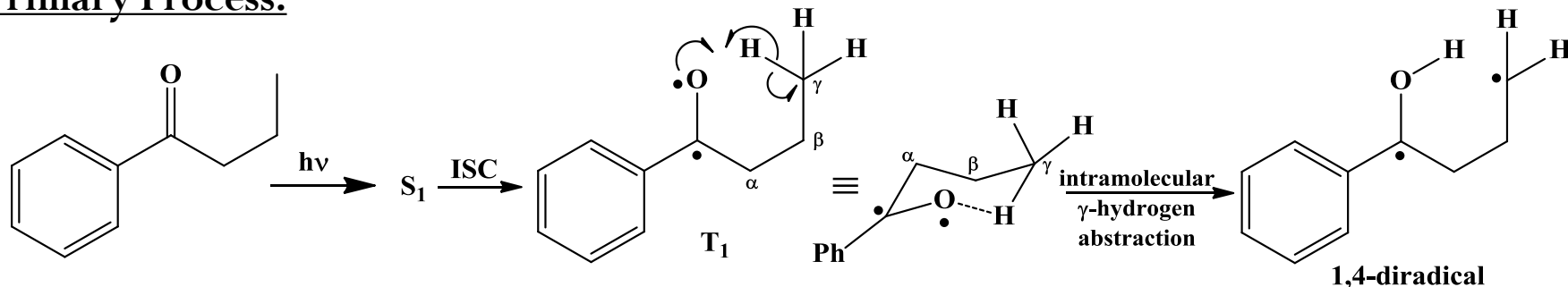
Secondary Process:
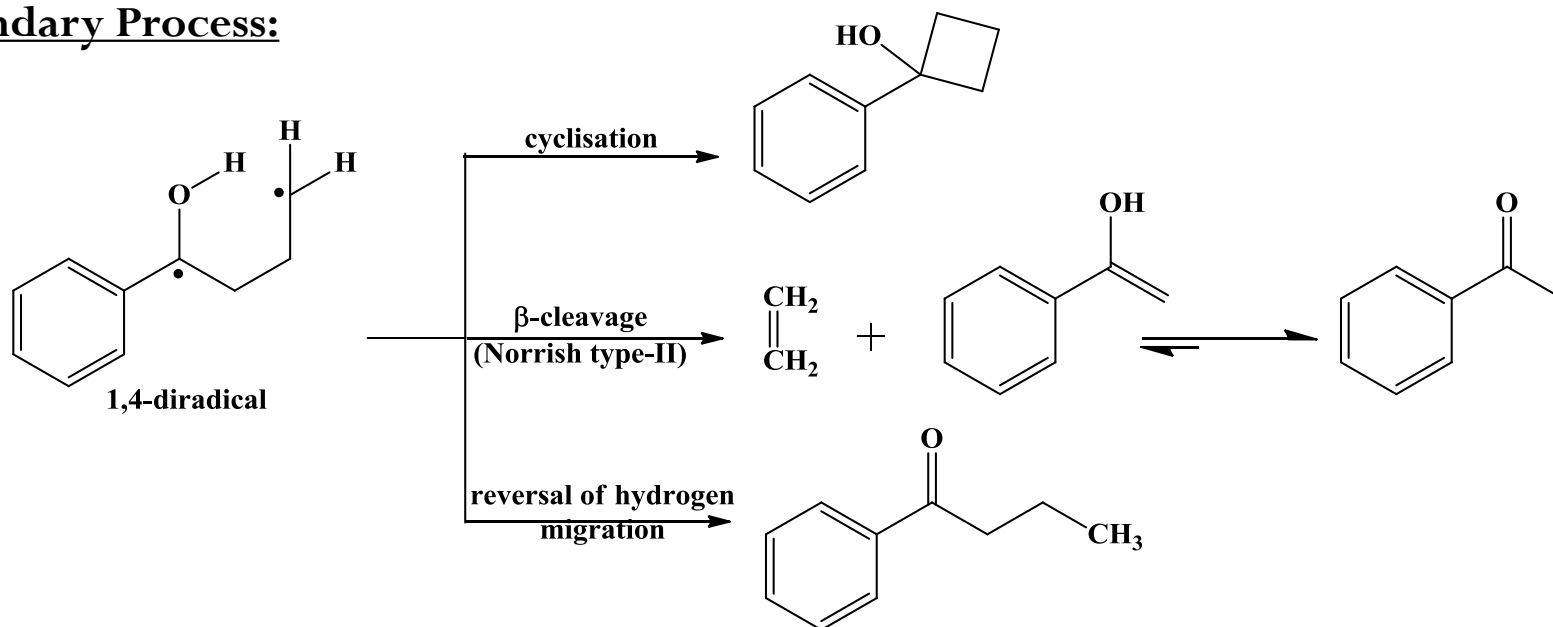
<u>Some features you should understand before starting the problems:</u>

❑ 1,4-Diradicals give cyclization major products in one case and Norrish type-II major products in the other case . (<u>Direction of the diradical orbitals</u>)

❑ Aromatic ketones do the photochemistry from T_1 excited state whereas aliphatic ketones use both S_1 and/or T_1 excited states.

❑ γ-Hydrogen abstraction is the fastest process comparing with other positions. In the absence of γ-hydrogen, the oxygen radical can abstract hydrogen from distance side depending on the proximity. (<u>Distance and proximity</u>)

❑ There is a good relation between the structure of reactants and its products. (<u>Position of the substituents</u>)

Example (1).
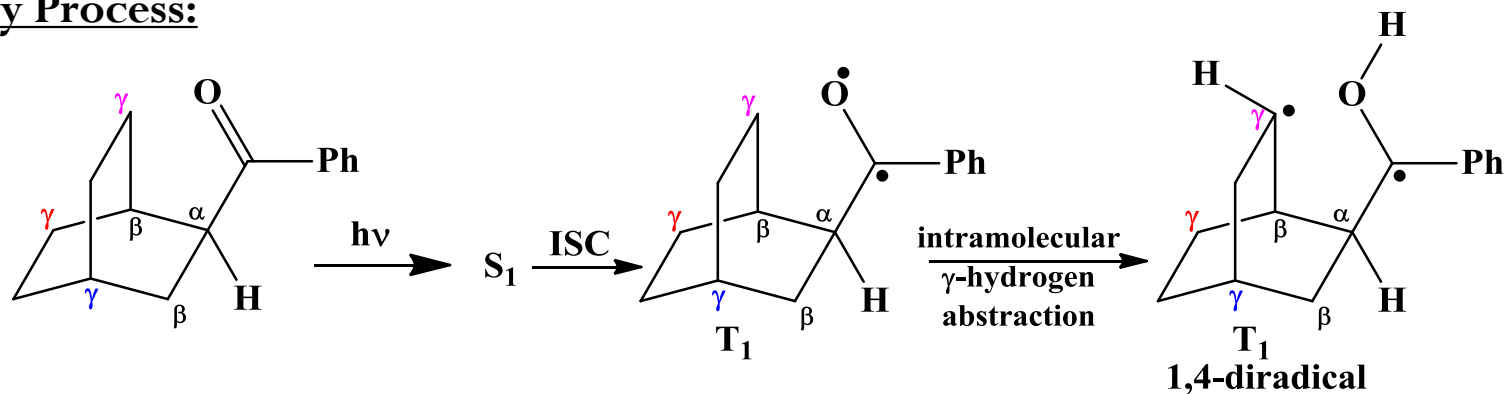
Primary Process:

Secondary Process:
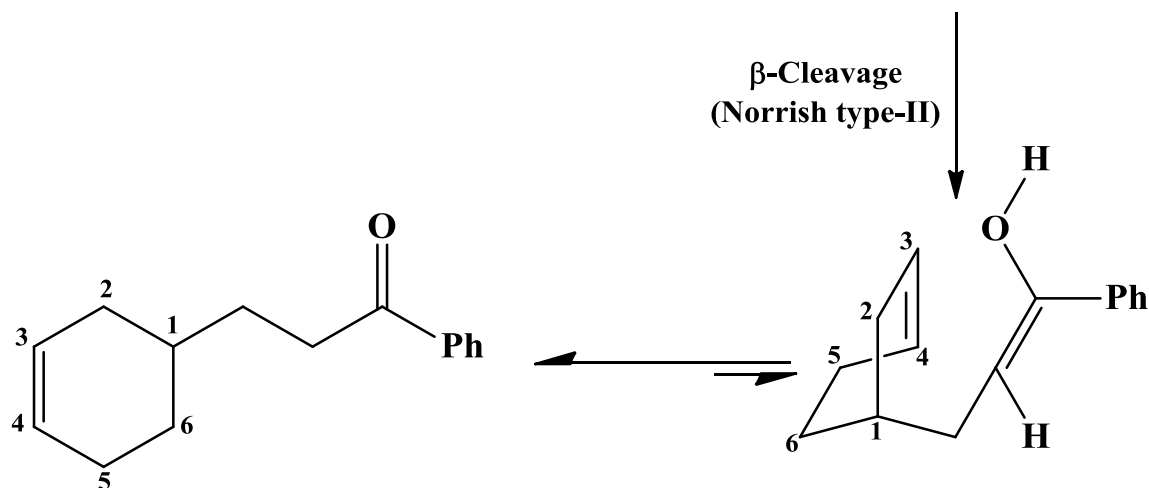
Problems.

Problems.

β-Hydrogen abstraction.

δ-Hydrogen abstraction.

Problems.
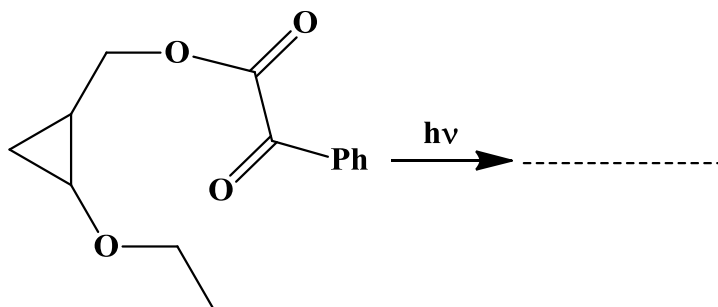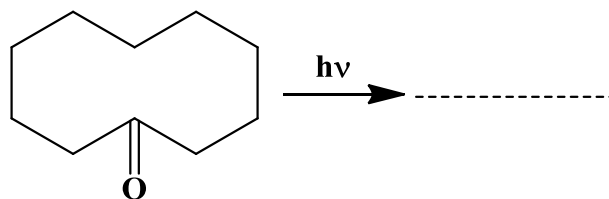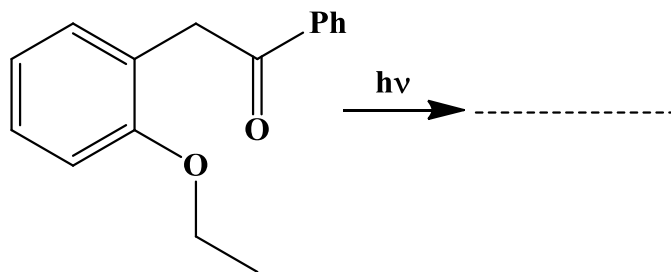
This reaction is a sort of [2+2]photocycloaddition of C=O to C=C. **[2+2] Photocyclo-addition** is the combination of an excited state enone with an alkene to produce a cyclobutane.

Example:
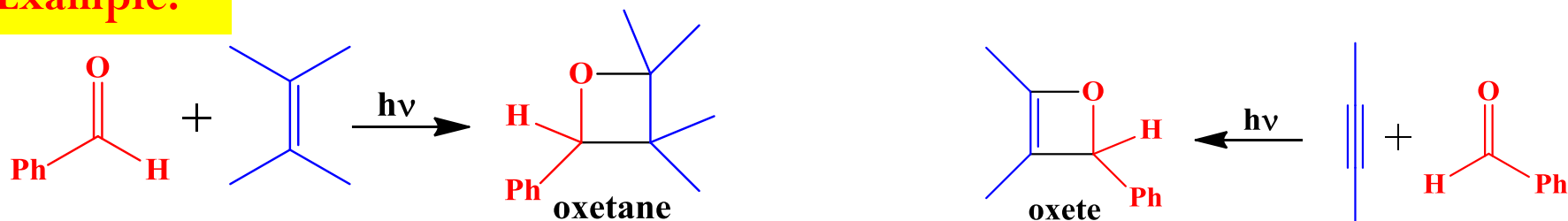
Mechanism:
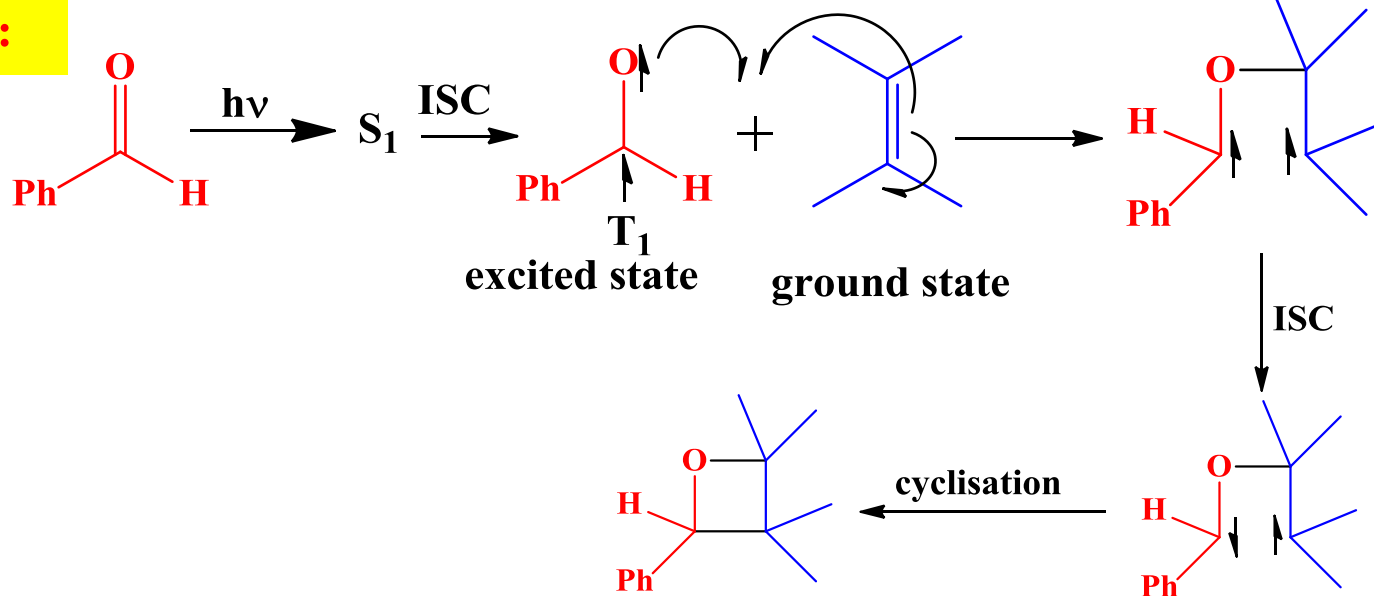
❑ Electron rich alkenes cycloadd with the excited carbonyl group by **free radical mechanism** and as a result **nonstereo-** and **nonregio-specific** cycloadducts are obtained.

▪ The diradical is sufficiently long lived for the stereochemical memory to be lost by bond rotation (**Stepwise Reaction**).

▪ the stability of the biradical plays an important factor in the isomeric ratio of the product.

❑ Whereas, electron deficient alkenes cycloadd with the excited carbonyl group by **ionic like mechanism** and as a result **stereo-** and **regio-specific** cycloadducts are obtained.
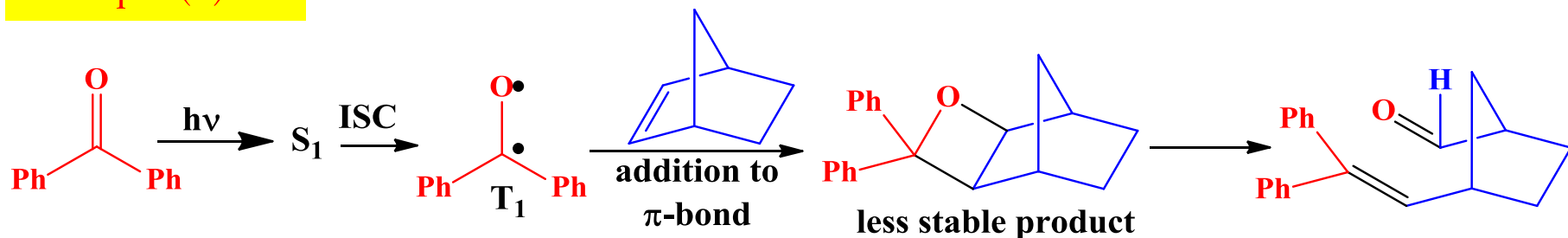
▪ The excited carbonyl group has different behaviour from that of the ground state one.

▪ Association of the excited carbonyl group with the deficient alkene generates exciplex complex which has only one way/chance to react (**Concerted Reaction**) and produce regio- and stereospecific cycloadducts.
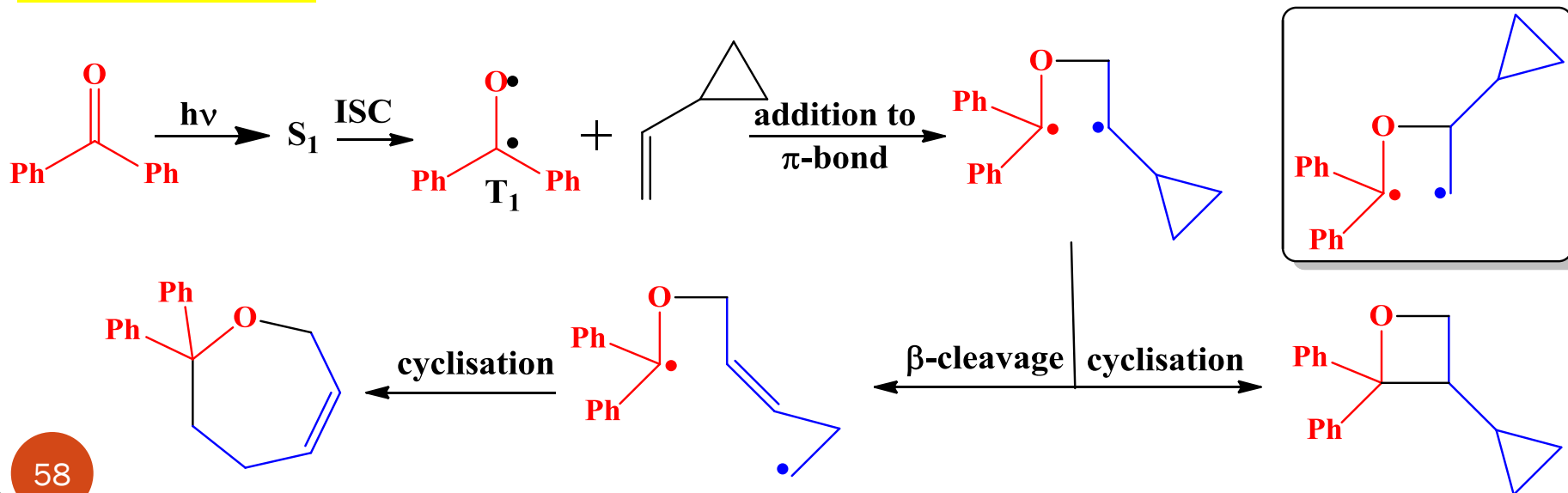
(a) Intermolecular Paterno-Buchi Reaction

Example (1):

Example (2):

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(a) Intermolecular Paterno-Buchi Reaction

Example (3 and 4):
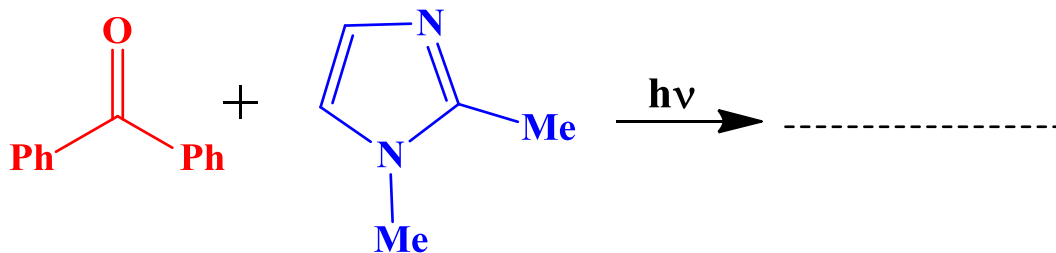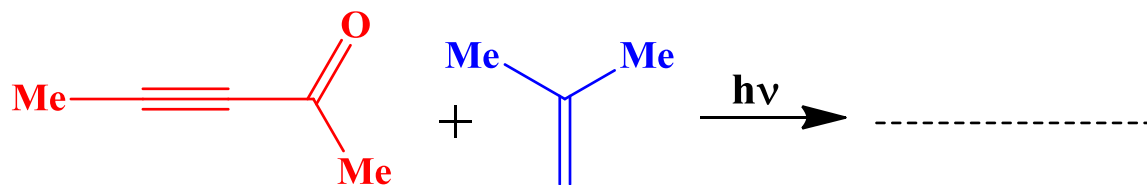
(b) Intramolecular Paterno-Buchi Reaction

Example (1):

Example (2):

(b) Intramolecular Paterno-Buchi Reaction

Example (3):

Problems:
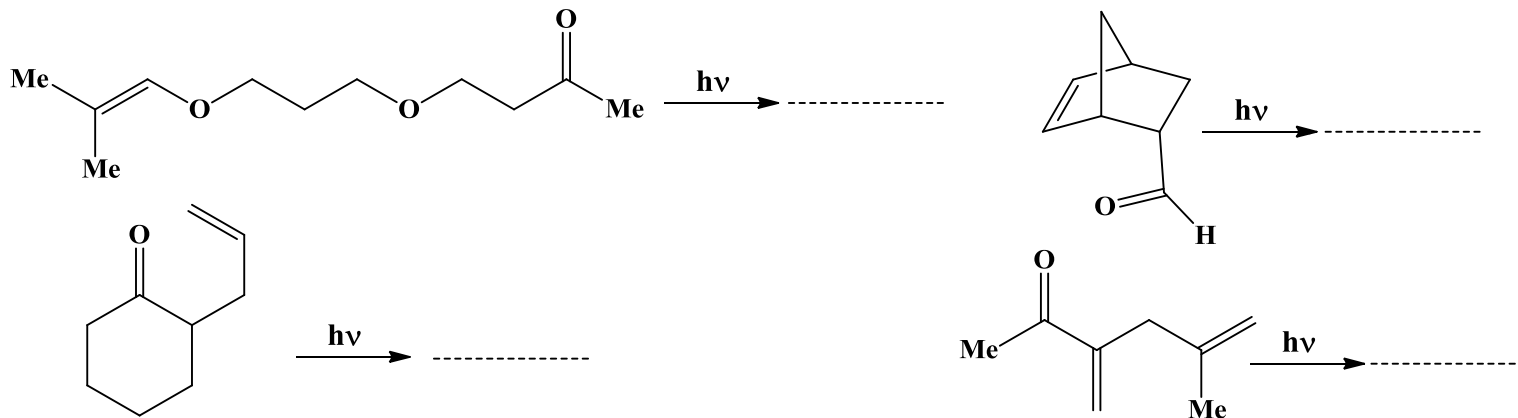
The energy transfer reaction is not a photochemical reaction but it is a photophysical process.

(1) $Z \xrightarrow{h\nu} Z_{(S)}* \xrightarrow{ISC} Z_{(T)}*$

ground state

excited state

(2) $Z_{(T)}* + M \xrightarrow[\text{Energy transfer process}]{\text{Collision}} M_{(T)}* + Z$

excited state · ground state · excited state · ground state

(2) $Z(\uparrow\uparrow)* + M(\uparrow\downarrow) \xrightarrow[\text{Energy transfer process}]{\text{Collision/Spin exchange}} M(\uparrow\uparrow)* + Z(\uparrow\downarrow)$

excited state · ground state · excited state · ground state
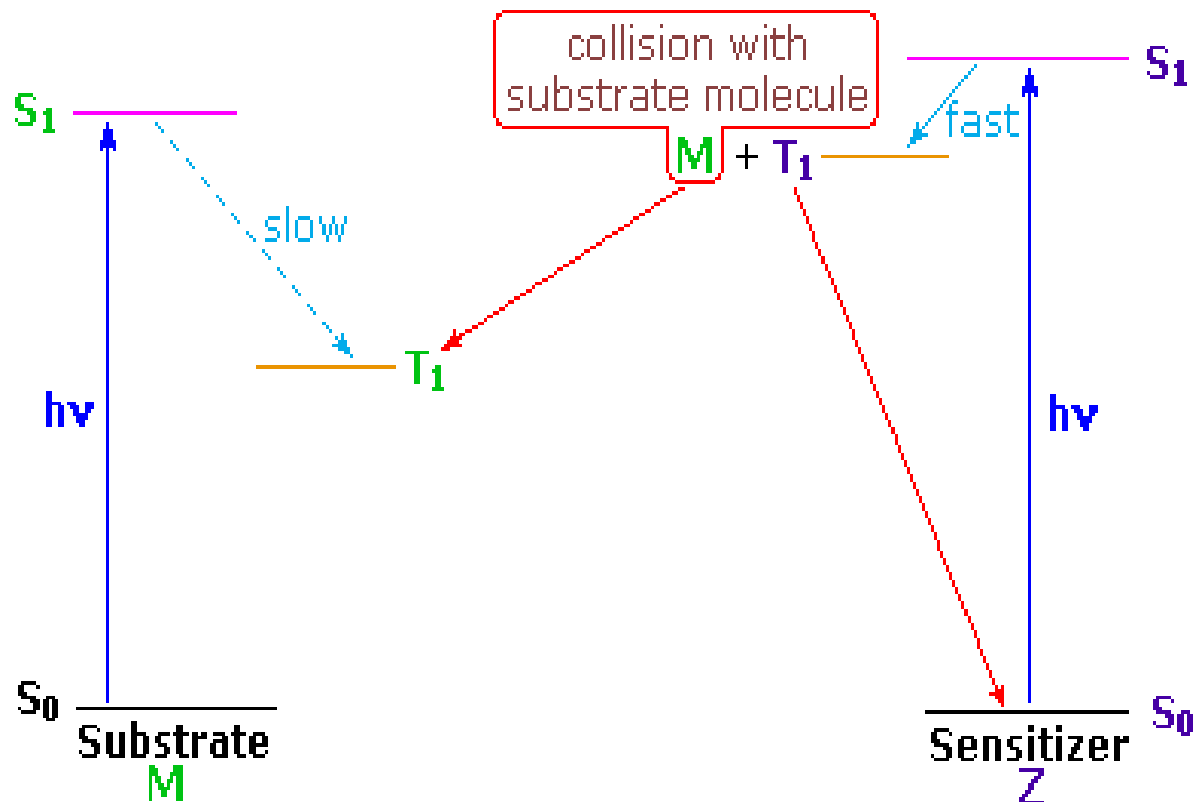
Applications of ETR: - Quenching reaction

- Triplet sensitizers (sensitizer reactions)

Chemistry of π-π* reactivity

This type of chemistry deals with systems like alkenes, dienes, and aromatic compounds.

We want to understand how this type of chemistry works:

❑ The ground state alkene is planar. The two p-orbitals on both carbon are overlapped…… (**Steric Rotation**)

❑ Shining the alkene with a suitable UV light transfers the alkene to the excited state. At the beginning of the excitation, the p-orbitals are planar as in the ground state because the excitation process is very fast. No overlapping between p-orbitals are possible and as a result rotation is possible. (**Planar, No overlapping**)

❑ Overtime, rotation around the bond becomes possible (< 2 Kcal/mol), and one carbon starts to rotate gradually to 90°, which is a very stable excited state…… (**Perpendicular-Relaxed twisted state**).
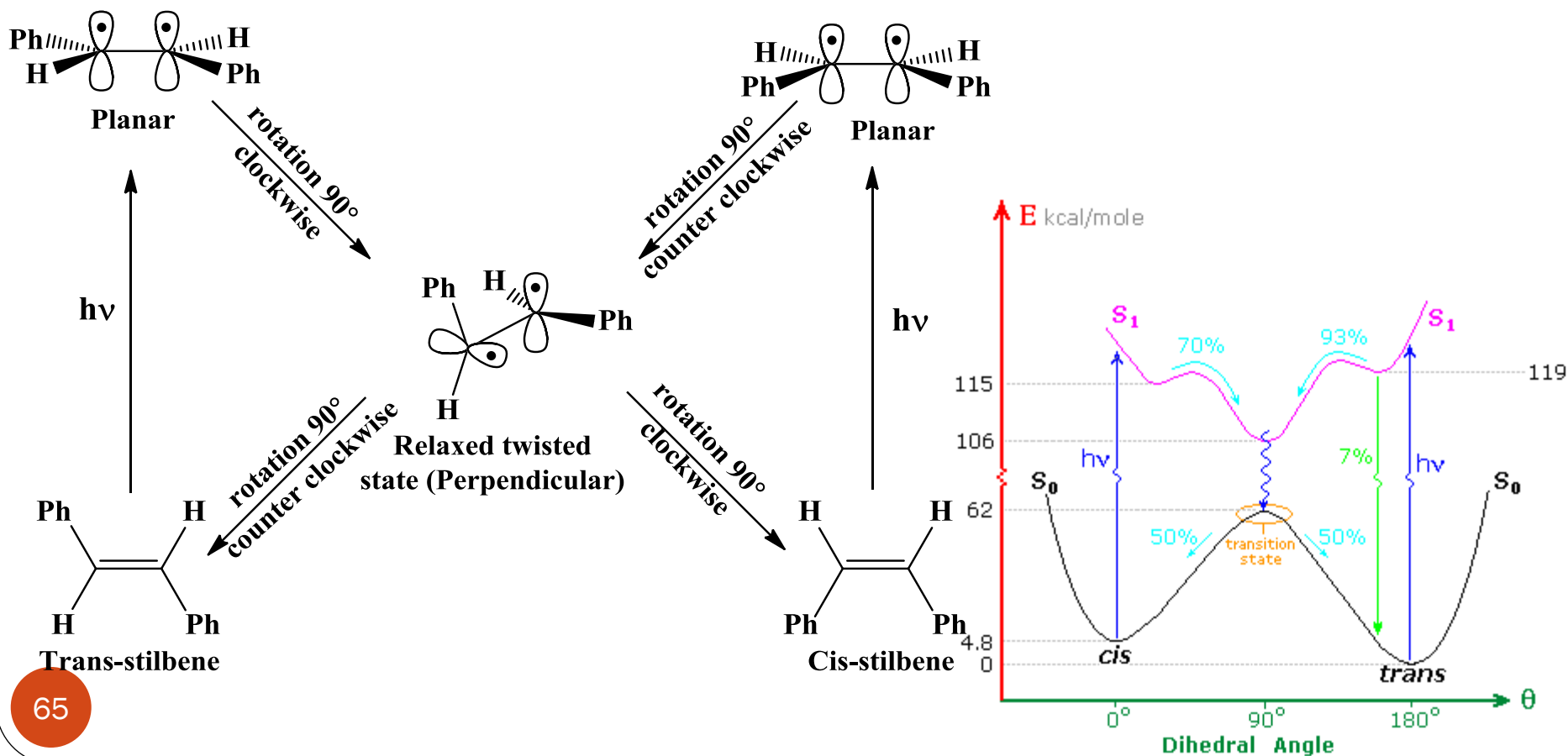
Both S_1 and T_1 excited states have the same previous behaviour but with different results…….. (**Ionic/Free radical Chemistry**)

This process is a simple configurational isomerisation about a single double bond. (**One Bond Flip event**)
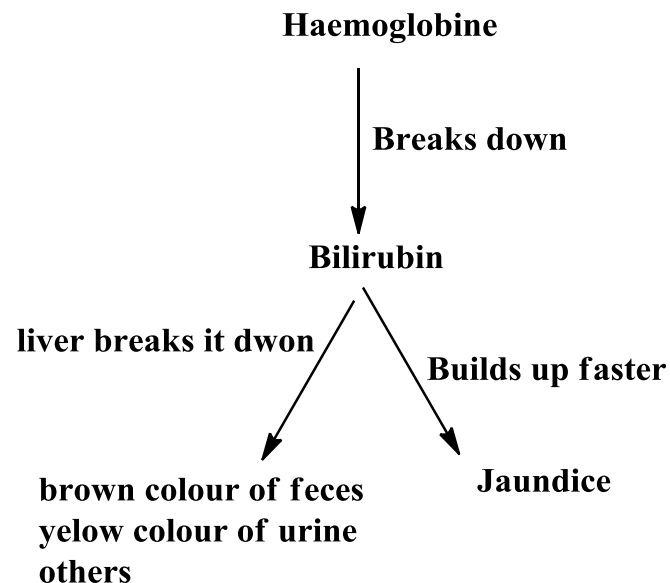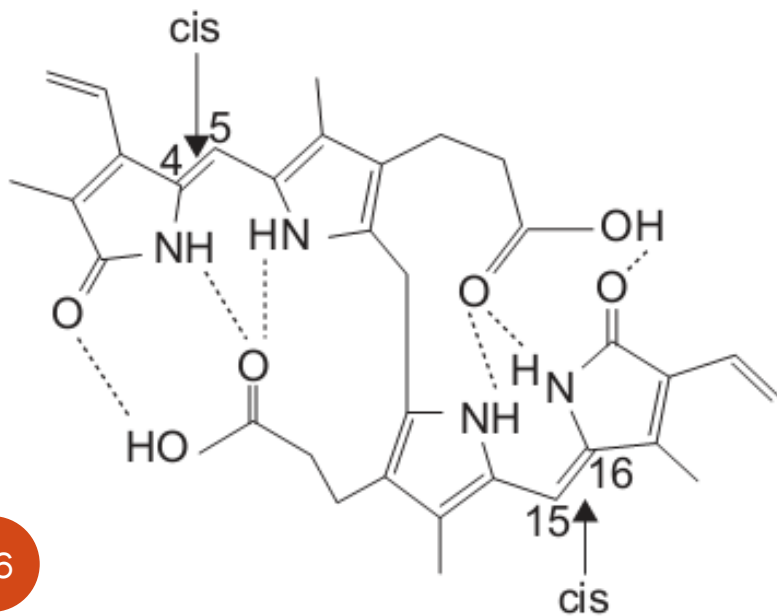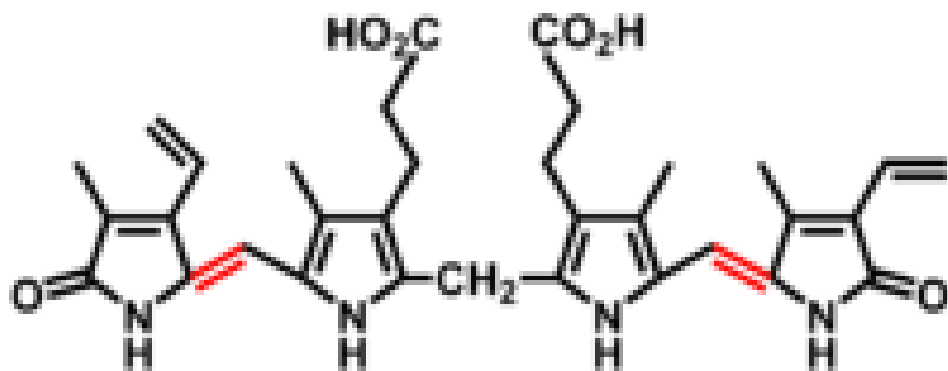
NB: ΔE between S_1 and T_1 in π-π* transition is very big. Hence, ISC is very slow and as a result the chemistry will be predominated from S_1 state.

Phototherapy: Bilirubin

Haemoglobine

↓ **Breaks down**

Bilirubin

liver breaks it dwon ↙   ↘ **Builds up faster**

brown colour of feces yelow colour of urine others   **Jaundice**

❑ Isomerisation of 3,4 and 5-membered ring systems are not possible

❑ Isomerisation of 6 and 7-membered ring systems are possible, but with very short life time (9-10 μs).

❑ Higher ring systems are easily isomerised.

➤The chemistry of alkenes take place from the singlet excited state (**Ionic like mechanism, Concerted, stereospecific)**

➤Stereospecific in a manner that preserve the ground state geometry.

➤The S1 excited state retains the stereochemical memory of its original ground state. (**Planar geometry**)

➤To let alkenes do chemistry from the triplet state, you need a triplet sensitizer.

➤The T1 excited state can not retain the stereochemical memory of its ground state. Two plannar T1 states are possible (cis and trans). (**Free radical mechanism**)

(a) Intermolecular dimerisation of alkenes….. [2+2]cycloaddition
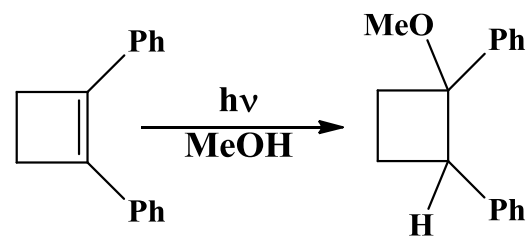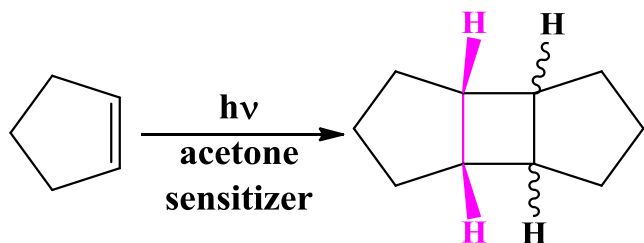
DNA Damage by UV
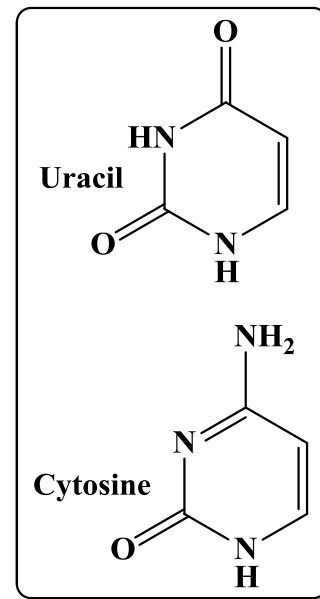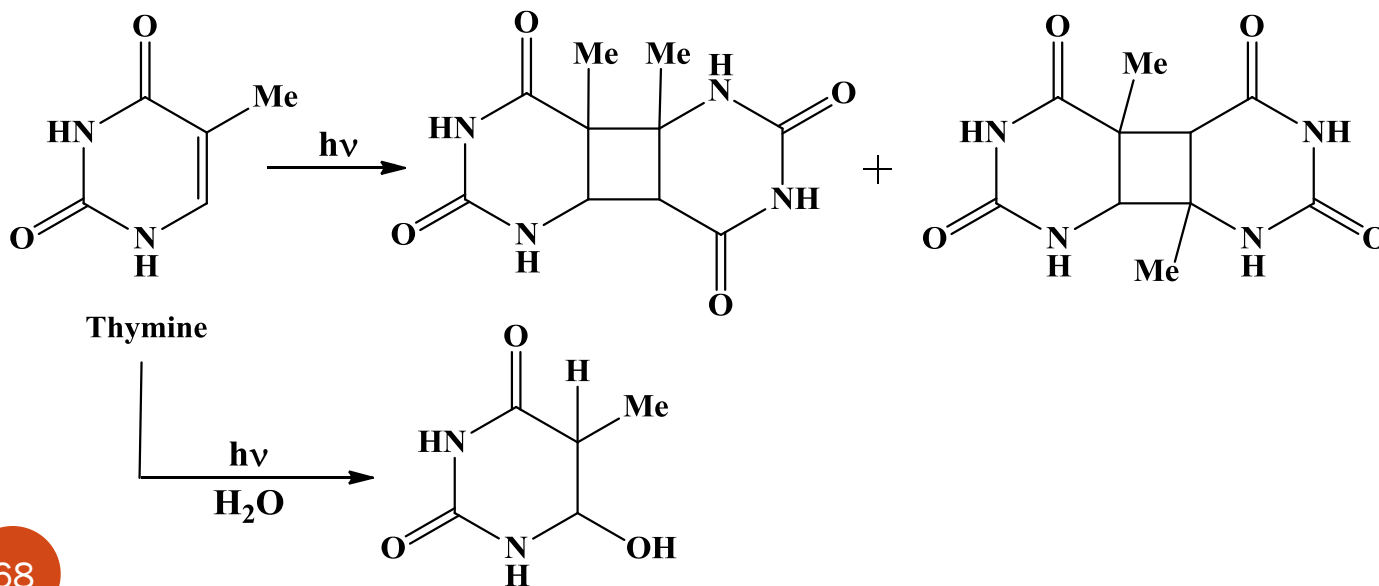
Thymine

Uracil

Cytosine

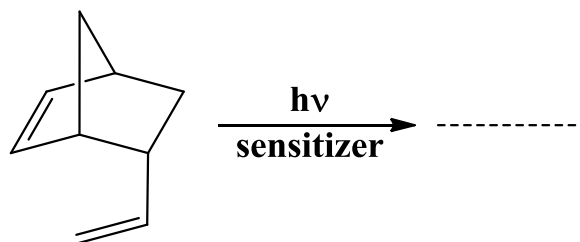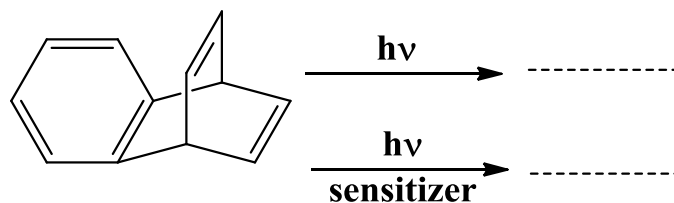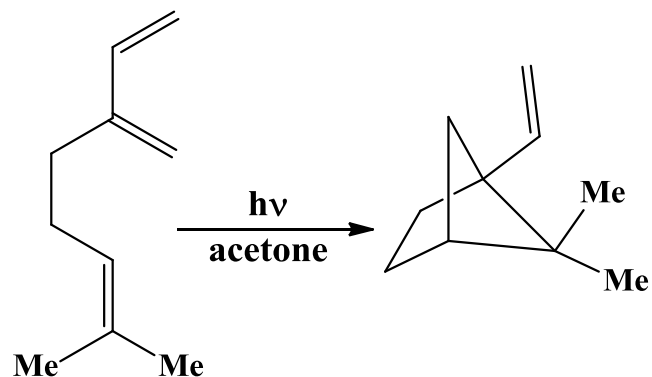(b) Intramolecular dimerisation of alkenes….. [2+2]cycloaddition

Odd number of CH_2-spacer between two alkenes will lead to a type of direct addition, while even number of CH_2-spacer will lead to a type of cross addition….. This description agrees with Rule of Five to some extent.
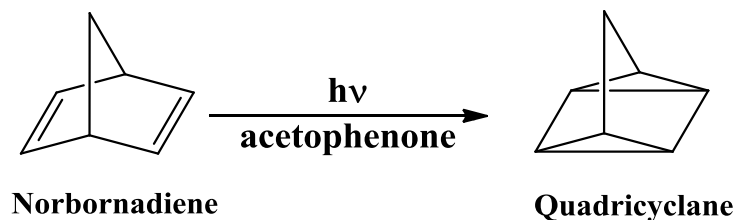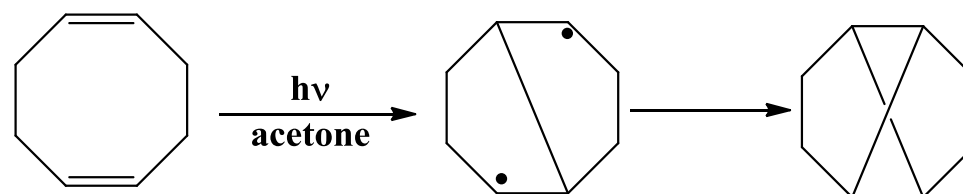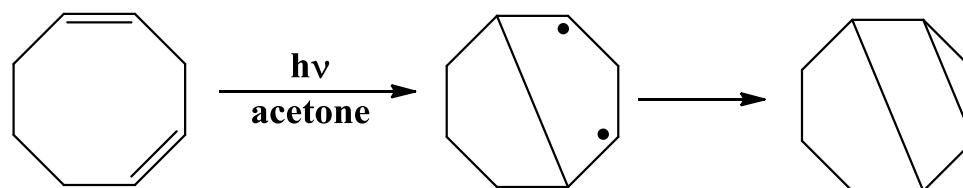
Norbornadiene   Quadricyclane

(b) Intramolecular dimerisation of alkenes..... [2+2]cycloaddition

(c) Inter- and Intra-molecular addition of conjugated dienes.

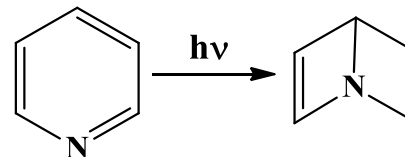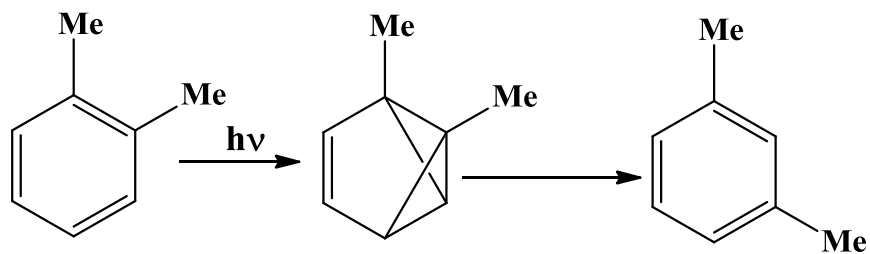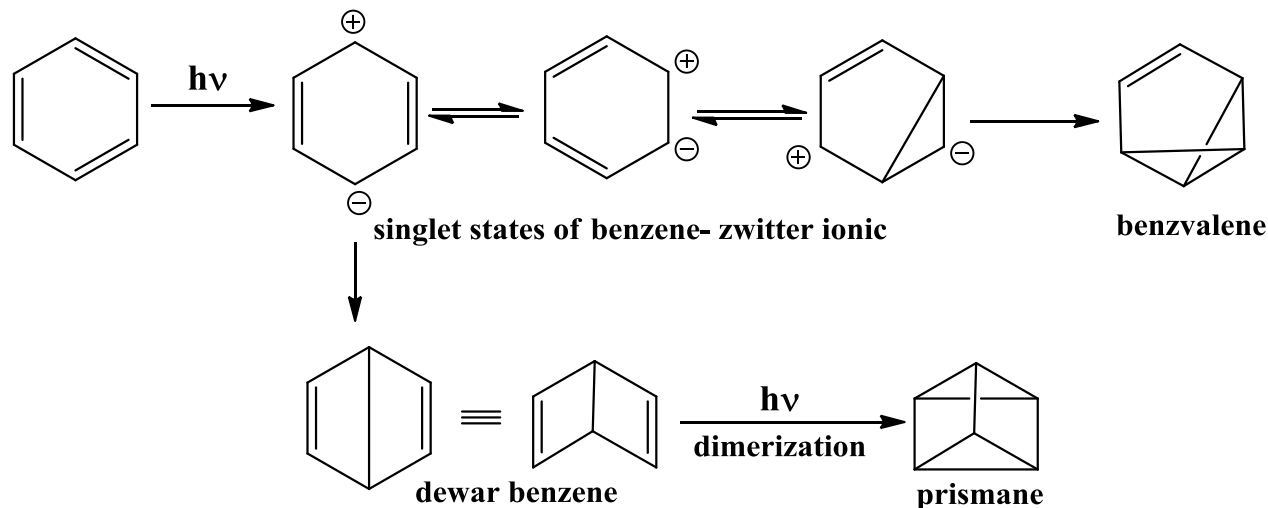Due to the presence of diene in two conformations, two skeletal products are possible.

Mechanism
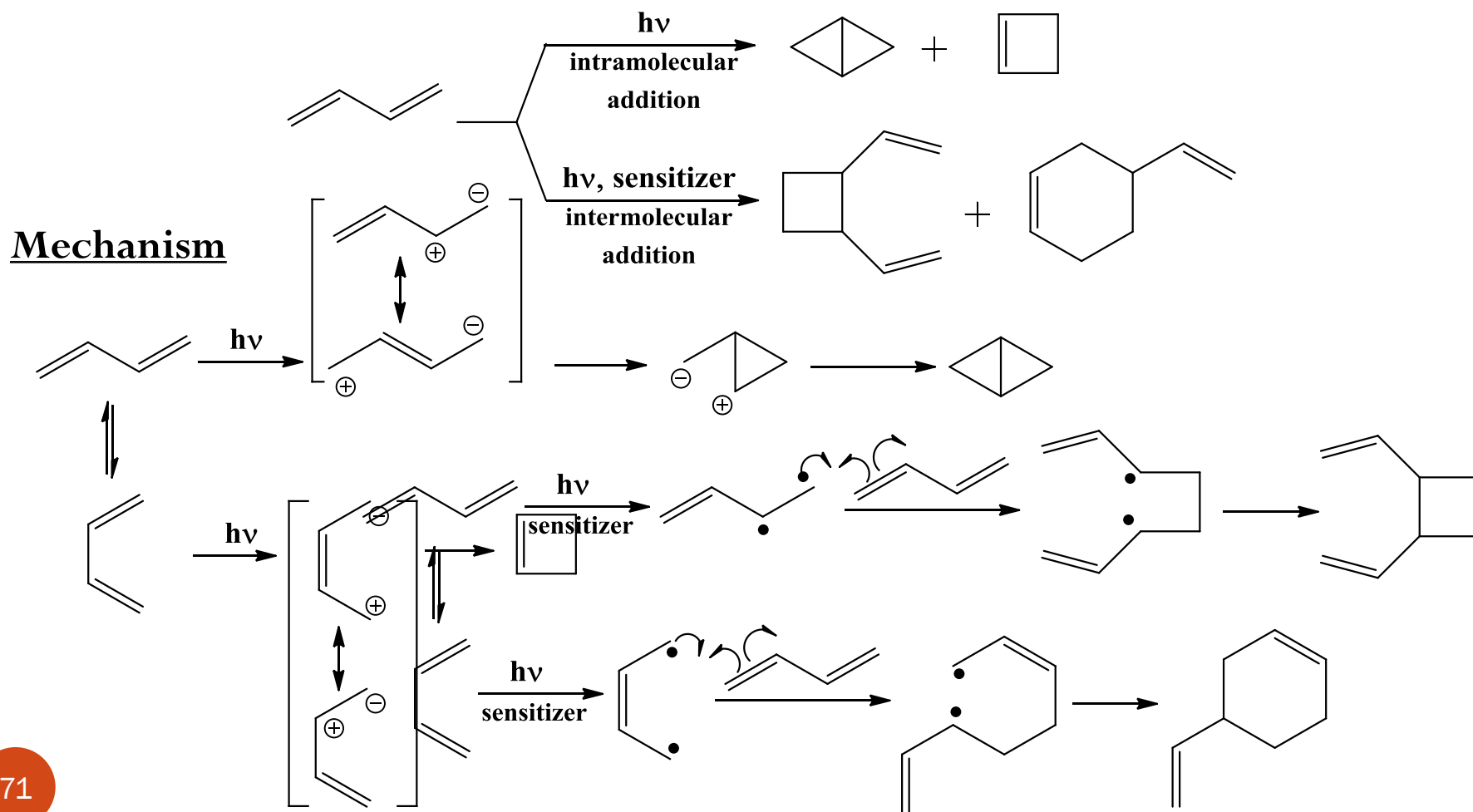
(d) Photoisomerisation of benzene.

What simple benzene can do when irradiated <u>solely</u> by UV light?

singlet states of benzene- zwitter ionic

benzvalene

dewar benzene

prismane

(e) Photocycloaddition of benzene and related compounds.

Benzene and related compounds in the presence of double bond (alkene, alkyne, diene) can undergo cycloaddition reactions.

(e) Photocycloaddition of benzene and related compounds.