Notes on
Organic photochemistry

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By

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Photochemistry is the study of reactions that are brought about by the action of visible or ultraviolet light.

$$6CO_2 + 6H_2O \xrightarrow[\text{Chlorophyll}]{\text{Sunlight}} C_6H_{12}O_6 + 6O_2$$

Chapman's definition: It is the science arising from application of photochemical methods to organic chemistry and organic chemical methods to photochemistry.

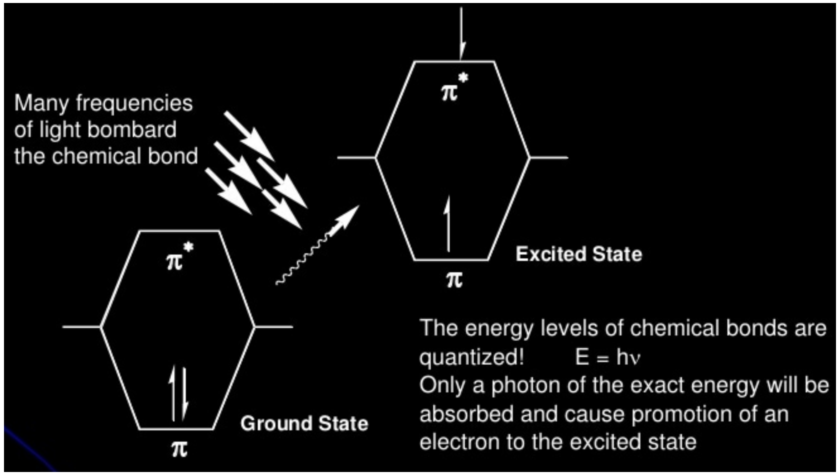
Basic Principles

In order to bring about a chemical transformation, a certain amount of energy is provided to molecules by irradiating the molecule with certain wavelength of electromagnetic radiation when the molecule absorbs a photon and gets excited. The wavelength of elctromagnetic region in general lies in the ultraviolet region or less frequently in the visible region of the spectrum. The basic relationship of energy of radiation to frequency and wavelength are given by the expression-

$\varepsilon = h\upsilon$; ε= energy per quantum, h= Planck's constant= 6.63×10^{-34} Js, υ= frequency of radiation

The energy absorbed per mole at a specific wavelength can be calculated by following the equation-

$E = Nh\upsilon = Nhc/\lambda$; E= energy per mole, N= Avogadro's number,
c= velocity of light, λ= wavelength of radiation



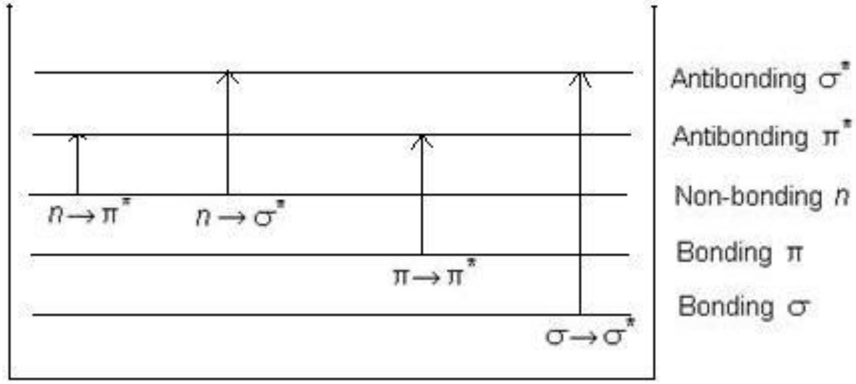
The energy levels of chemical bonds are quantized! E = hν
Only a photon of the exact energy will be absorbed and cause promotion of an electron to the excited state

Light in the visible and ultraviolet region has sufficient energy to cover the range of chemical bond energies. When a molecule absorbs a photon of the appropriate energy, one of its electrons is raised to an orbital of higher energy i.e. an electron from its highest occupied molecular orbital (HOMO) is excited to the lowest unoccupied molecular orbital (LUMO) of the molecule. The resulting molecule may take part in a reaction in this excited state. The reaction so induced may be either intramolecular e.g. rearrangement or dissociation, or intermolecular, for example-addition reactions. On the other hand, the excited molecule may also transfer its energy to another molecule which in turn can undergo reaction. These variants open up a wide range of synthetic possibilities.

Different types of electronic transition in organic molecules

The valence electrons of organic compounds in the ground state are accommodated in σ-MOs , π-MOs, and nonbonding molecular orbitals . For each of the bonding σ or π-MO, there is a corresponding antibonding σ^* or π^* orbital.

Electronic transition due to photochemical excitation of molecules involve the promotion of an electron from σ or π-MO or NBMO to one of the antibonding orbitals σ^* or π^*.



The order of energy required for various electronic transition is given below-

$$\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$$

$\sigma \rightarrow \sigma^*$ - Alkanes (no n or pi electrons)

$n \rightarrow \sigma^*$ -Alcohols, amines, ethers etc.

$\pi \rightarrow \pi^*$ - aldehydes, carboxylic esters, alkenes.

$n \rightarrow \pi^*$ - aldehydes, ketones, carboxylic esters

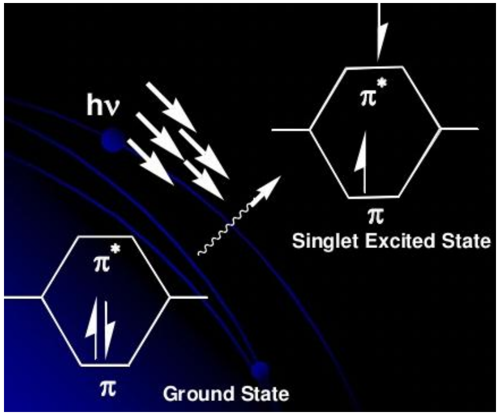
In photochemical reactions, the most important type of electronic excitation in organic molecules are $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. These transitions have lower energy requirements and occur at longer wavelengths, usually well within uv light. The energies required for $\sigma \rightarrow \sigma^*$ and $n \rightarrow \sigma^*$ are usually very high, requiring a wavelength far below 200 nm. Therefore, photochemical reactions are usually limited to those in which at least one of the reactants is unsaturated or aromatic.

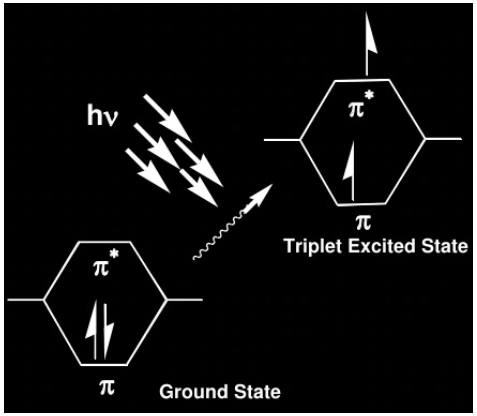
Photophysical processes

In the ground state of the molecules, most of the organic compounds remain in spin paired state. This state is denoted by S_0 state. When a molecule absorbs a photon of a particular wavelength, an electron from the bonding level is promoted to an antibonding level depending on the size of the quantum of energy provided by the photon.

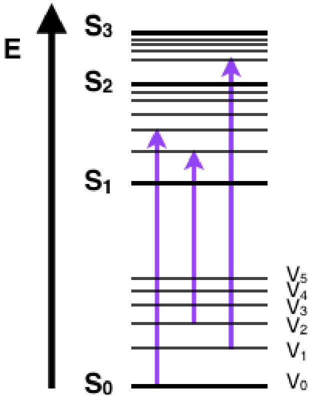
❖ If an electronic transition takes place with the conservation of spin state of the molecule, this means that the molecule is photoexcited from S_0 to S_n state, n= 1,2,3...etc. The excited state is known as singlet excited state.

❖ In many cases, electronic excitation is followed by spin inversion, thus giving rise to a new excited state. This state is called triplet excited state or T_n.



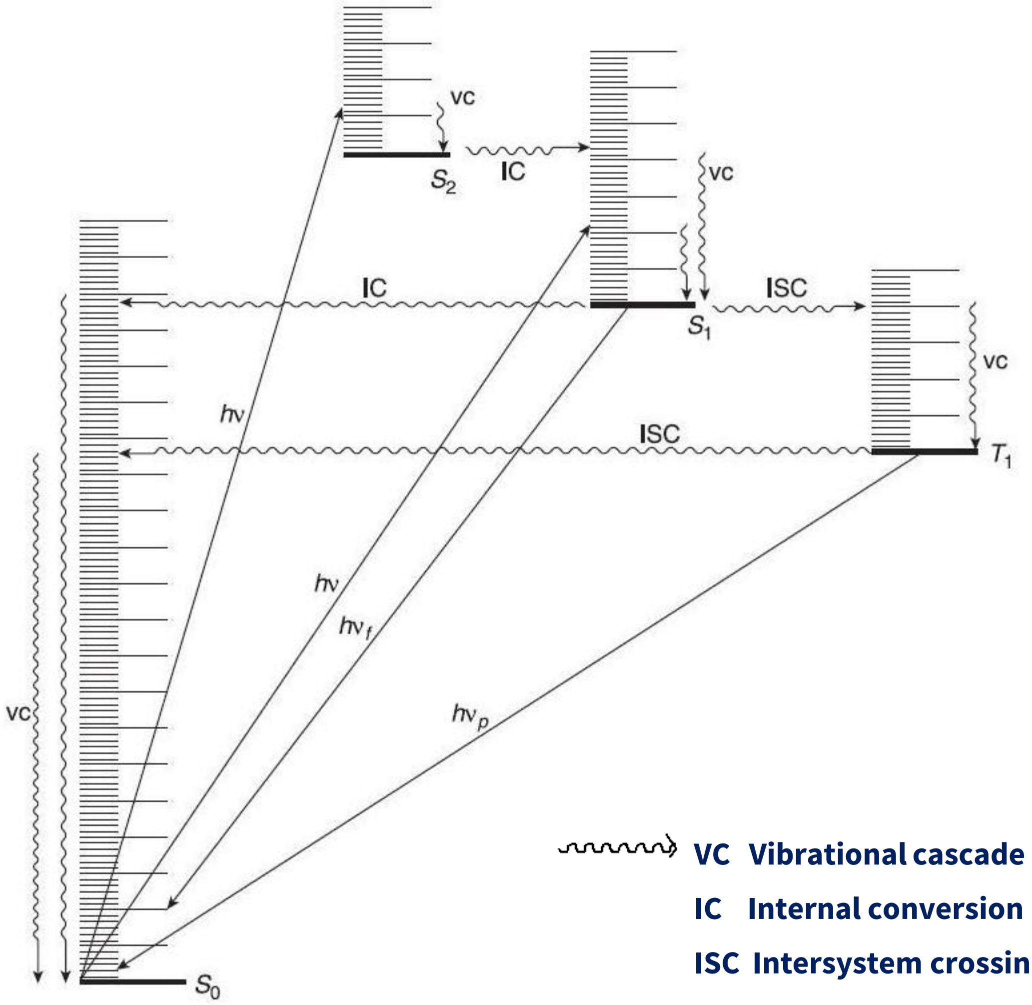


Suppose, a molecule is photoexcited from S_0 to S_n state, where n is the higher electronic state of the molecule. There are many more photophysical processes which can cause energy dissipation by the photoexcited molecule. Of these, the uni- and bi-molecular processes are given below-



Unimolecular processes-	Bimolecular processes-
❖Internal conversion (IC)	❖Solvent quenching
❖ Fluorescence ($h\upsilon_f$)	❖ Self-quenching
❖ Intersystem crossing (ISC)	❖ Impurity quenching
❖ Phosphorescence ($h\upsilon_p$)	❖ Electronic energy transfer (ET)

Jablonski diagram



⇝ VC Vibrational cascade

IC Internal conversion

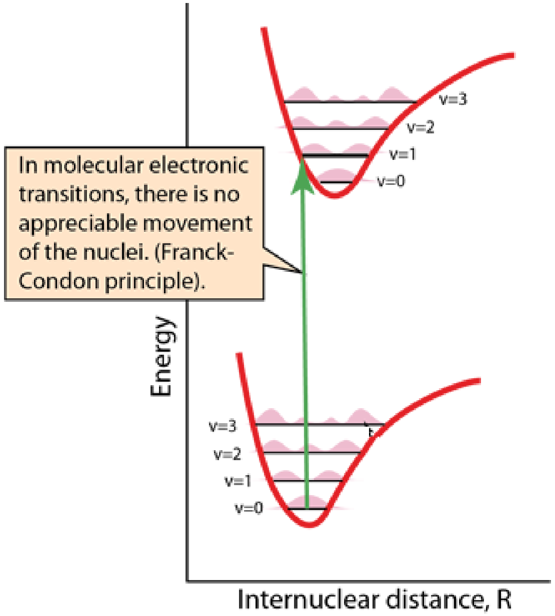
ISC Intersystem crossing

$h\nu_f$ Fluoroscence

$h\nu_p$ Phosphorescence

Franck Condon principle

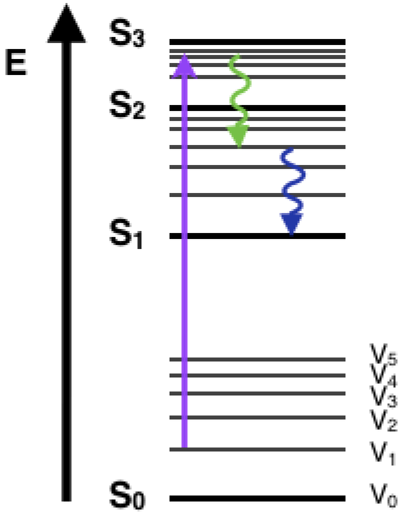
Franck-Condon principle provides a useful guiding principle for investigating the vibrational structure of electronic spectra. It states that an electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition. The principle is true in the sense that since the electrons move so much faster than the nuclei that during the electronic transition the nuclei do not change their position. Hence an electronic transition may be represented by a vertical line on a plot of potential energy versus internuclear distance.



Internal conversion:

This is a non-radiative unimolecular energy dissipation process. When a molecule absorbs a photon of a particular wavelength, the molecule is raised to ground electronic state to higher electronic states depending on the amount of energy provided by the photon, i.e. the molecule is photoexcited from S_0 to S_n state where n=1,2,3....etc. The life time of upper excited singlet states (n=2,3,4....) is usually less than 10^{-11} s and they rapidly decay to the lowest level S_1 by successive release of energy. These energy cascades of the electron involve overlapping vibrational states of each electronic state of the molecule. So, these energy cascades are called vibrational cascades (VC) in which excess electronic energy is dissipated in the form of heat called nonradiative path. Such VC from one electronic state to the other is called internal conversion (IC). IC from S_n, S_{n-1},.....to S_2 are quite common but IC from $S_1 \rightarrow S_0$ is not so fast due to the high energy gap between S_0 and S_1 levels. Most of the higher electronic states S_2, S_3,.....etc. cannot lead to chemical transformation due to their short life time compared with the collision frequency (~10^{-8} s) required for any chemical transformation. Of all the excited singlet states, S_1 has the longest life (10^{-8} s) and is very important in photochemistry.

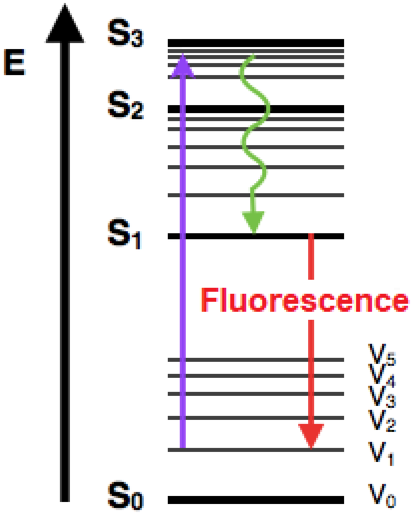
S_1 may undergo one of the following four energy degrading processes- (i) It may emit the energy as photon and drop to S_0. This process is called fluorescence and generally occurs within 10^{-9} to 10^{-6} s. (ii) It may return to S_0 by nonradiative process in which excess energy of the excited state is shuffled into vibrational modes. (iii) S_1 may undergo chemical reactions and finally (iv) its decay to triplet state may occur before any of the above processes take place.



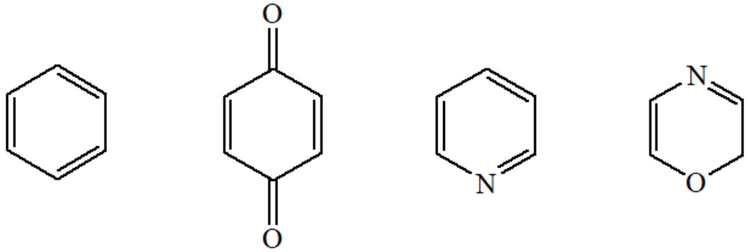
Fluorescence:

It is the process where a material absorbs light at a higher energy, short wavelength and emits light at a lower energy, usually visible, wavelength. In other words, it is a radiative unimolecular energy dissipation process and is caused due to $S_1 \rightarrow S_0$ transition. The emitted radiation is of lower frequency than the absorbed radiation due to the vibrational relaxation of the primary excited state $S_1(V=V_n)$ to S_1 $(V=V_0)$ state.

Organic molecules that possess more or less rigid structure and cannot lose their energy through many vibrational levels generally fluoresce. Certain groups that are part of such molecules are called fluorophores. The following groups are the examples of fluorophores:



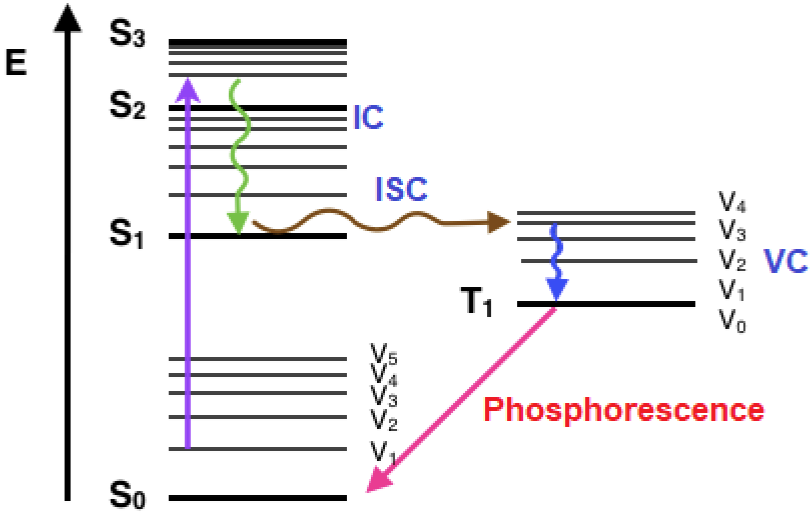
$C=C$ $N=O$ $N=N$ $C=O$ $C=N$ $C=S$



Intersystem crossing:

If the singlet state S_1 is sufficiently long-lived, as in aromatic and carbonyl compounds, and if S_1 and the corresponding triplet state T_1 are close in energy, then the $S_1(v_0)$ state may crossover to the $T_1(v_n)$ state in a slow process. The crossover is slow in accordance with the spectroscopic rule that change in multiplicity is a formally forbidden process. The $T_1(v_n)$ state then vibrationally cascades down to $T_1(v_0)$ state. Therefore this process can be looked upon as $S_1(v_0) \rightarrow T_1(v_0)$ transition with loss of heat energy. This non-radiative unimolecular energy dissipation by the $S_1(v_0)$ state is called intersystem crossing (ISC).

This process is very important for photochemical reactions as T_1 exists for a much longer period of time (10^{-3} to 1 s). This implies that molecules in the T_1 state may undergo many effective collisions leading to chemical reactions. So, photochemical reactions are favored by the long life of T_1 state. Many aromatic ketones and other aromatic compounds have high intersystem crossing efficiencies while due to the rather high energy gap between two states of olefin, the latter have a lower tendency to intersystem crossing.



Intersystem crossing leads to several interesting routes back to the ground electronic state. T_1 state may either undergo a chemical reaction or may return to the ground state (S_0) by emission of a photon, a process known as phosphorescence. The third alternative for the triplet state is to return to S_0 by radiationless decay.

Phosphorescence:

The photoexcited molecules in the $T_1(v_0)$ state is most likely to undergo photochemical changes. But this may also lose or dissipate energy through a unimolecular radiative path called phosphorescence. The lifetime of phosphorescence is usually in the range of 10^{-3} to 10 s. It is a slow process due to the spin forbiddenness and is caused due to $T_1(v_0) \rightarrow S_0$ transition. When a molecule has both fluorescence and phosphorescence, the wavelength of phosphorescent light is always longer than that of fluorescent light (since the energy gap of $S_1 \rightarrow S_0$ is higher than the energy gap of $T_1 \rightarrow S_0$). It is always a delayed process.

Energy transfer:

T_1 state cannot be directly populated from S_0 state by irradiation due to spin forbiddenness and also due to the fact that in most cases the energy gap between $S_1(v_0)$ and T_1 (v_n) states is too large for any crossover from $S_1(v_0)$ to $T_1(v_n)$ state. Energy transfer is a means to populate T_1 state. Some photoexcited molecules called donors, where the T_1 state can be easily populated via ISC from S_1 state, can transfer their T_1 energy to the S_0 state of some other molecules called acceptor molecules, where populating the T_1 state is not possible by ISC and thereby can directly populate the T_1 state of the acceptor molecule and themselves return to the ground state. This process is called energy transfer (ET) and plays a very important role in bringing about photochemical reactions. The phenomenon is called photosensitization. It is a process of initiating a reaction through the use of a substance capable of absorbing light and transferring the energy to the desired reactants.

The basic requirement for energy transfer is that the donor molecule should have at least 5 kcal/mole more energy than the energy required to excite the acceptor molecule to its lowest excited state. Under these conditions, energy transfer does take place on every collision between the excited donor molecule and the ground state acceptor molecule. Ketones and aldehydes are good examples of donor molecules and alkenes are examples of acceptors. A typical mechanism for triplet energy transfer involves the excitation to S_1 of donor molecule on irradiation, and the subsequent decay of S_1 to T_1. Collision of the T_1 donor with the ground state acceptor molecule produces a T_1 acceptor and ground state donor molecules. This photosensitization phenomenon can be represented as follows with symbols D for donor and A for acceptor.

$$D(S_0) \xrightarrow{h\nu} D(S_1)v_0 \overset{\text{ISC}}{\rightsquigarrow} D(T_1)v_n \rightsquigarrow D(T_1)v_0$$

$$D(T_1)v_0 + A(S_0) \xrightarrow{\text{ET}} D(S_0) + A(T_1)v_0$$

Laws of photochemistry

Photochemical processes are governed by two laws, namely

First law of Grotthus-Draper law: It is an empirical law, which states that when a substance is irradiated, only that fraction of the radiation that is absorbed by the substance can bring about photochemical changes. The reflected or scattered or transmitted portions of the incident light play no role in the chemical changes.

Second law of Stark-Einstein's law of photochemical equivalence: It states that each quantum or photon absorbed by a substance can activate only one molecule of it in the primary step of a photochemical equivalence.

But this rule does not imply that each excited or activated molecule will take part in the chemical change. Only in ideal cases, such things happen, i.e., every activated molecule undergoes chemical transformation. But in most cases, it is not so. Many activated molecules undergo deactivation by various quenching and photophysical processes.

Quantum yield

The efficiency of a photochemical process is usually expressed in terms of quantum efficiency or quantum yield (Φ), which is defined as-

$$\Phi = \frac{\text{Number of molecules reacting in a given time}}{\text{Number of quanta of radiation absorbed in the same time}}$$

$$= \frac{\text{Number of molecules of the product formed}}{\text{Number of quanta absorbed}}$$

Only in ideal cases, $\Phi = 1$. In practice, however, Φ has been found to have a very low value (as low as 0.01) and also a very high value (as high as 10^6). The low Φ values are very common for those reactions where the activated molecules are readily deactivated by different quenching processes, or where the primary products formed recombine to give back the parent compound.

The high Φ values found in some chain reactions, where the primary products formed as free radicals can trigger a chain reaction involving the parent molecules.

Types of photochemical reactions

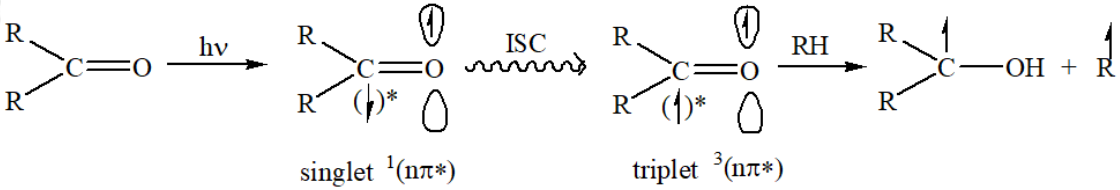
1. Photodissociation: Since the electrons are weakly held in the excited state, the molecule may be more easily dissociated.
2. Because of Franck-Condon principle, unusual vibraional and rotational levels may be achieved that can bring about chemical changes not normally possible in the ground state as in valence isomerization of benzene.
3. The photoexcited electron is more likely to be easily removed by an electrophile as in photooxidation.
4. The photoexcited state may interact with any other odd electron species to form a bond.
5. For systems with a variable valency as in the case of coordination compounds, a redox reaction may be set up either intramolecularly or intermolecularly.

The reaction of excited states including both singlet and triplet can be classified under the following headings: reduction, addition, rearrangement, oxidation, aromatic substitution and fragmentation.

Photolytic reactions of carbonyl compounds:

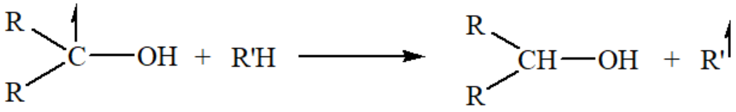
- Two readily accessible transition in a carbonyl group are n → π* and π → π* transitions. These transitions take place at around 285 nm (n → π*) and 180 nm (π → π*).
- Since NBMO and antibonding π* MO are perpendicular to each other, the n → π* transition in carbonyl compound is overlap forbidden. But due to unsymmetrical molecular vibrations, this transaction takes place slowly. The π → π* transition is an allowed process.
- Due to the small energy gap between S1 and T1 states, ketones undergo intersystem crossing with high degree of efficiency. As a result, most of the photochemistry of ketones arises from their triplet states. The nature of products of such reactions, very frequently depends on the structure of ketone and medium of irradiation.

Photoreduction: Carbonyl compounds can be converted into 1,2-diols (pinacol) and alcohols by irradiation in presence of a hydrogen donating compound such as alcohols, amines or hydrocarbons. Reaction occurs through triplet state of the carbonyl compound which abstracts a hydrogen atom from the second reactant. The lowest singlet excited state of ketones is $S_1(n\pi^*)$ state.

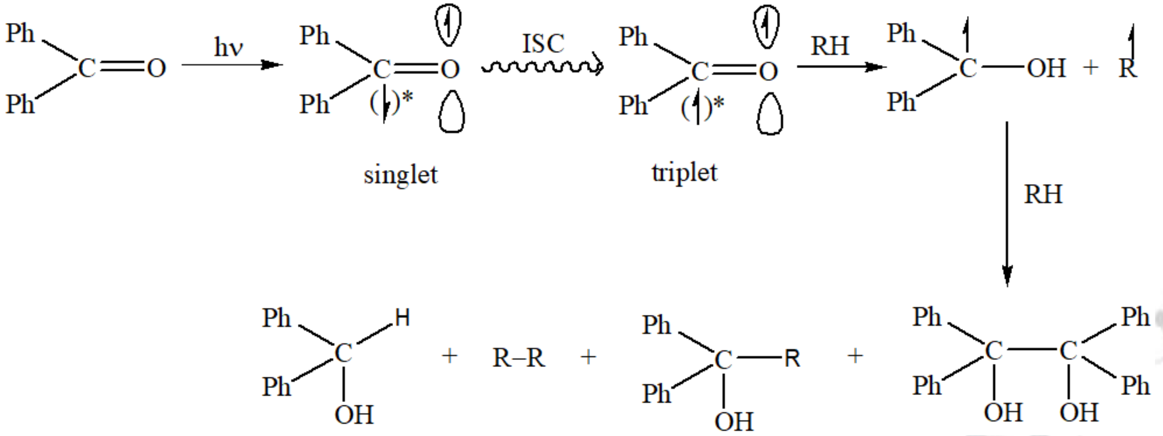


The resulting radicals either combine,

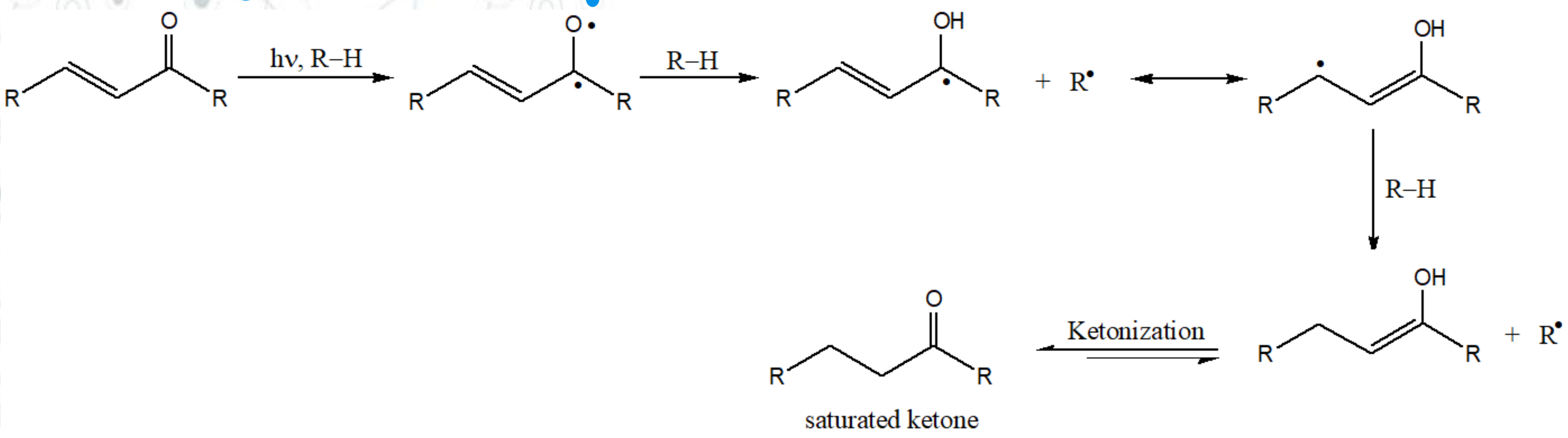
Or abstract hydrogen from the solvent,



The latter reaction is favoured when R’· is a stabilized radical (e.g. tertiary) and the coupling reaction is favoured when R is a radical stabilizing group (e.g. aryl). The coupling reaction is usually most efficient when the hydrogen donor is itself the alcoholic reduction product of carbonyl compound. For example, in case of benzophenone



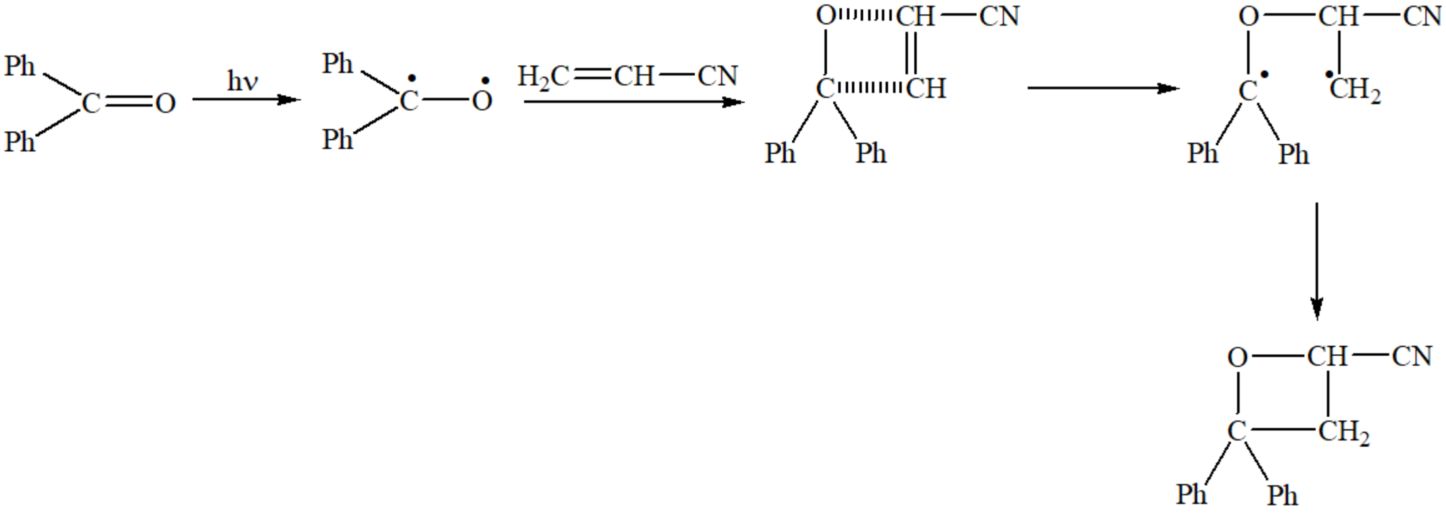
α,β-unsaturated ketones under similar condition often form saturated ketones.



$$R^{\bullet} + R^{\bullet} \longrightarrow R{-}R$$

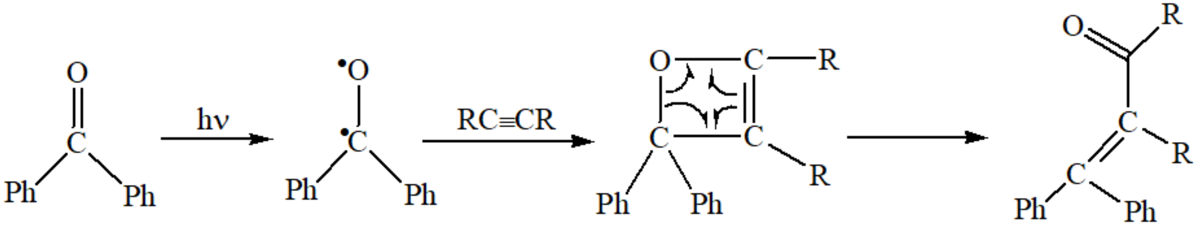
The hydrogen abstraction reaction is much more efficient in the n,π* state of ketones than in the π,π* state, because of the high electron density on O-atom in 3(ππ*) ketones , such oxygen atom cannot abstract a hydrogen atom but shows a tendency to abstract a proton instead.

Photocycloaddition of ketones with C=C and C≡C (Paterno-Buchi reaction): Carbonyl compounds yield oxetanes on irradiation in presence of olefins. This photocycloaddition is usually referred to as Paterno-Buchi reaction. This photoaddition normally occurs by reaction of the triplet state of the carbonyl compound with the ground state of the alkene. As in photoreduction, it is more efficient when the triplet is of (n,π*) type rather than (π,π*) type.



Oxetanes

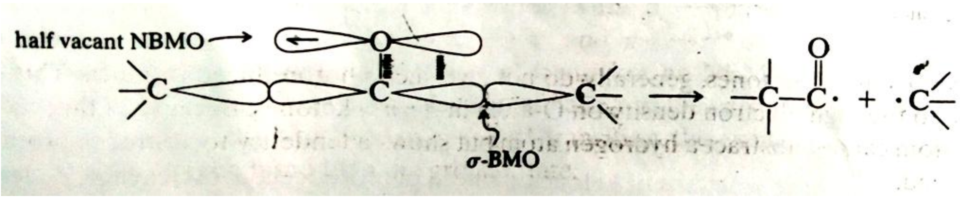
^{3}(nπ*) undergo cycloaddition with C≡C to form unstable oxetenes that quickly isomerize to α,β-unsaturated ketones.



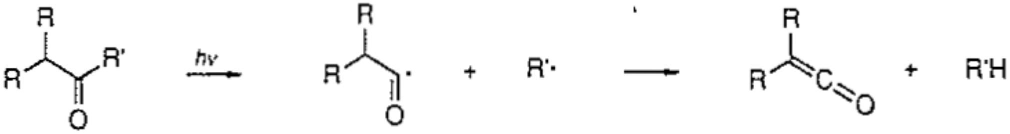
Photolysis of carbonyl compounds: Carbonyl compounds on irradiation alone generally undergo a cleavage of C-C bond giving a number of products. The n → π* excitation of aldehydes and ketones can bring about two types of fragmentation.

First, fragmentation can occur of the C-C bond adjacent to carbonyl-

Thus, when cleavage of the C-C bond α to the carbonyl group takes place, it is called ***Norrish type I reaction***. This cleavage takes place by the $^3(n\pi^*)$ state of the ketones. The half vacant NBMO of $^3(n\pi^*)$ state overlaps the σ-BMO of the α-C-C bond. This facilitates the cleavage of the α-C-C bond.

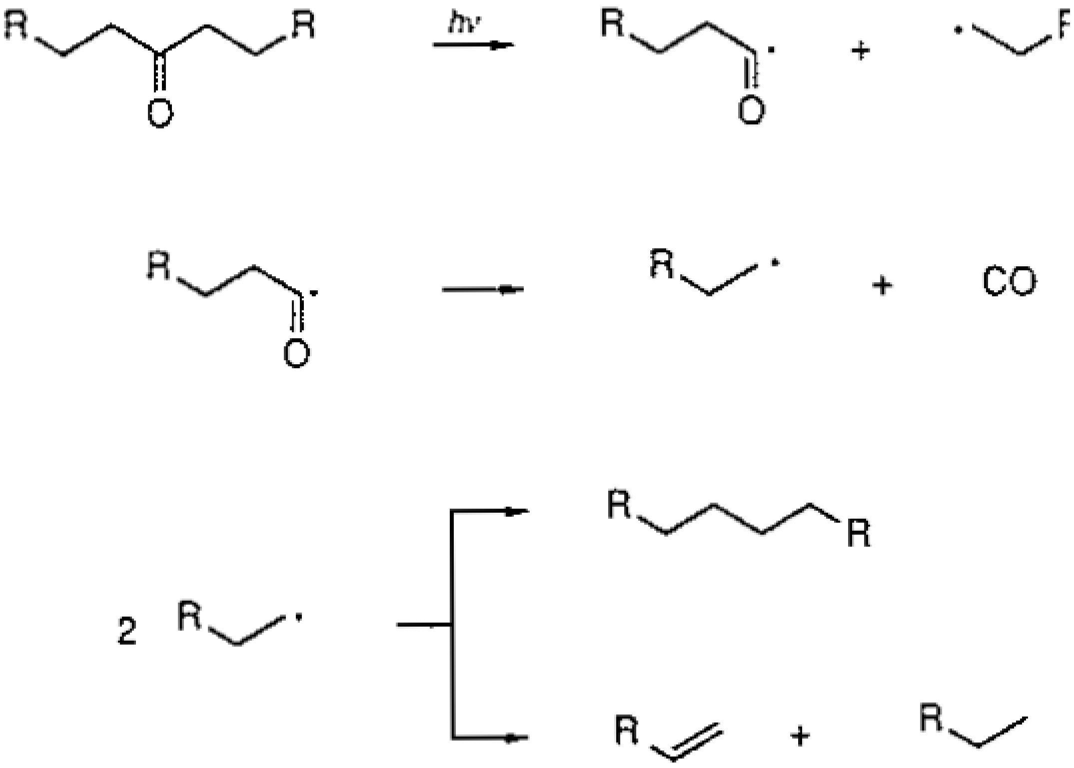


The cleavage is generally followed by one or more of three reactions depending on the reaction conditions: disproportionation to give a ketene,

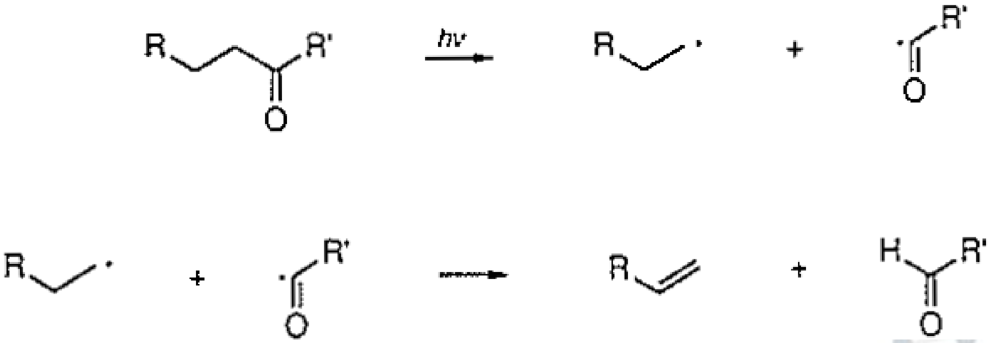


Decarbonylation and then dimerization and/or disproportionation or intermolecular H atom abstraction by acyl radical.

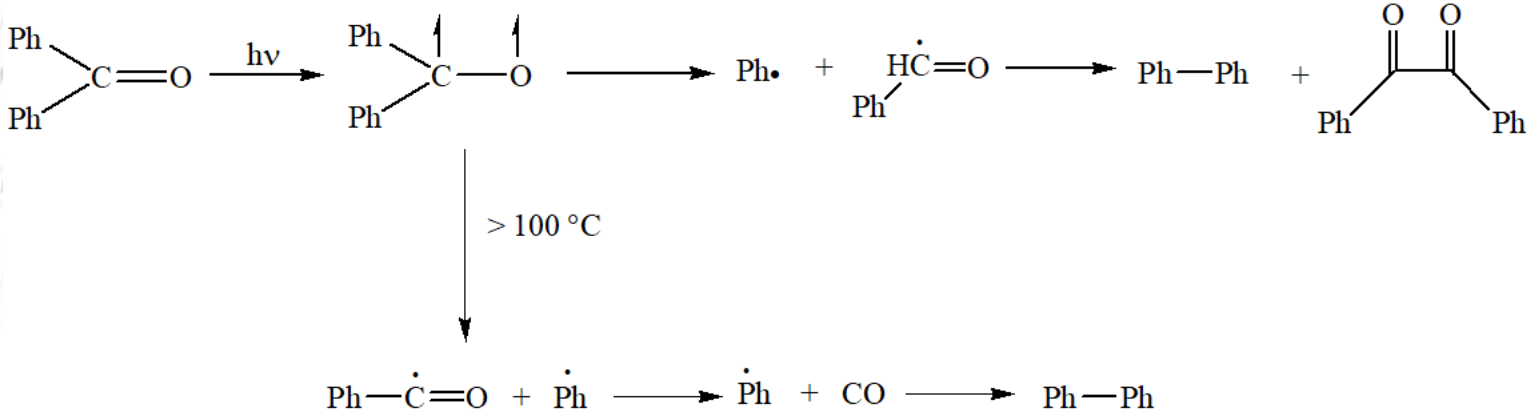
For example,



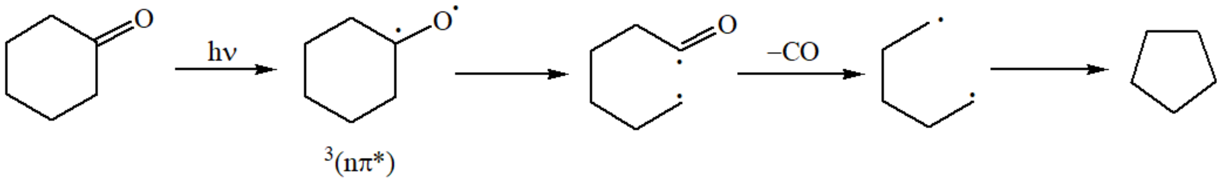
Intermolecular H atom abstraction by acyl radical



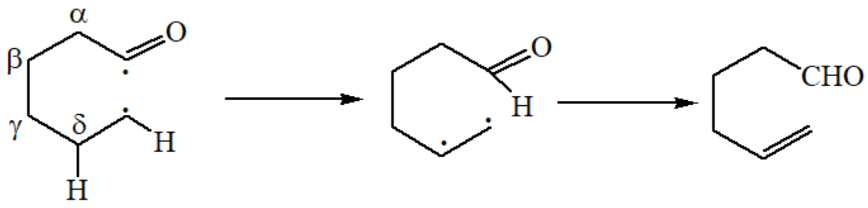
Benzophenone on α-cleavage at room temperature gives benzil and biphenyl as main products but above 100 °C, practically no benzil is formed. The benzoyl radical decarbonylates to form biphenyl as the main product.



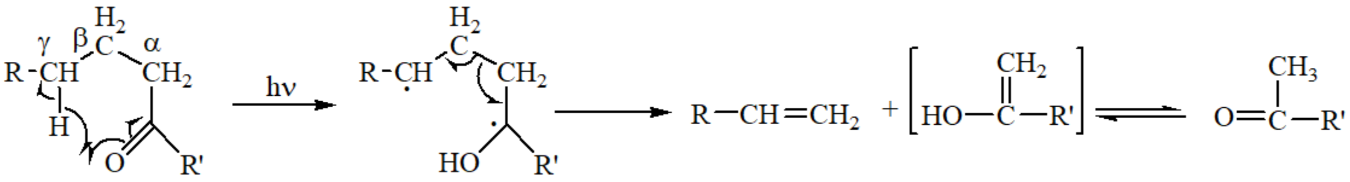
In case of cyclic ketones, it forms diradicals in the primary reaction. The diradical may decarbonylate, and the resulting new diradical may cyclize if a strainless ring formation is possible.



The diradical formed in the primary reaction may also abstract a δ-H atom to form an unsaturated aldehyde.

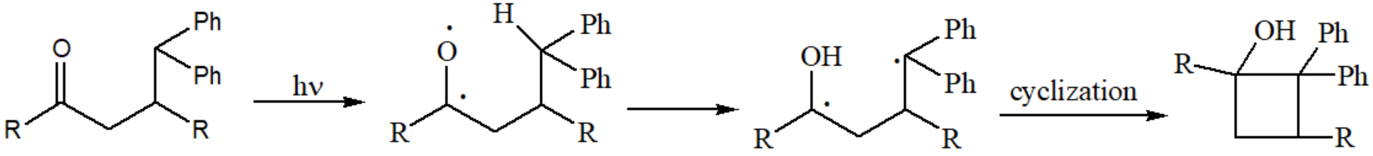


If the carbonyl compound contains a γ-H atom, intramolecular H-atom abstraction can occur. This β-cleavage is known as ***Norrish type II reaction***. The reaction proceeds by the initial γ-H abstraction by the oxygen atom yielding a 1,4-biradical which subsequently cleaves to an olefin and an enol. In some cases, ring closure also occurs.

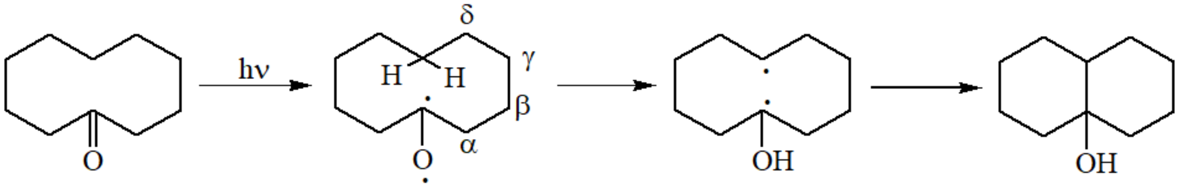


Both n,π* singlet and n,π* triplet participate in the intramolecular hydrogen abstraction reactions while ketones with a low lying π,π* state do not undergo this reaction.

If alkyl or aryl group is present in the γ-C atom of the ketone, then cyclization reaction of the primary diradical competes with β-cleavage.



In case of smaller cyclic ketones, type I process predominates, while for larger rings type II process can occur. In case of some cyclic ketones, H abstraction may take place from a C atom beyond the δ-position and the formation of cyclized product may compete with β-cleavage if conformation allows.

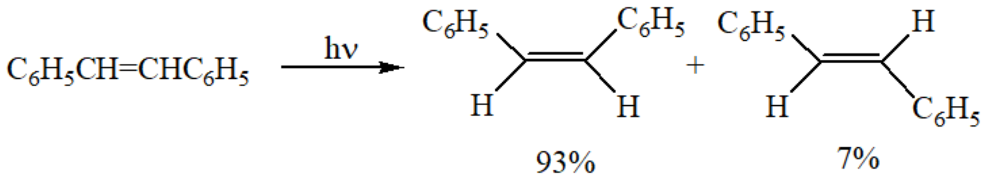


Photochemistry of alkenes: In the phtoexcitation of a C=C bond in alkenes, only (ππ*) state is involved. But since ISC of S1 → T1 is inefficient, the 3(ππ*) can only be populated via photosensitization.

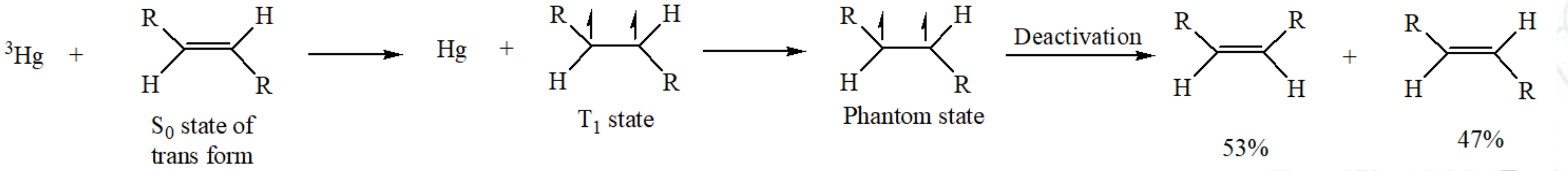
The products formed in the photoreaction of alkenes depend on the following factors:

1. Nature of the olefin
2. The number of C=C present in the molecule and their relationship with one another
3. The excited state

Cis-trans isomerization of alkenes (Photostereomutation): Olefins usually undergo cis-trans isomerization upon irradiation with ultraviolet light. The usefulness of the reaction lies in the fact that in photostereomutation, the thermodynamically less stable cis isomer may be obtained as the major component of the product mixture.



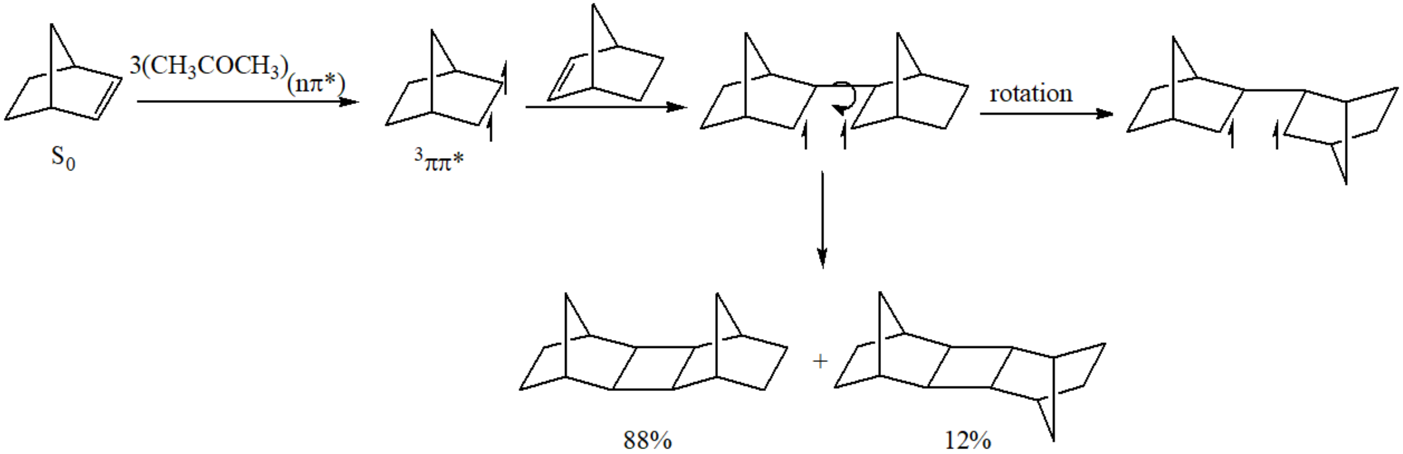
The transformation can be effected by direct irradiation of the olefins or by irradiation in the presence of a sensitizer. It may either take place through a singlet or triplet excited species. It is however known that isomerization in the triplet state possess a lower barrier to rotation around the carbon-carbon bond.



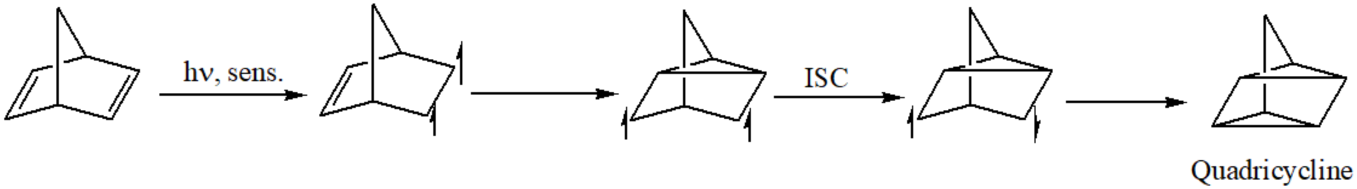
Here, mercury photosensitized isomerisation takes place through T_1 state of the alkenes. Isomerization can occur because π bond which normally prevents it, is lost in passage to the excited state. In the excited state, the structure around the C-C σ-bond is twisted by approximately 90°. This distorted configuration of the excited state is called phantom state in which the distinction between cis and trans form is lost. The phantom state then collapses to the ground state by conventional deactivation process. In doing so, C-C σ bond can be twisted in either of the two directions to give both cis and trans isomers. Since more of the trans isomers are preferentially excited to the phantom state, therefore the photostationary state obtained by the deactivation of the phantom state will contain a higher percentage of the thermodynamically less stable cis form.

This process of obtaining the less stable stereoisomer by photostereomutation is called optical pumping.

- **Dimerization of alkene**: Olefins may also undergo dimerization reaction. The process involves generation of an excited triplet molecule which subsequently reacts with a ground state olefin molecule. It occurs through $^3(\pi\pi^*)$ state. For example- acetone sensitized photodimerization of norbornene.



Similar dimerization may also take place intramolecularly.



Alkenes can also be photodimerized by direct irradiation in [2 + 2] cycloaddition reaction giving stereospecific products..