

Photochemistry of enones

M.Sc. Sem II

Dept. of Chemistry

Presented by

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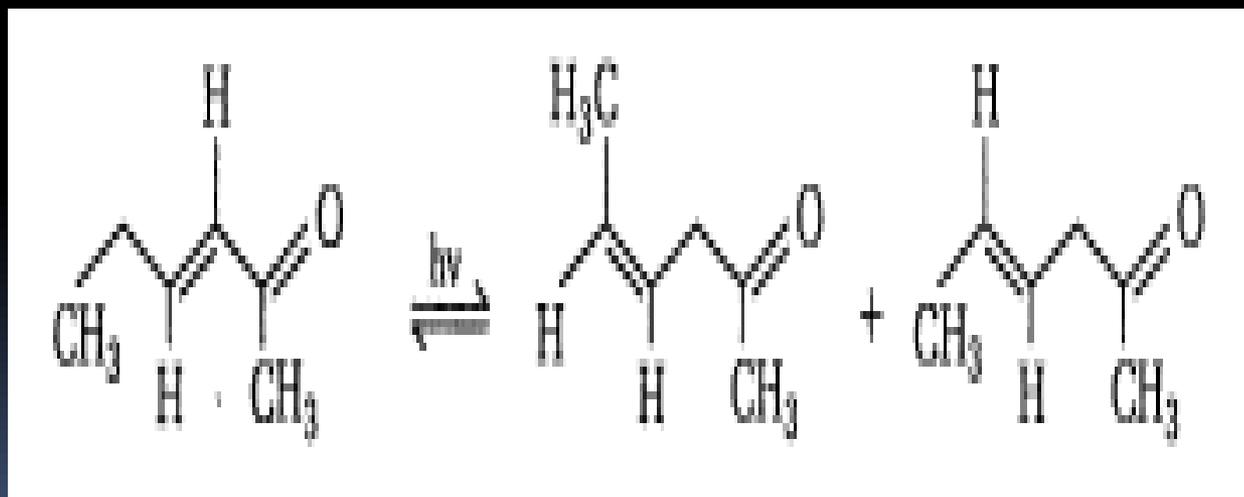
Patna University

*α - β unsaturated carbonyl
Compounds*

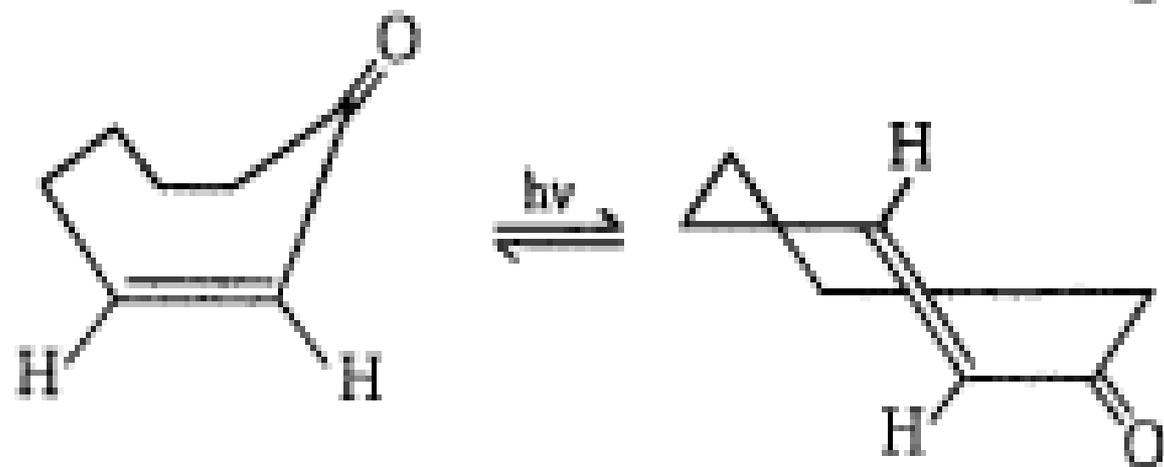
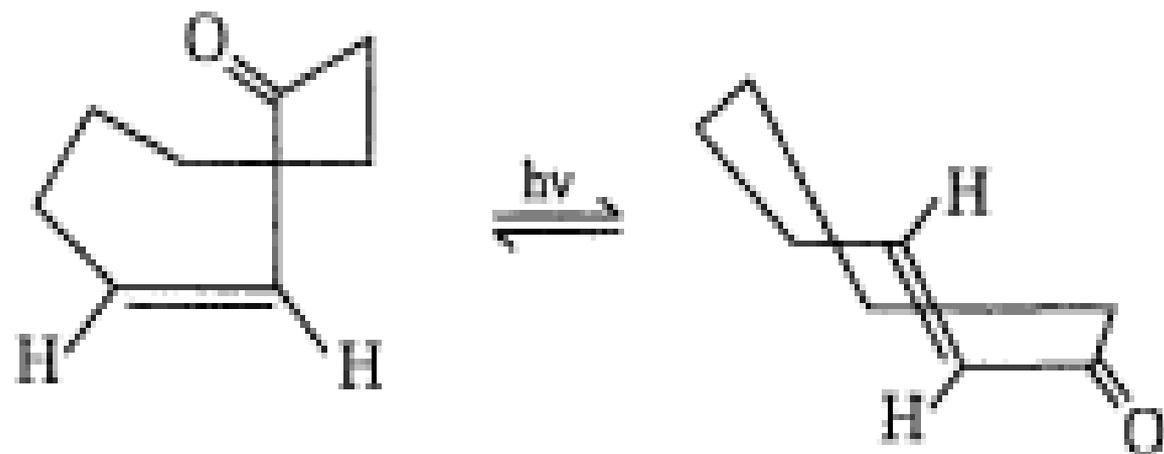
- Most of the α - β unsaturated carbonyl compounds undergo photochemical change by migration of the π bonds to β - γ unsaturated ketones, dimerise photochemically [$\pi^2s+\pi^2s$], cycloaddition and rearrangement

Photoisomerisation

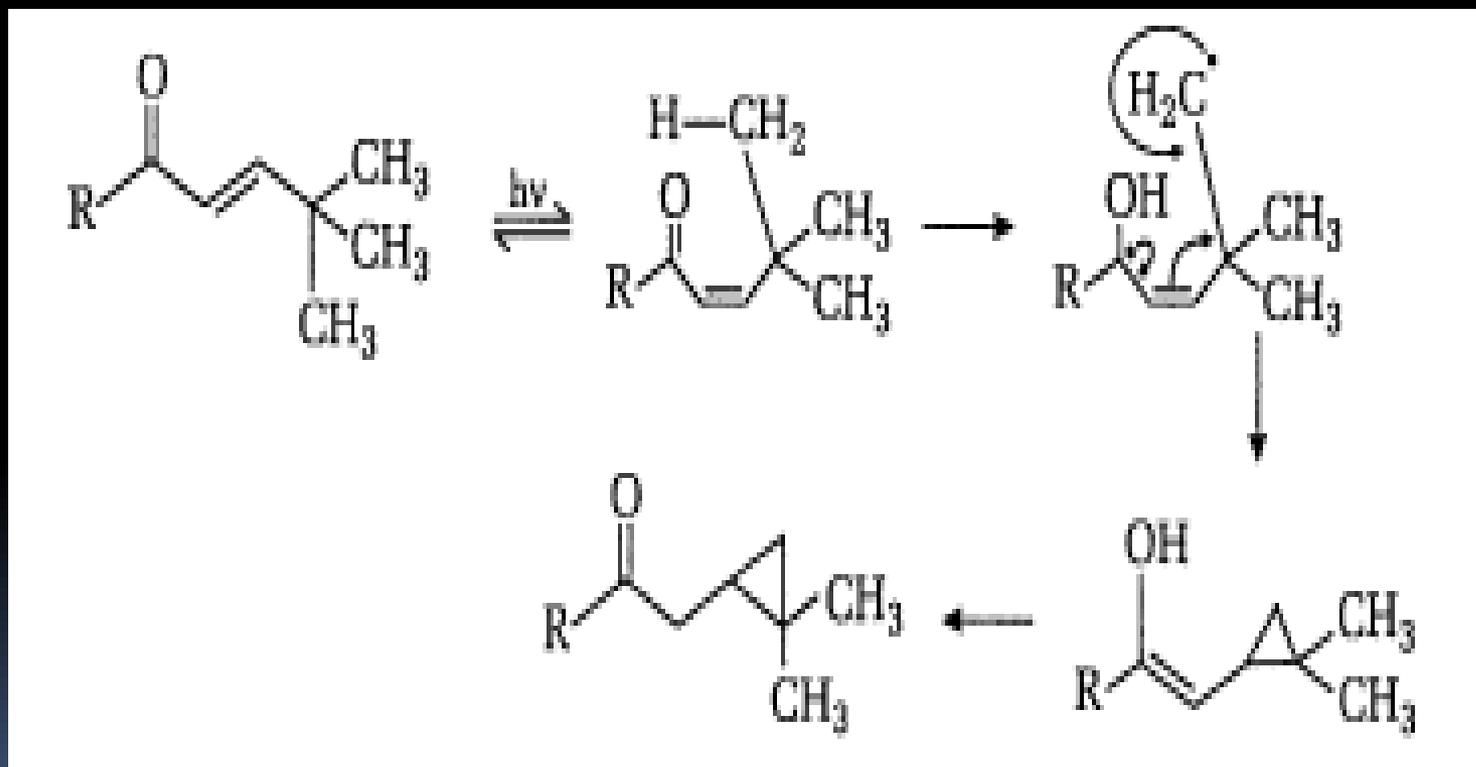
- Easiest and fastest photochemical reaction of acyclic and cyclic α - β unsaturated carbonyl compounds is cis-trans isomerisations. This is expected to involve triplet π - π^* transition



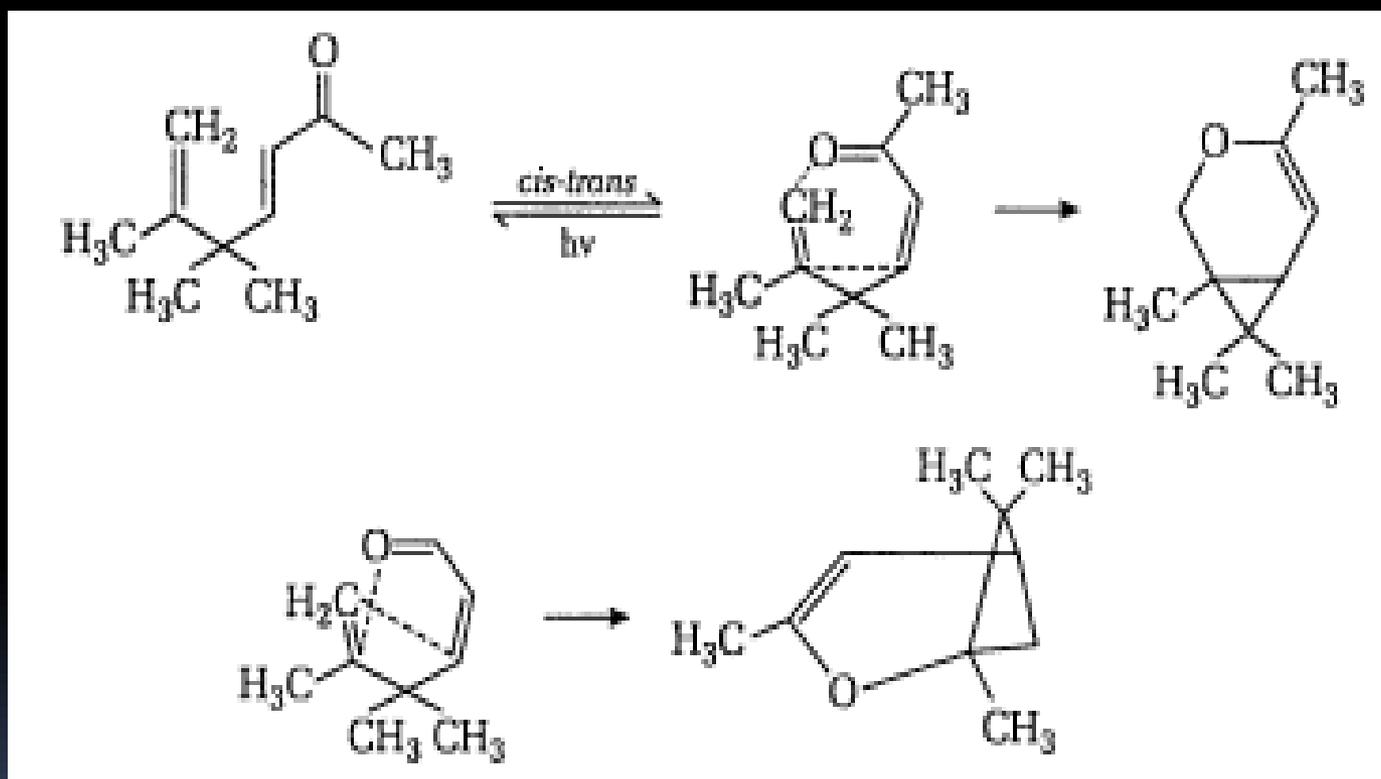
- The rearrangement is due to intramolecular hydrogen abstraction from γ carbon
- Both cyclic as well as acyclic compound undergo such reaction.
- not expected for cyclopent-2-enone because of high strain energy, but it has been reported for cis cyclo-2enone and cis cyclohept-2-enone.



- When there is lack of γ hydrogen to the carbonyl group, photolysis result in an intramolecular δ -hydrogen transfer through a seven membered cyclic transition state.

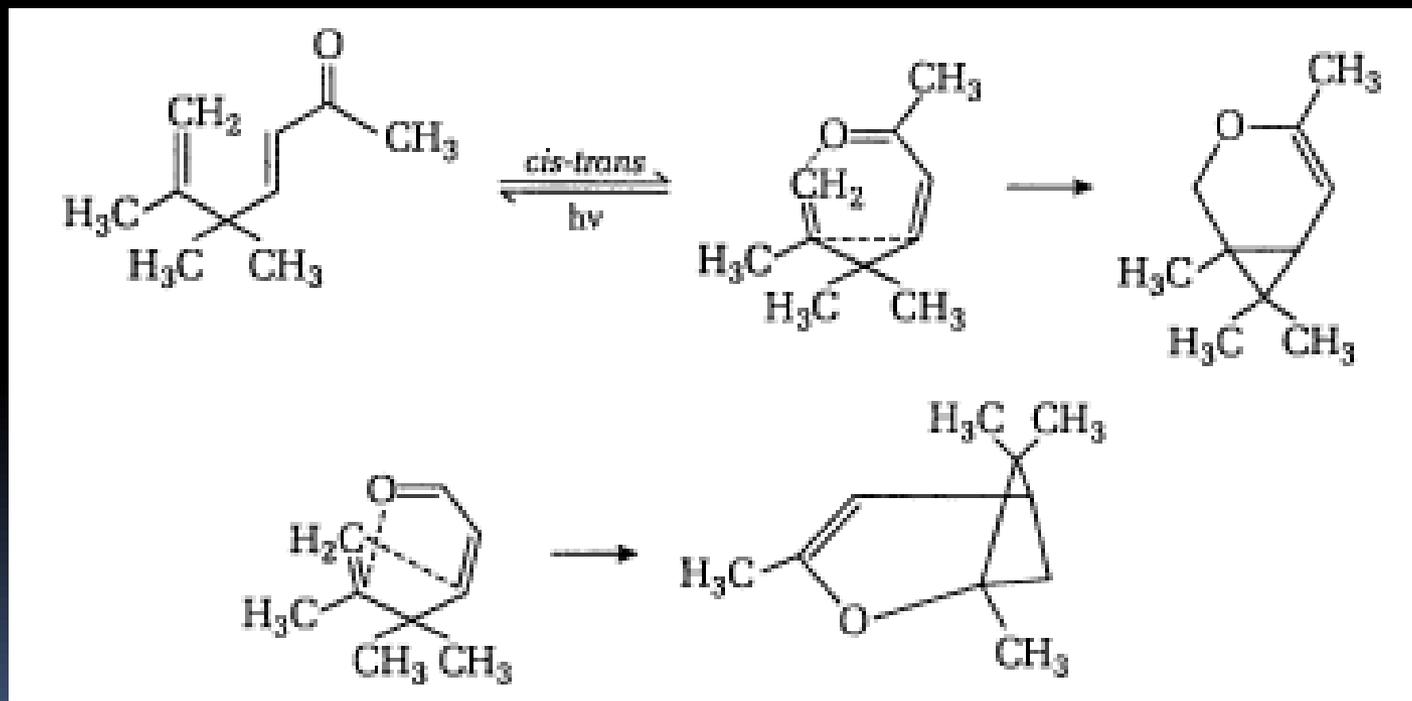


- Intramolecular cycloaddition have also been reported

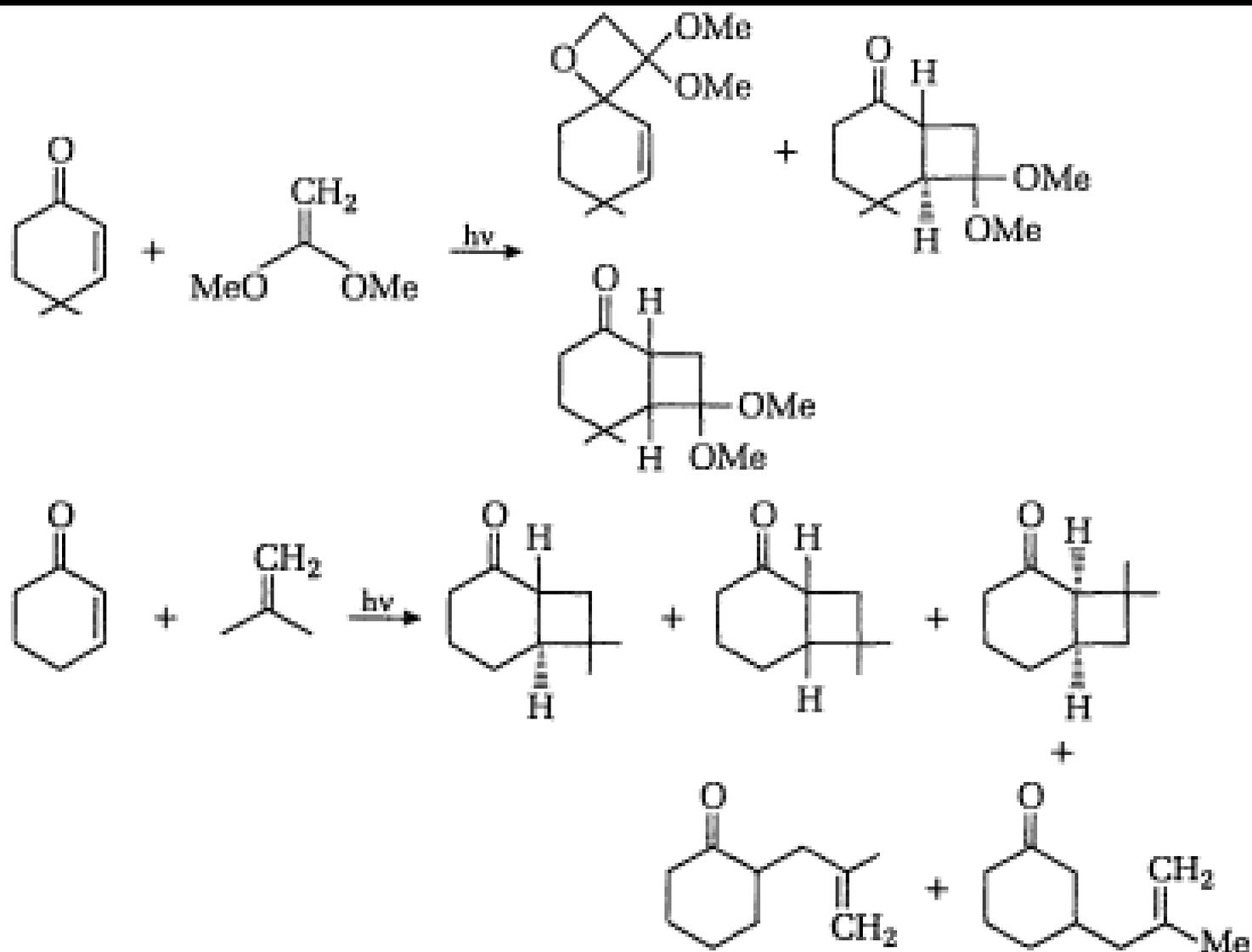


Cycloaddition reaction

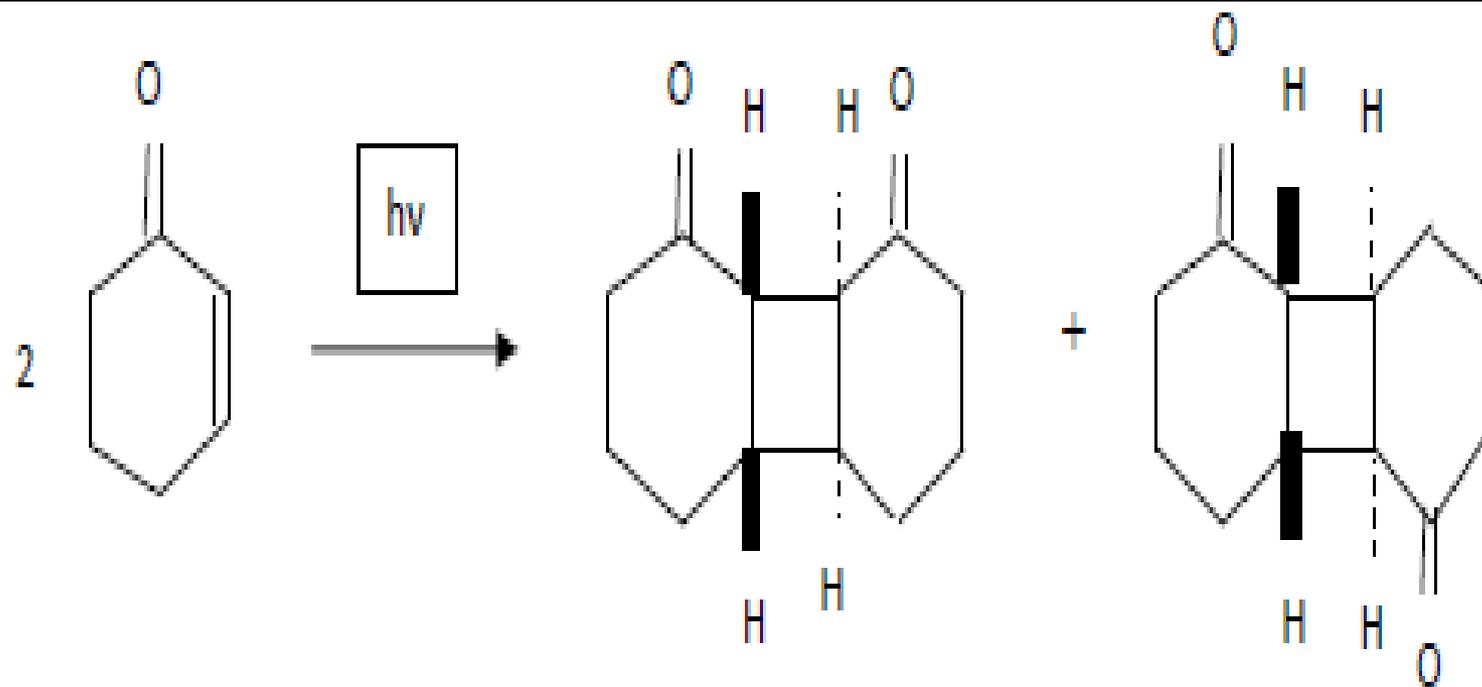
- Intramolecular cycloaddition reaction
- Intermolecular $[\pi^2-\pi^2]$ type



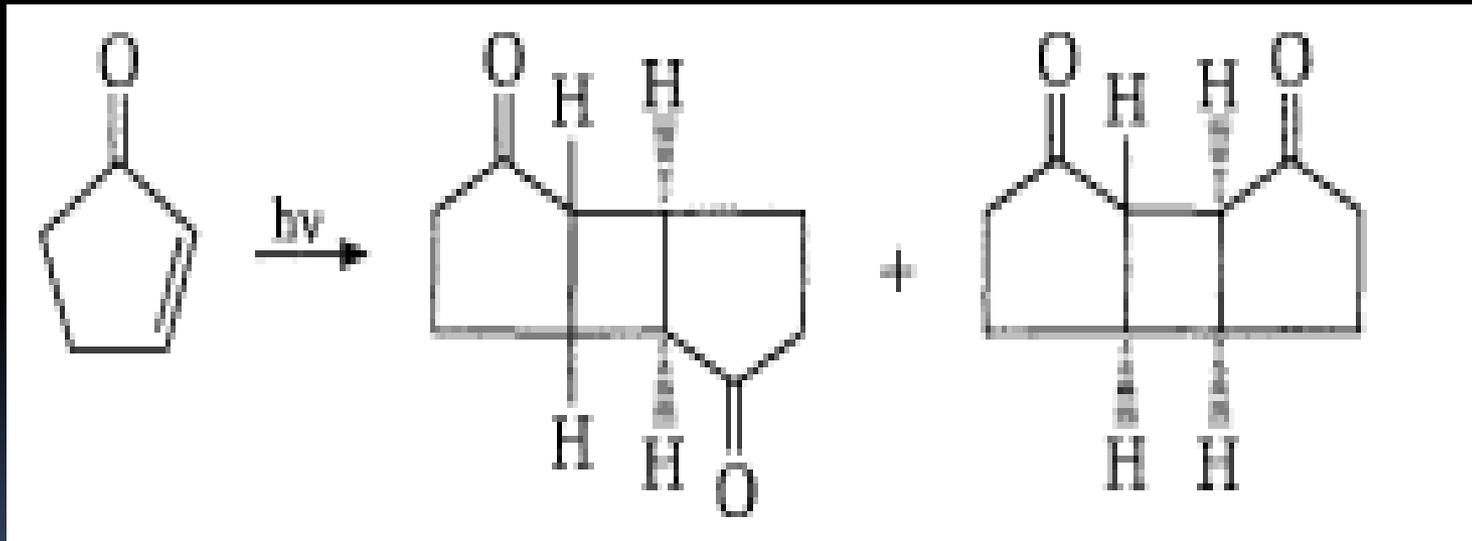
- Photo induced geometrical isomerisation followed by a ground state reaction of highly reactive trans-cyclic enone.
- Reaction of cyclohexenone with 2-methyl propene gives both of the possible cis fused cyclobutane adducts, but the major product is the trans fused ketone.
- Formation of trans-fused adducts is more common for reaction of enones with electron rich alkene



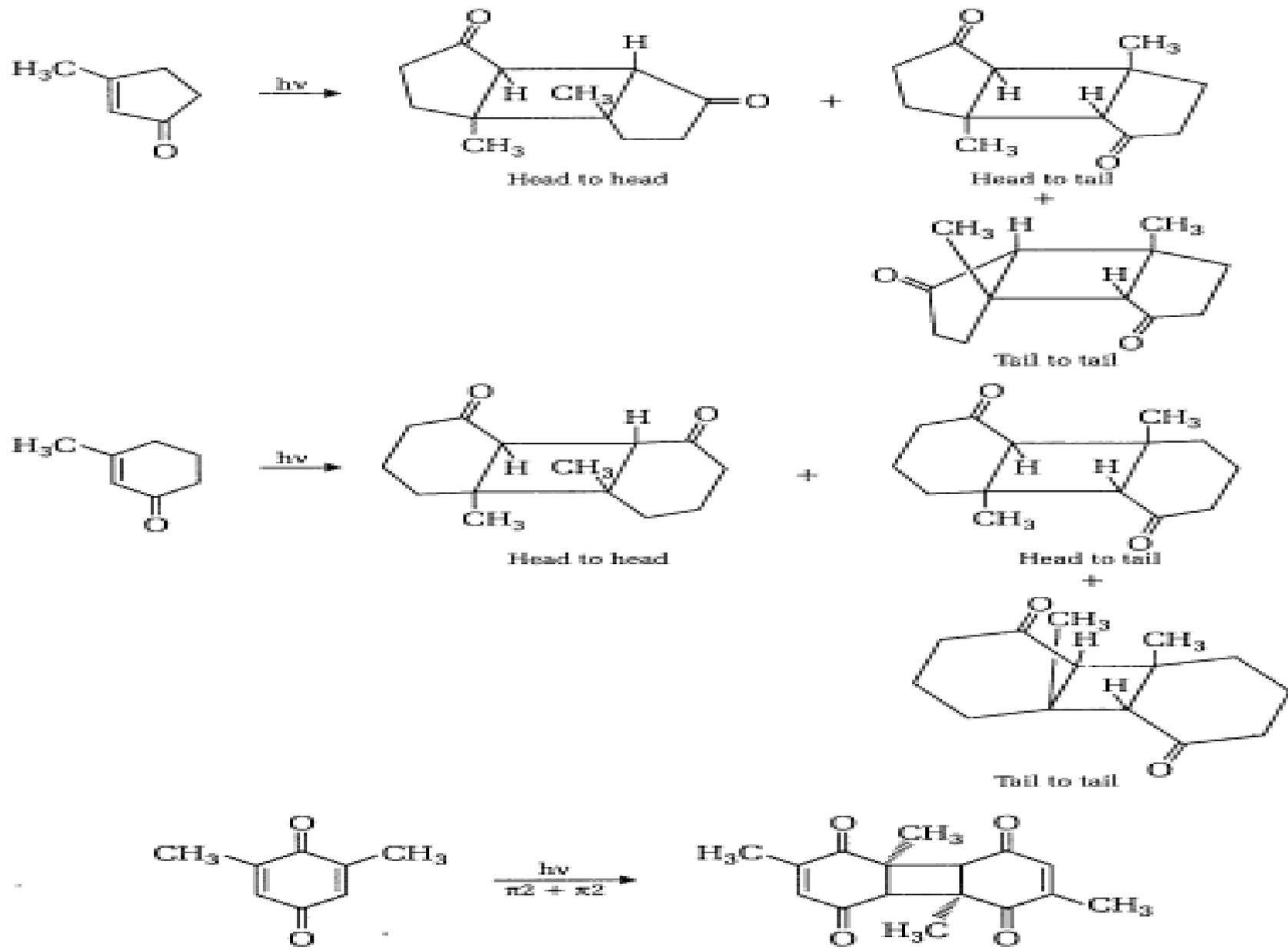
Dimerisation



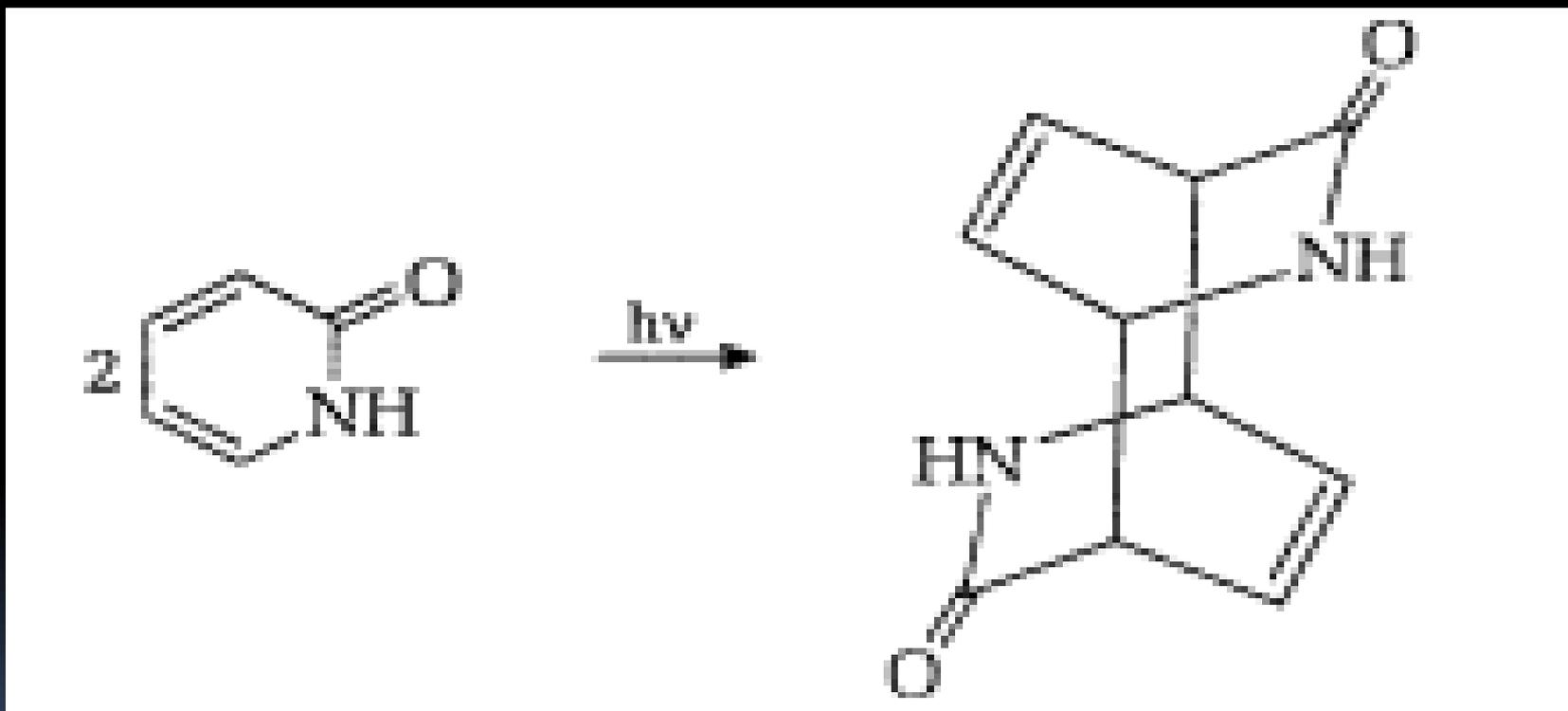
- The $[\pi^2s+\pi^2s]$ photodimerisation reactions proceeds by the involvement of 2π – electrons from each enone. The two π -bonds converted into intermolecular σ bonds.
- The photodimerisation of cyclopentenone $[\pi^2s+\pi^2s]$



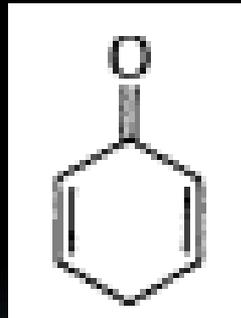
- The photodimerisation of α,β -unsaturated ketones provides a further class $[\pi^2-\pi^2]$ cycloaddition and is demonstrated for a 3-methylcyclopent-2-enone, with the formation of head to head dimers and head to tail dimers. The α,β -unsaturated enones absorb light of wavelength 300nm and get n,π^* excitation. The reaction is believed to occur from triplet state because ISC is efficient. While $\pi-\pi^*$ triplet excited enone also cause dimerisation



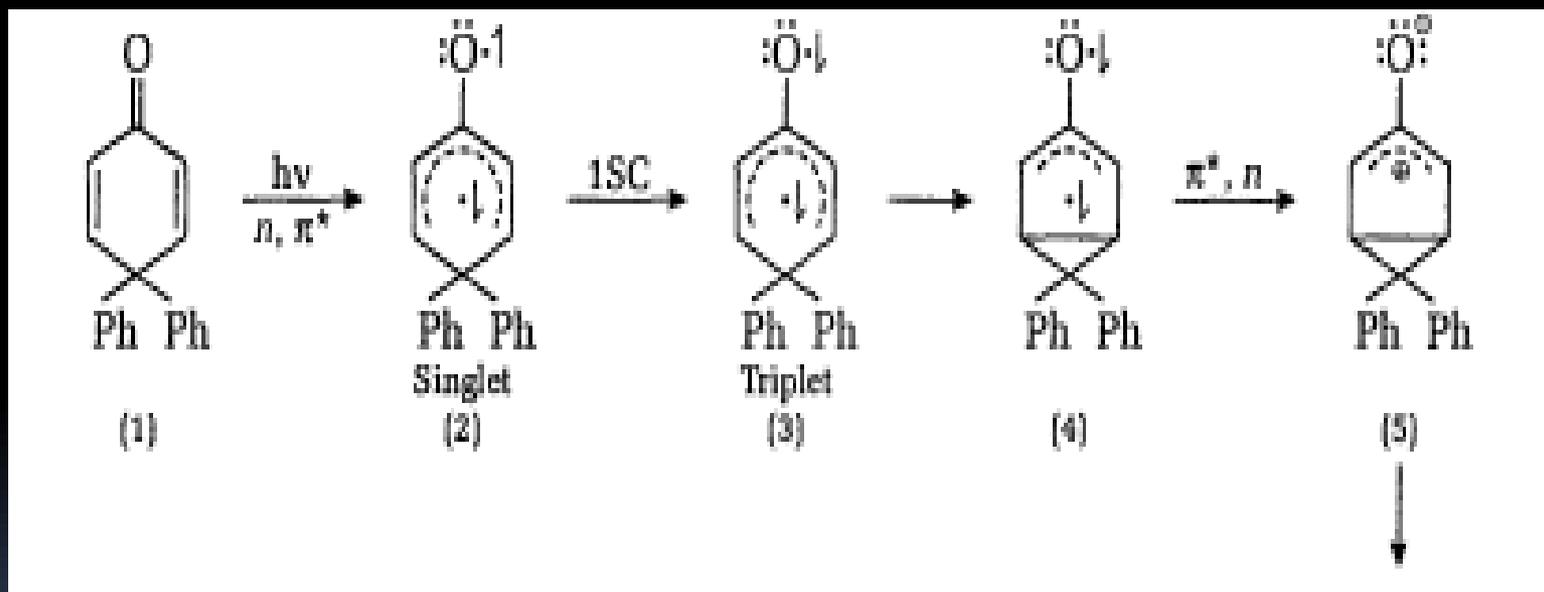
- 2-pyridones are known to undergo photodimerisation through $[\pi^4s-\pi^4s]$ cycloaddition.

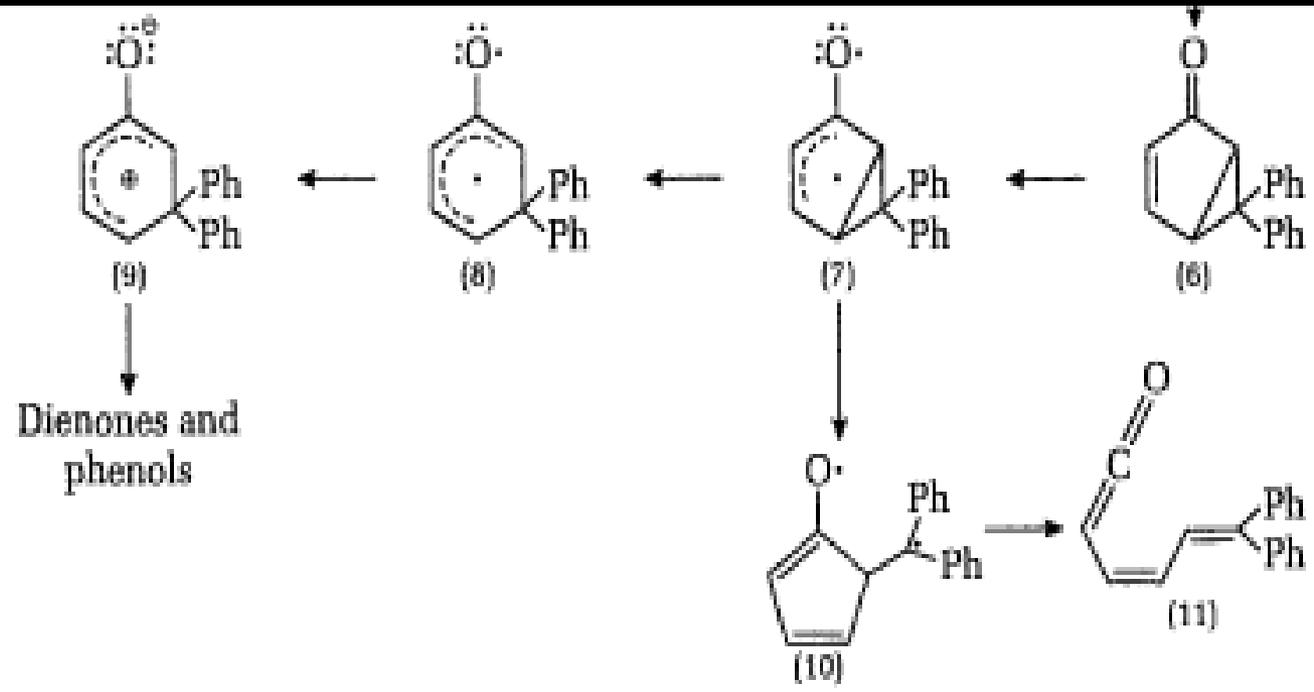
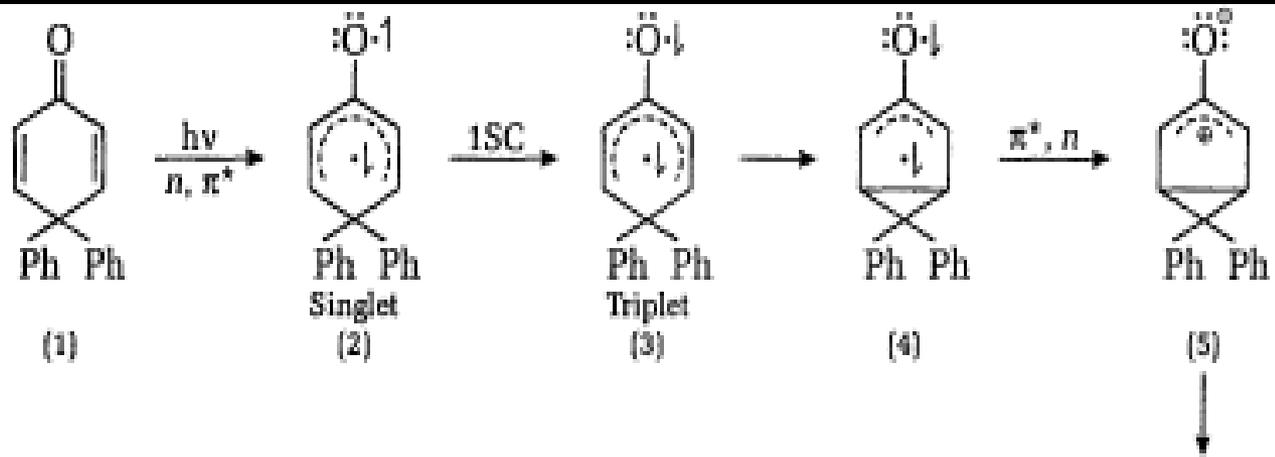


Cyclohexadienone



- The reactive excited state of dienone is $n-\pi^*$ triplet state.
- Excited cyclohexadienone undergoes rearrangement reactions.



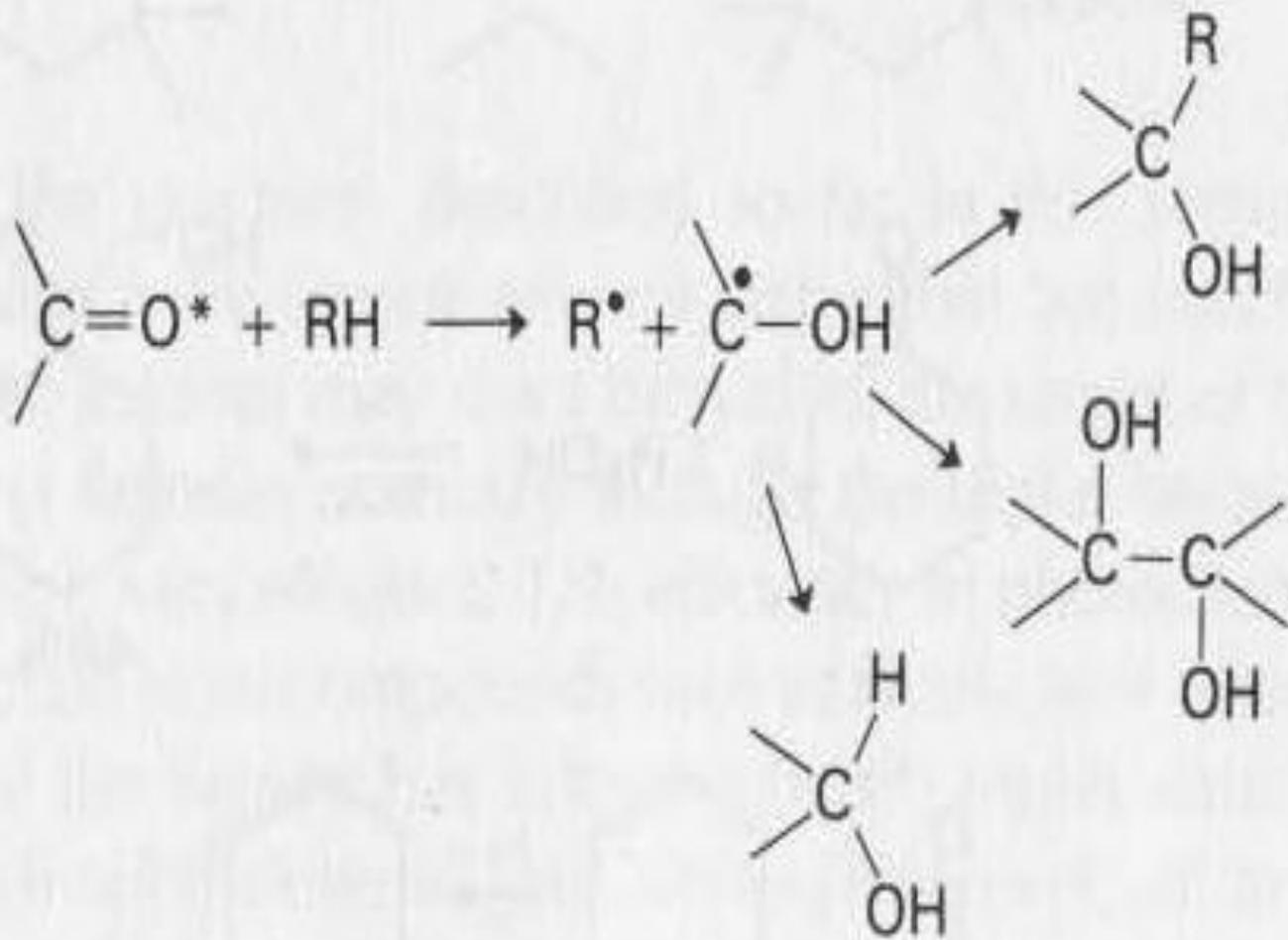


- For the rearrangement of 4,4-diphenyl cyclohexa-2,5-dienone, the suggested mechanism involves C₃-C₅ bonding from the excited triplet state(3).
- n-π* triplet state of the dienone indicates that an increase in C₃-C₅ bonding results from electron occupying the lowest π* molecular orbital(1) to the excited triplet state(3) is lost after C₃-C₅ bonding (4) to give the zwitter ion(5) which subsequently rearranges to the product 6,6-diphenyl bicyclo[3,1,0] hex-2-en-2-one(6). The product (6) is itself photochemically labile and undergoes further rearrangement as shown above.

Hydrogen abstraction

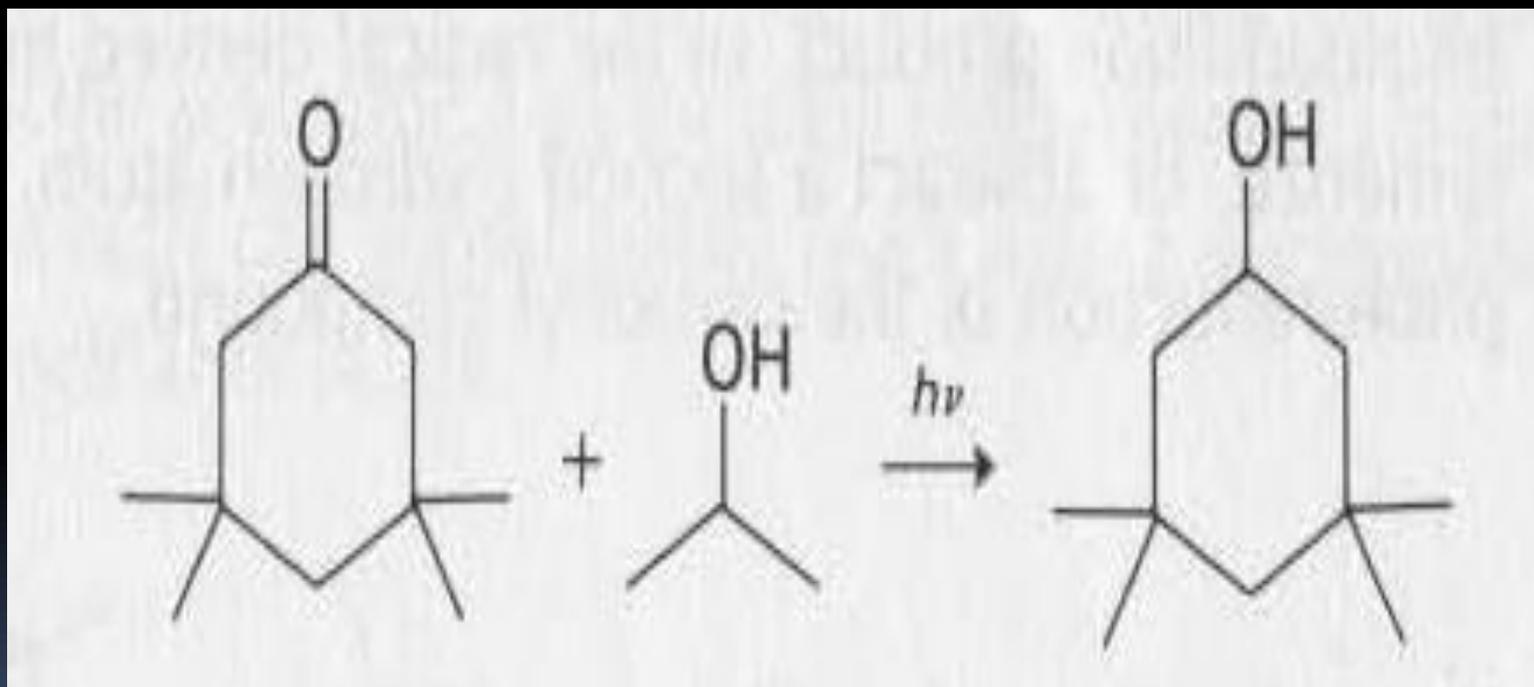
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- $n-\pi^*$ excited ketones exhibit radical like behavior in their alpha cleavage reactions, so they resemble alkoxy radicals in their ability to abstract a hydrogen atom from a suitable donor. The initially formed pair of radicals may combine to give an overall photoaddition product, or the radical derived from the ketone may dimerize, or abstract a second hydrogen atom, resulting to overall photoreduction of the carbonyl compound

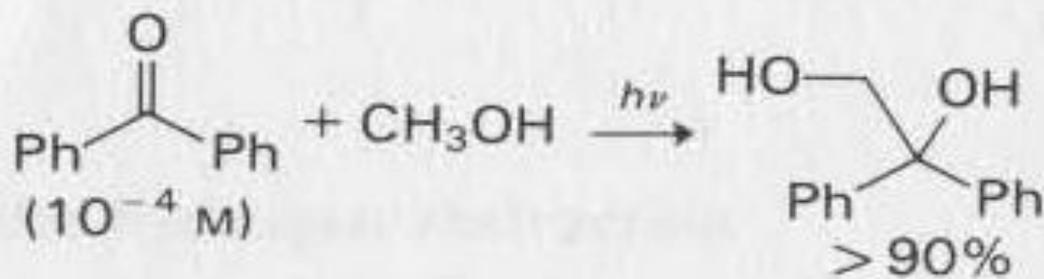
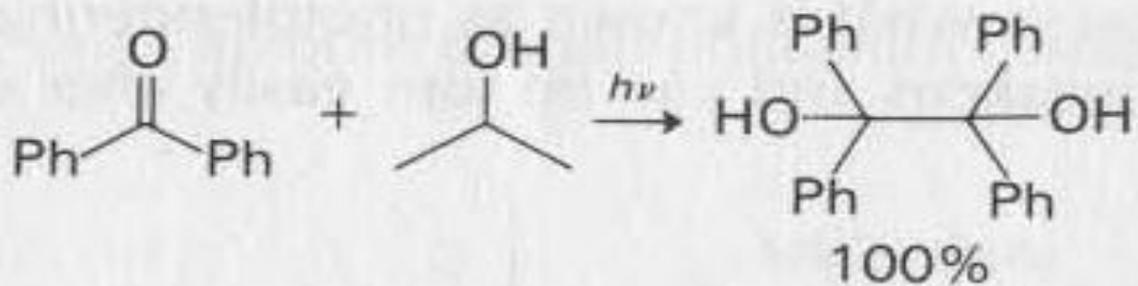


- the hydrogen donor(R-H) may be an alkane, but often the use of a saturated hydrocarbon leads to inefficient reaction, the balance of energy is quite fine, and for the reaction to be efficient a compound with a slightly weaker C-H bond is required.
- Suitable donors are primary or secondary alcohols or ethers (C-H adjacent to oxygen); these all give radicals that are stabilized relative to the corresponding alkyl radicals.
- One outcome of the facile reaction between excited state ketones and these compounds is that some of the commonly used solvents for thermal reactions, such as ethanol, diethyl ether or tetrahydrofuran are often not appropriate for use for the photochemical reactions of carbonyl compounds.

- the overall course of reaction depends on the relative rate constants for the various secondary radical processes. Aliphatic ketones are often photoreduced to secondary alcohol.



- aryl ketones such as benzophenone or acetophenone give good yields of the dimeric reduction product, a pinacol, on irradiation in methanol or propan-2-ol and this is the convenient method for making such symmetrical pinacols.
- The mechanism has been studied in detail and only one photon is required to generate two aryl ketyl radicals, since the radical derived from aliphatic alcohol exchanges a hydrogen atom with a second molecule of ground state aryl ketone.
- As a support of this mechanism is seen in the predominance of photoaddition product when extremely dilute solution of benzophenone in methanol is irradiated –under these conditions the rate of reaction between methanol and ground state benzophenone is markedly reduced.



- aliphatic ketones may react by way of the singlet or triplet state and aryl ketones normally reacts through the triplet state because intersystem crossing is efficient in latter.
- The efficiency of photochemical hydrogen abstraction from compounds such as alcohols or ethers is very much lower if the ketone has a lowest $\pi - \pi^*$ triplet state as 1-or 2-naphthalene.
- However, all aryl ketones regardless of whether their lowest triplet state is $n - \pi^*$ or $\pi - \pi^*$ react photochemically with amines to give photoreduction or photoaddition products.

Intramolecular photoreactions in β,γ -unsaturated carbonyl compounds

- intramolecular photoreactions in β,γ -unsaturated carbonyl Compounds consist of α -cleavage.

- the overall reaction follows following by two modes:

- (a) 1,3-acyl shift is involved, which form an isomeric β,γ -unsaturated ketones.

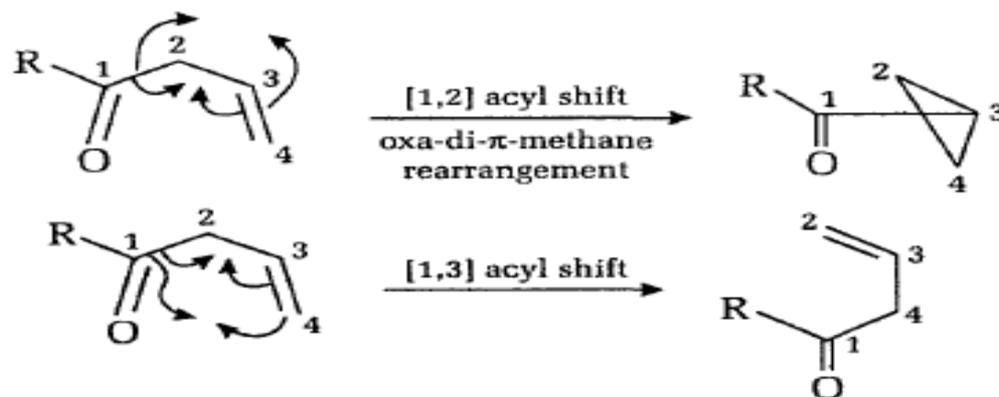
- (b) ring closure process takes place

The β, γ -unsaturated carbonyl compounds are non-conjugated systems and show remarkable properties in ultra-violet region. Bicyclo [2.2.1]-hept-5-en- 2-one is an example and shows absorption at 308 nm.



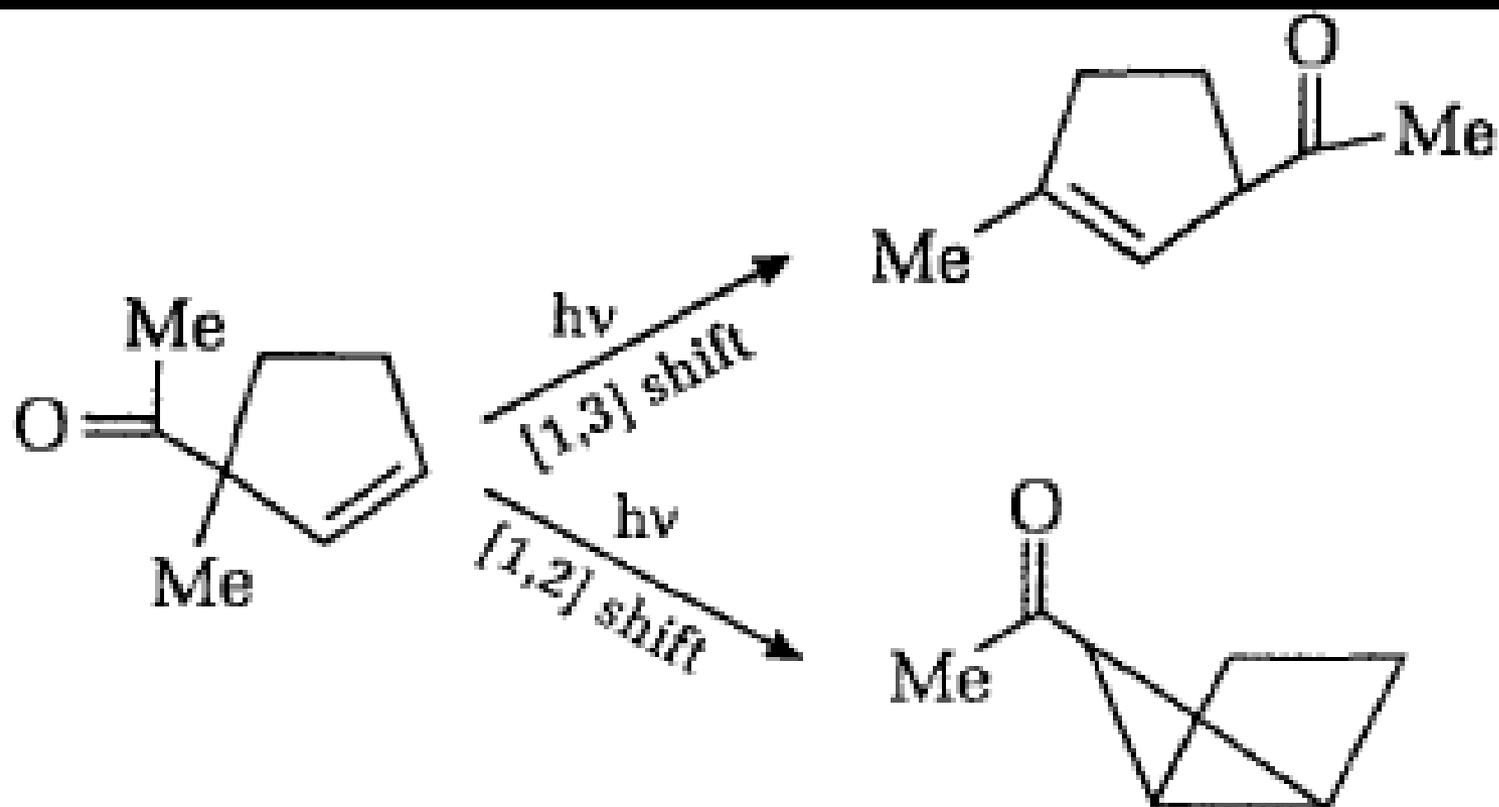
The $n \rightarrow \pi^*$ excitation is most favoured transition but some times, the absorption shifts to longer wavelength, because of mixing of $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition.

β, γ -unsaturated ketones exhibit two reactions that depends upon the bichromophoric interaction. These two characteristic reactions are [1, 2] and [1, 3] acyl shift.



The [1, 2] sigmatropic reaction is also known as the oxa-di- π -methane rearrangement and is analogous to the di- π -methane rearrangement of 1, 4-dienes. The reaction involves the migration of the acyl group from C_2 to C_3 (termed as [1, 2] acyl shift), and formation of a new bond between C_2 and C_4 . The [1, 3] acyl shift involves migration of the acyl group from C_2 to C_4 [termed as [1, 3] acyl shift) and relocation of the double bond between C_2 and C_3 .

Photolysis of β, γ -enone, yields product through both [1, 2] and [1, 3] acyl shifts.

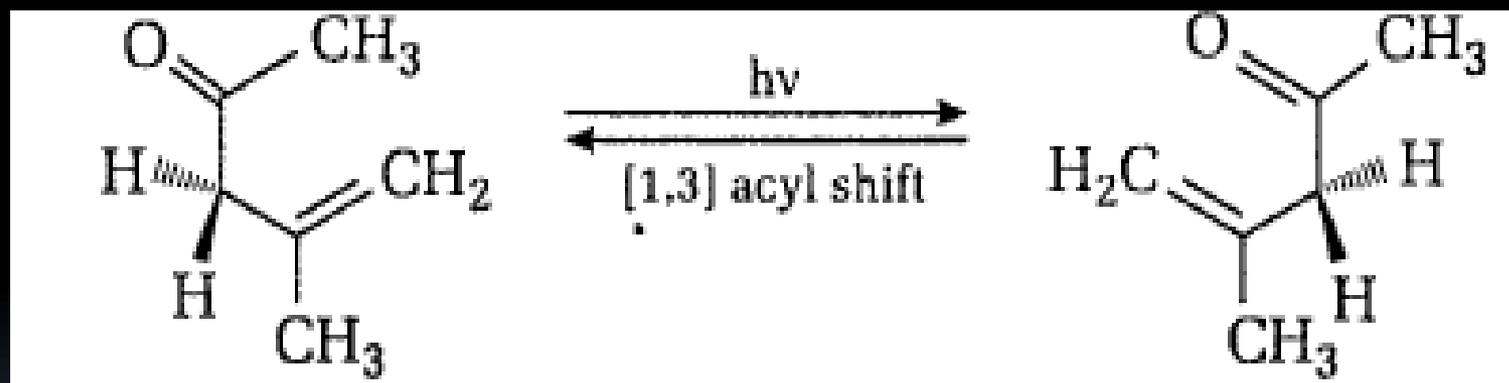


Beside [1, 2] shift and [1, 3] shift β, γ -unsaturated carbonyl compounds undergo characteristic reactions of chromophores, *i.e.*, dimerisation, oxetane formation, reduction, Norrish type I and Norrish type II reactions, are also reported.

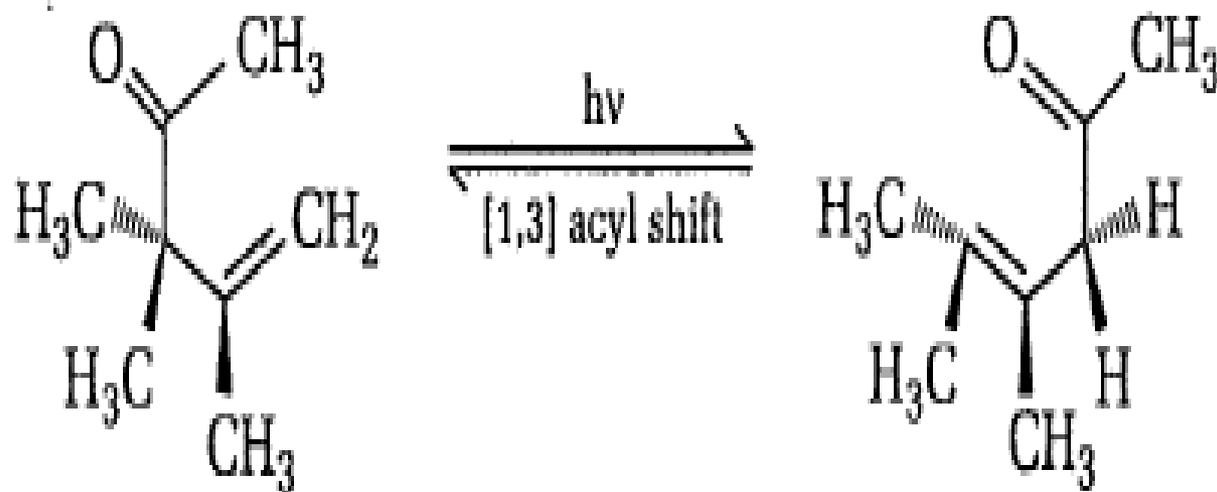
Solution phase photolysis of 4-methylpent-4-en-2-one gives more common Norrish type I and Norrish type II reactions. The Norrish type I (α -cleavage) yield minor products due to subsequent reorganization and recapture of the radical fragments (cyclobutanol). Norrish type II yields major product of the reaction which proceeds from $n \rightarrow \pi^*$ singlet or from an exceedingly short-lived triplet state. The other products expected from fragmentation of 1, 4-diradical, namely acetone and alkene were not detected.

For this simple substrate the [1, 2] shift product is not observed and this is also a common feature of substrates which geometrically isomerise, thereby dissipating triplet energy which might be otherwise used to effect the oxa-di- π -methane rearrangement.

A [1, 3] shift of acyl group cannot be detected for this substrate since product of the process is identical with the substrate.



The introduction of two methyl substituents adjacent to the carbonyl group destroys the symmetry of the enone and a product resulting from [1, 3] acyl shift is observed. The product may result from a concerted shift of the acyl group or from α -cleavage and radical recombination in the cage containing the acyl and allylic radicals.



Thank you