

**M.Sc. Semester-IV
Core Course-9 (CC-9)
Synthetic Organic Chemistry**



**III. Photochemistry
3. Cis-Trans Isomerisation of Alkenes**



**Dr. Rajeev Ranjan
University Department of Chemistry
Dr. Shyama Prasad Mukherjee University, Ranchi**

III Photochemistry 10 Hrs

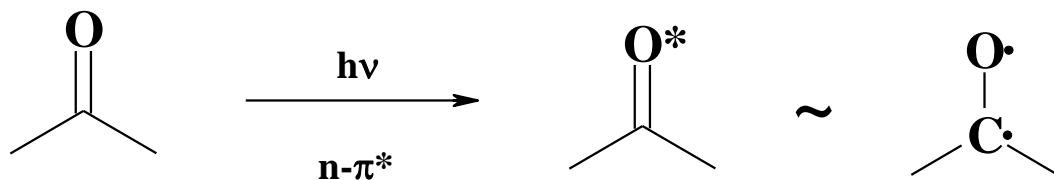
Thermal versus photochemical reactions, Electronic excitations: $n-\pi^*$ and $\pi-\pi^*$ transitions. Singlet and Triplet energy states: Comparison of energies, Lifetimes and Reactivity. Jablonski diagram, Allowed and forbidden transitions: Fluorescence, Phosphorescence and Internal conversion and Intersystem crossing.

Photochemical reactions of saturated ketones : Norrish Type I and Norrish Type II reaction, Photoreduction of ketone, Photoaddition reactions, Paterno Buchi reaction. Photochemistry of simple olefins : Cis-trans isomerization, Di-pi methane rearrangement. Photooxidation : Formation of peroxy compounds, oxidative couplings : Barton reaction. Photo rearrangements : Photo-Fries rearrangement and Photo rearrangement of 2,5-Cyclohexadienones.

Coverage:

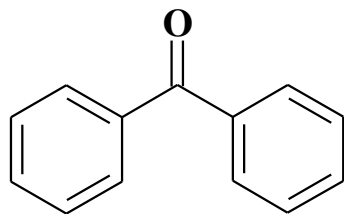
1. Electronic Configuration of Reactive States
2. Cis-Trans Isomerisation of Alkenes

Electronic configuration of Reactive states

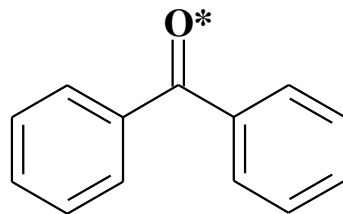


carbonyl chromophore

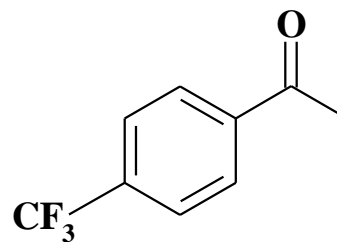
Dipolar species



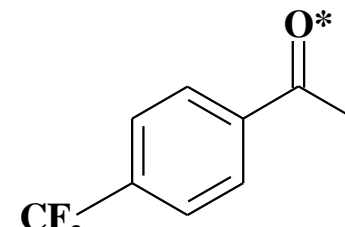
2.9 D
1665 cm⁻¹



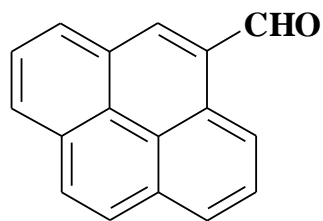
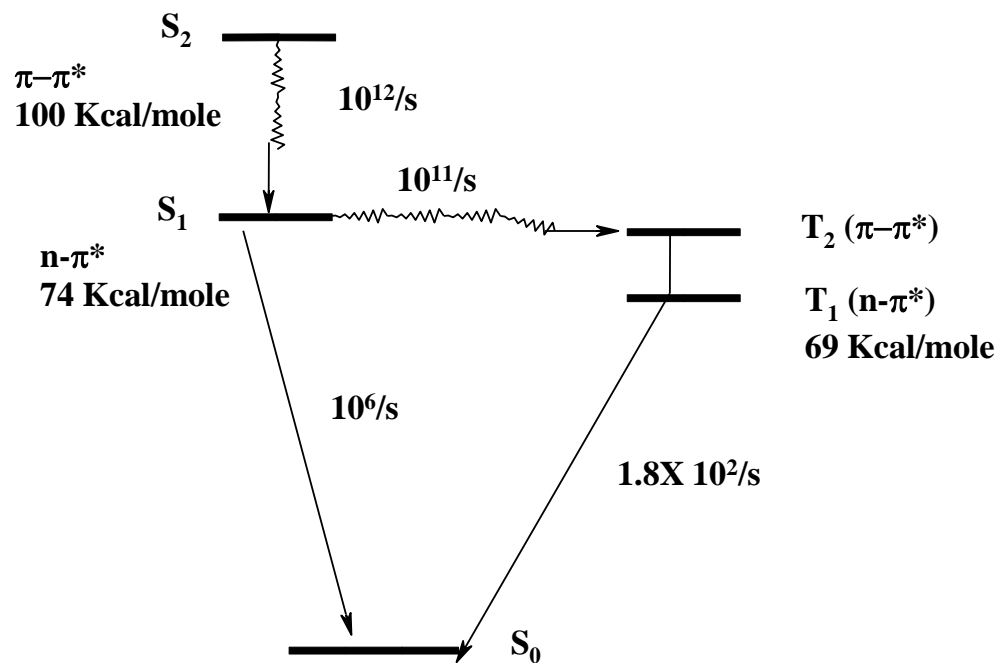
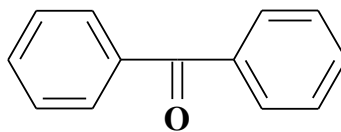
2.1 D
1225 cm⁻¹



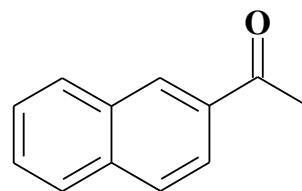
1696 cm⁻¹



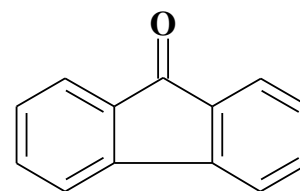
1326 cm⁻¹



pyrene aldehyde



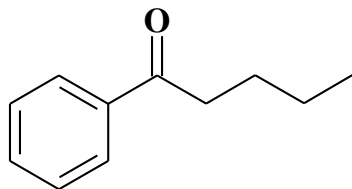
2-acetonaphthone



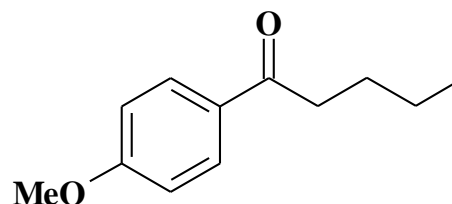
fluorenone

lowest triplet state is $\pi-\pi^*$

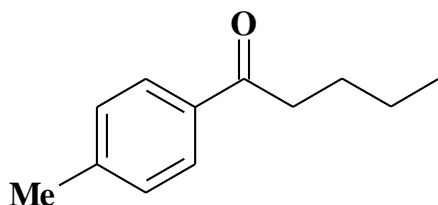
Triplet lifetime depends on the nature of lowest excited states



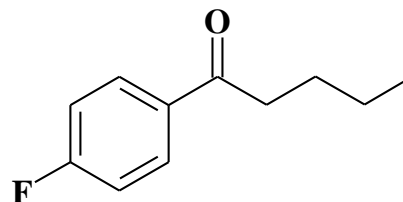
$\tau = 0.0064 \text{ s}, 77^\circ\text{K}$
 $n-\pi^*$



$\tau = 0.45 \text{ s}, 77^\circ\text{K}$
 $\pi-\pi^*$



$\tau = 0.13 \text{ s}, 77^\circ\text{K}$
 $n-\pi^* \text{ \& } \pi-\pi^*$

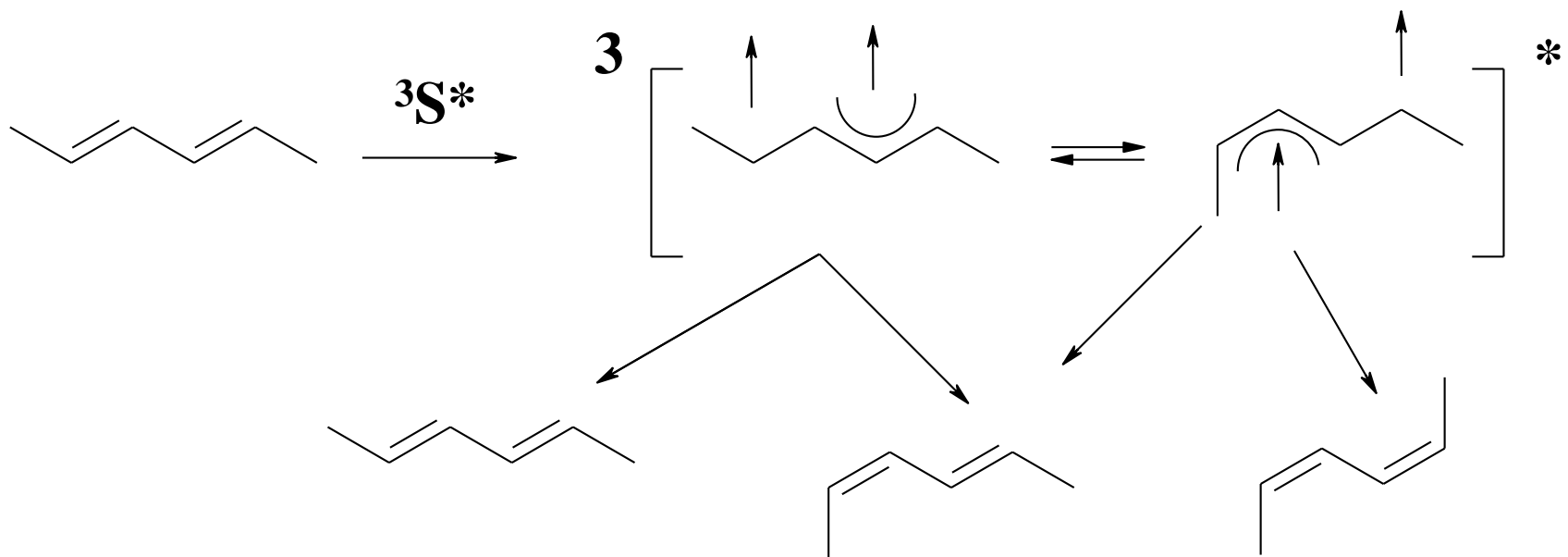
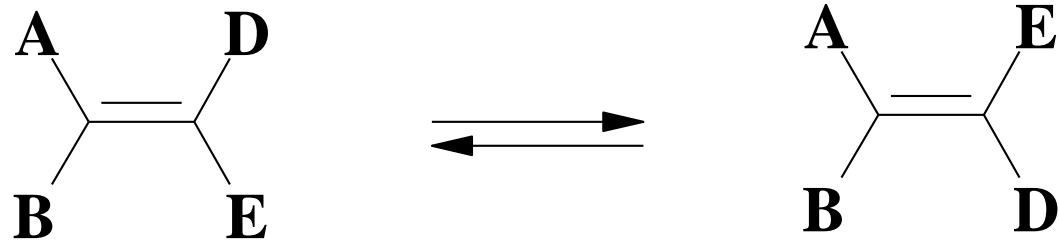


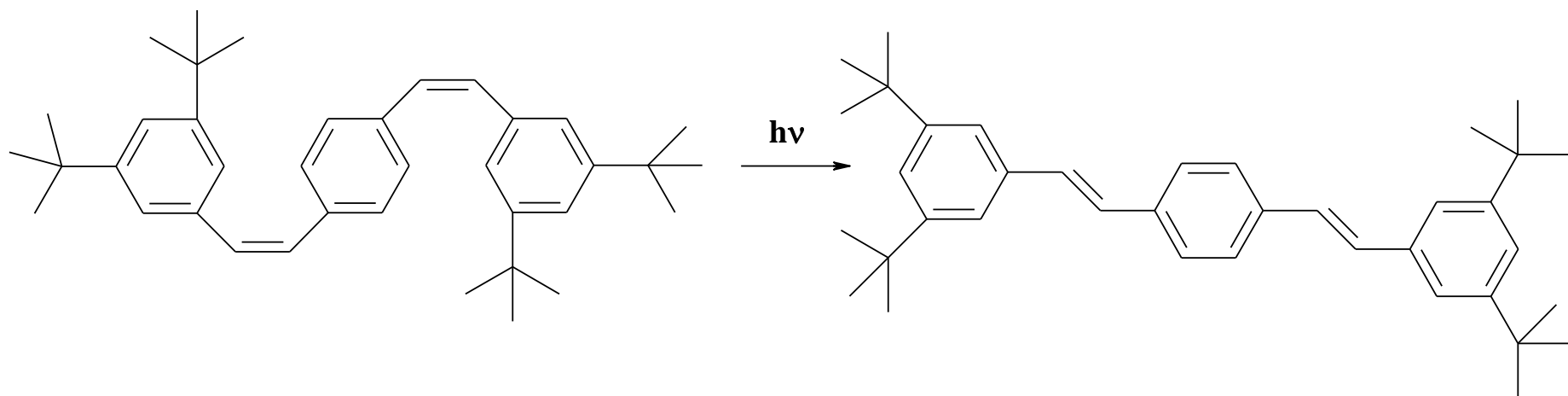
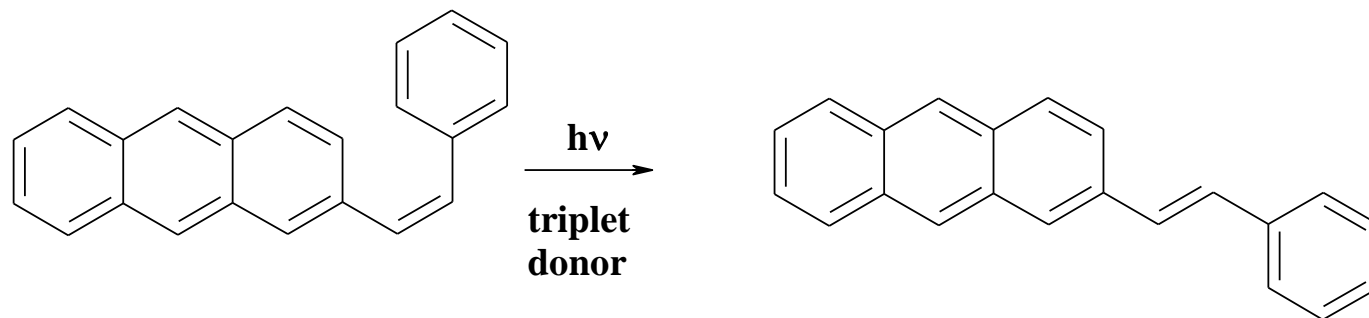
$\tau = 0.039 \text{ s}, 77^\circ\text{K}$
 $n-\pi^* \text{ \& } \pi-\pi^*$

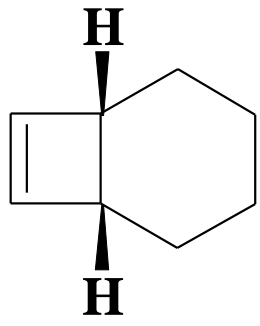
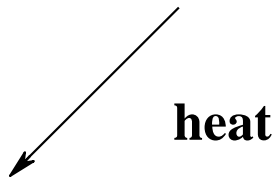
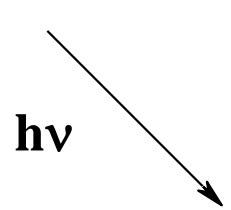
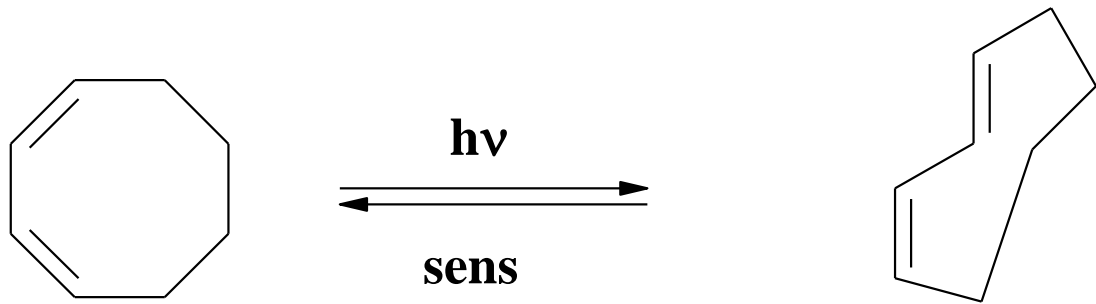
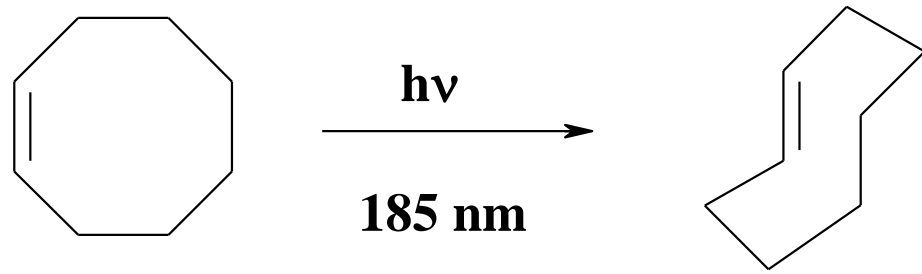
Electron donating substituents such as Me and -OMe stabilize $\pi-\pi^*$ state

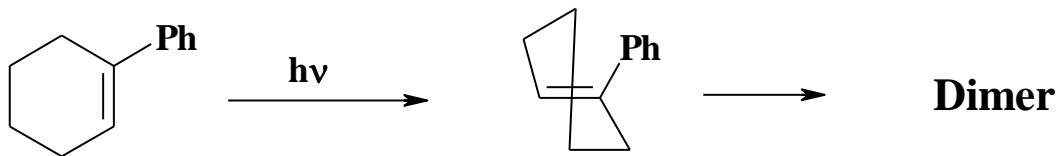
Electron withdrawing substituents such as CF_3 and CN stabilize $n-\pi^*$ state

Cis-Trans isomerization of alkenes

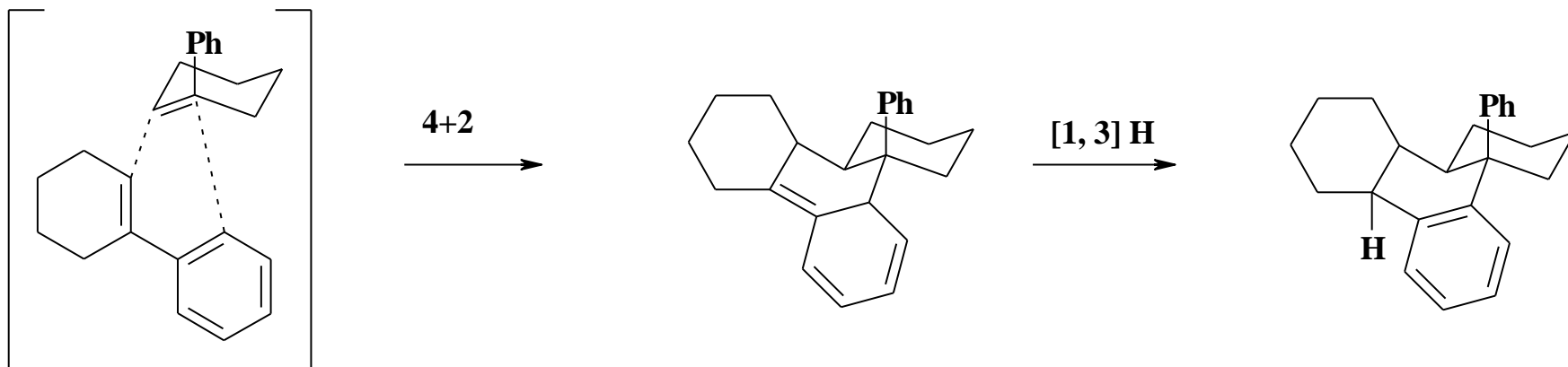




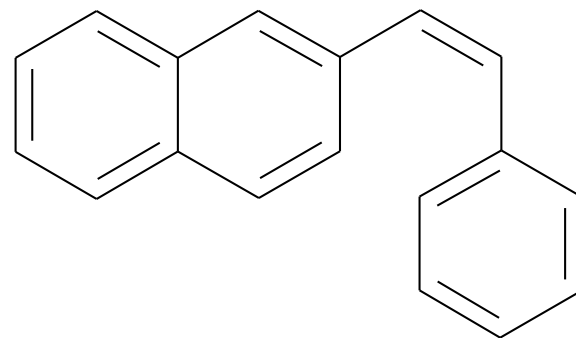
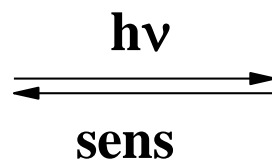
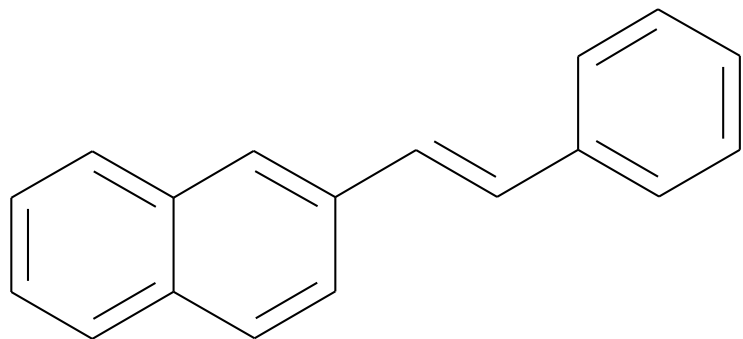
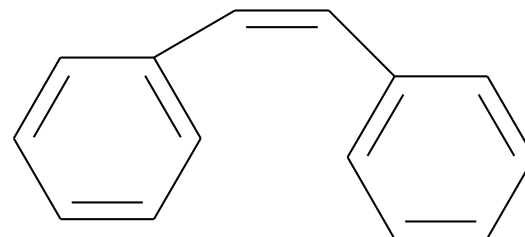
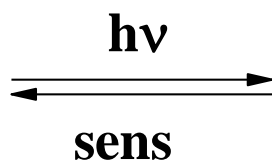
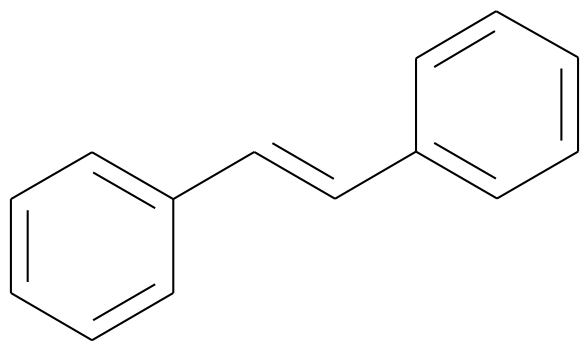


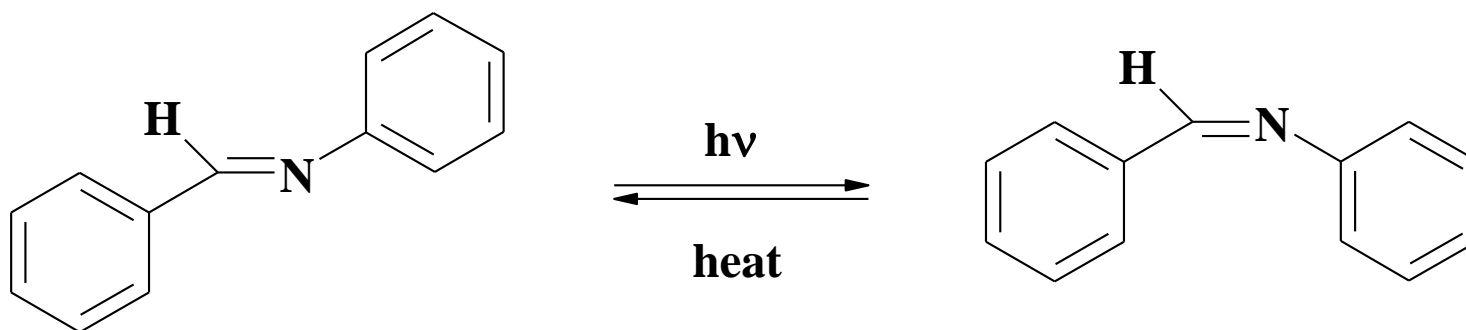
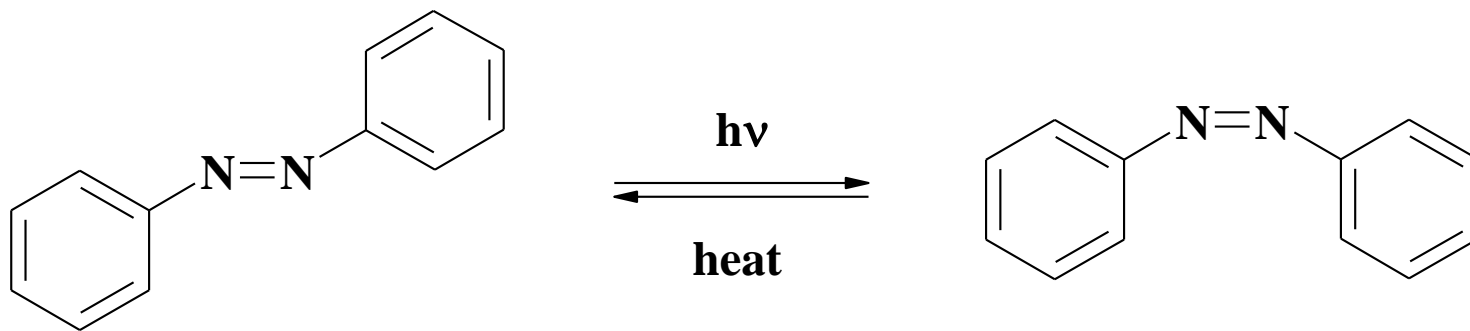
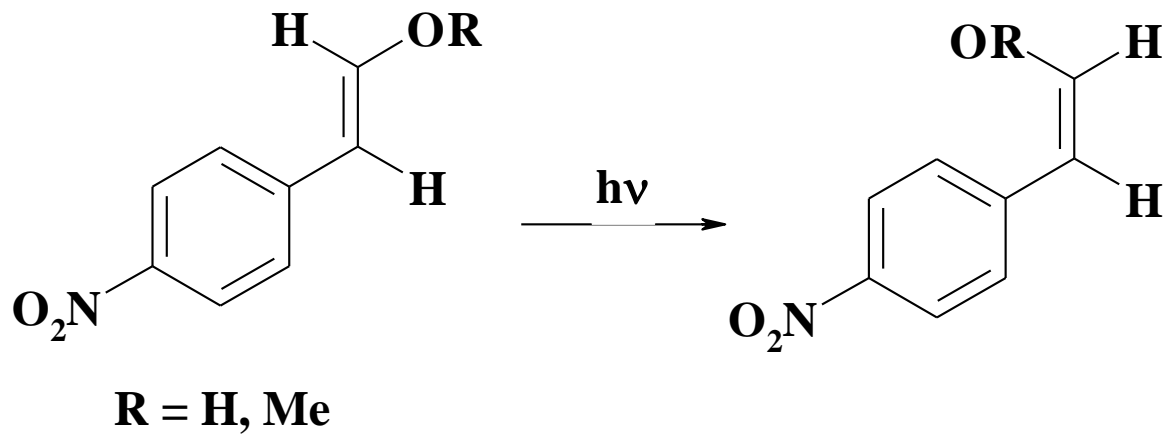


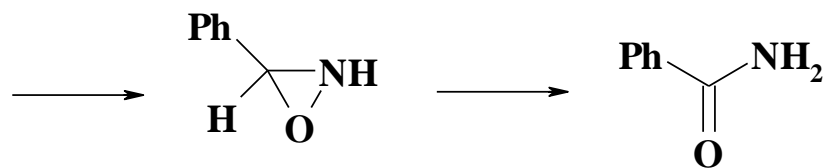
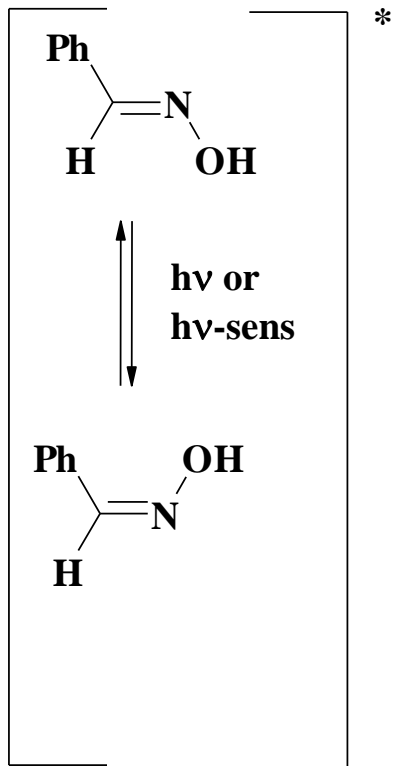
$\lambda_{\text{Max}} = 380 \text{ nm}$
 $\tau = 9 \mu\text{s}$



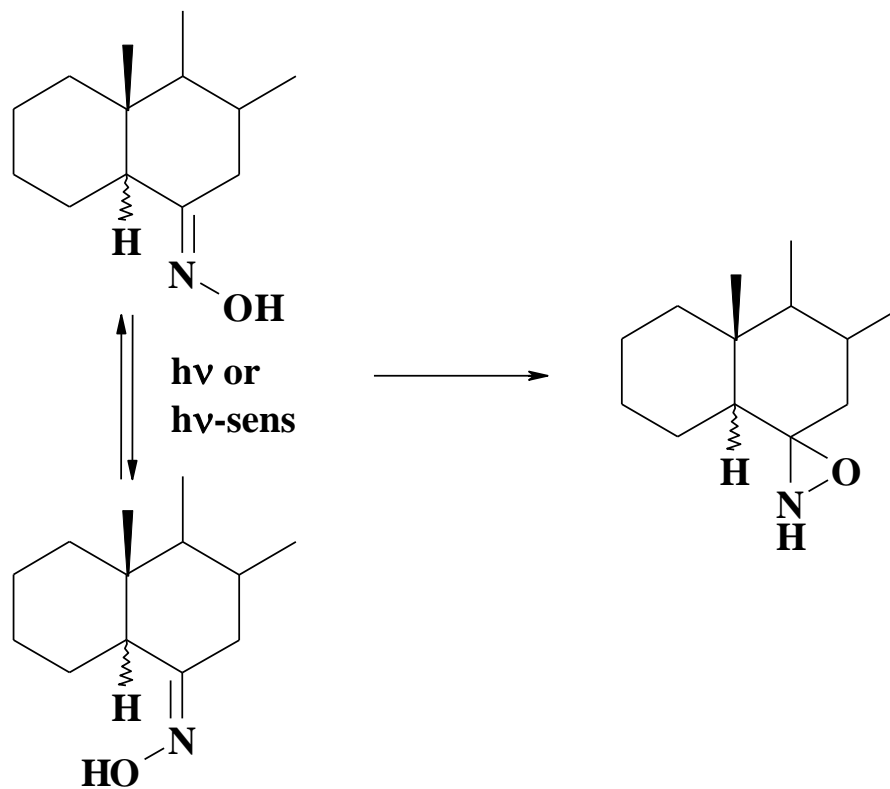
Trapping of a trans cyclohexene

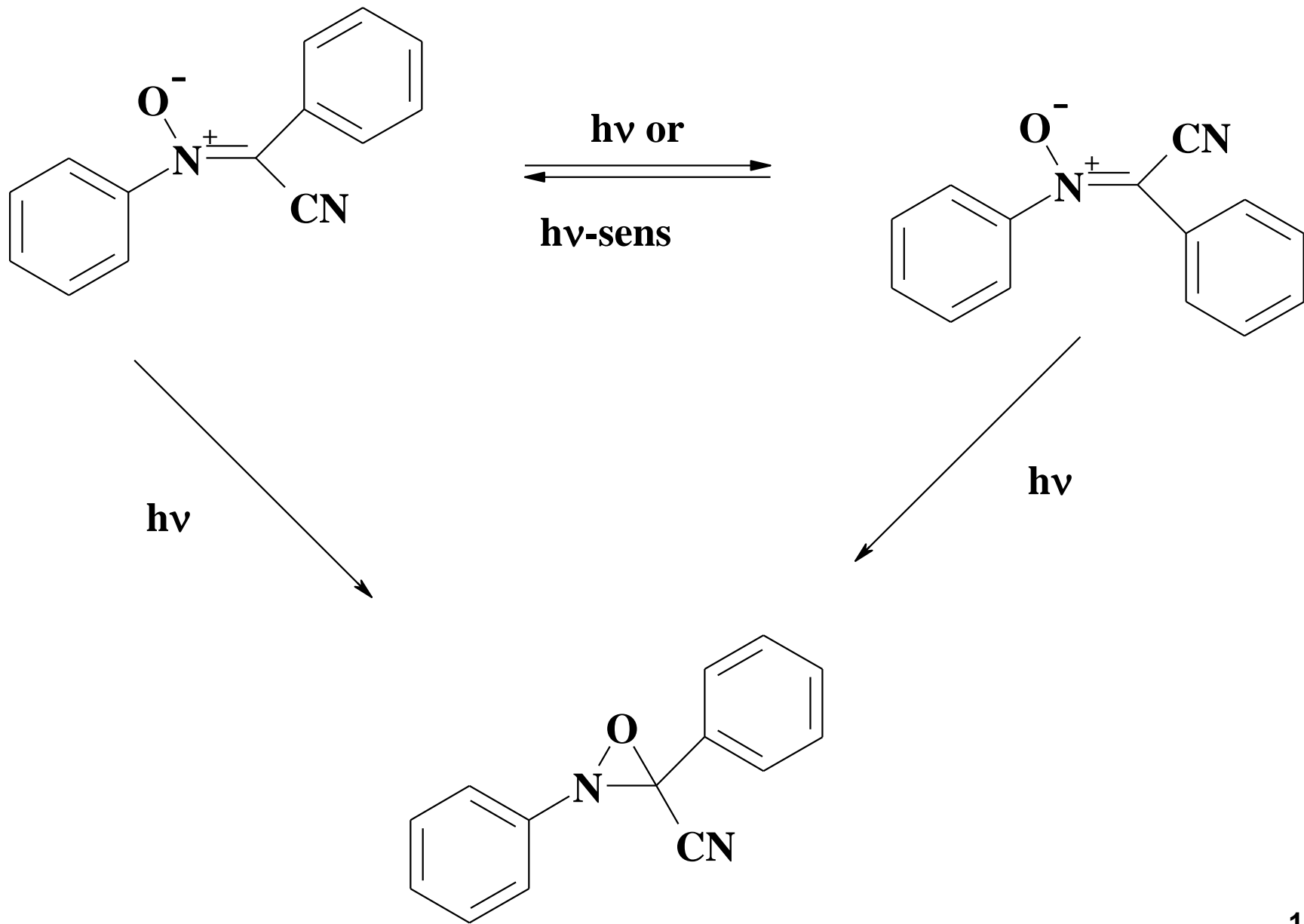


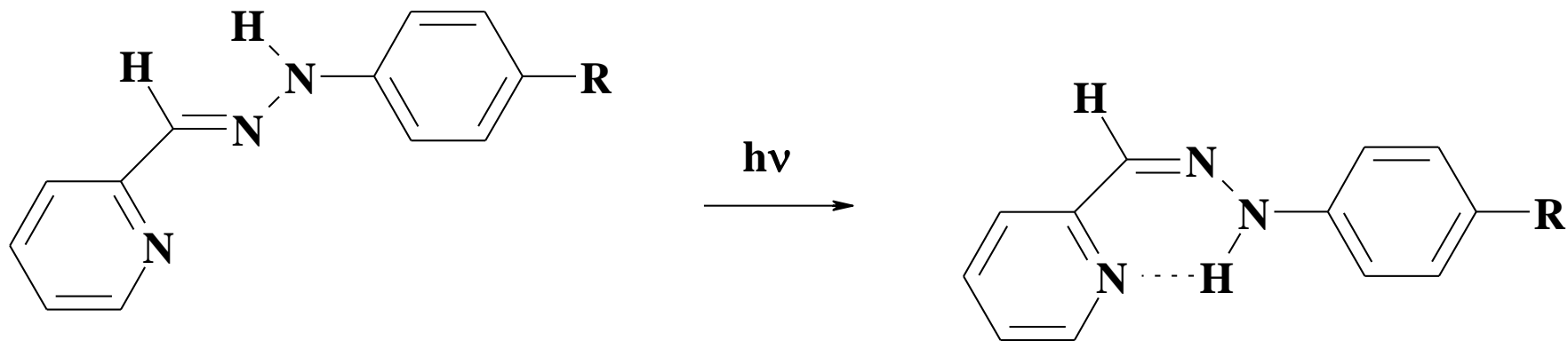
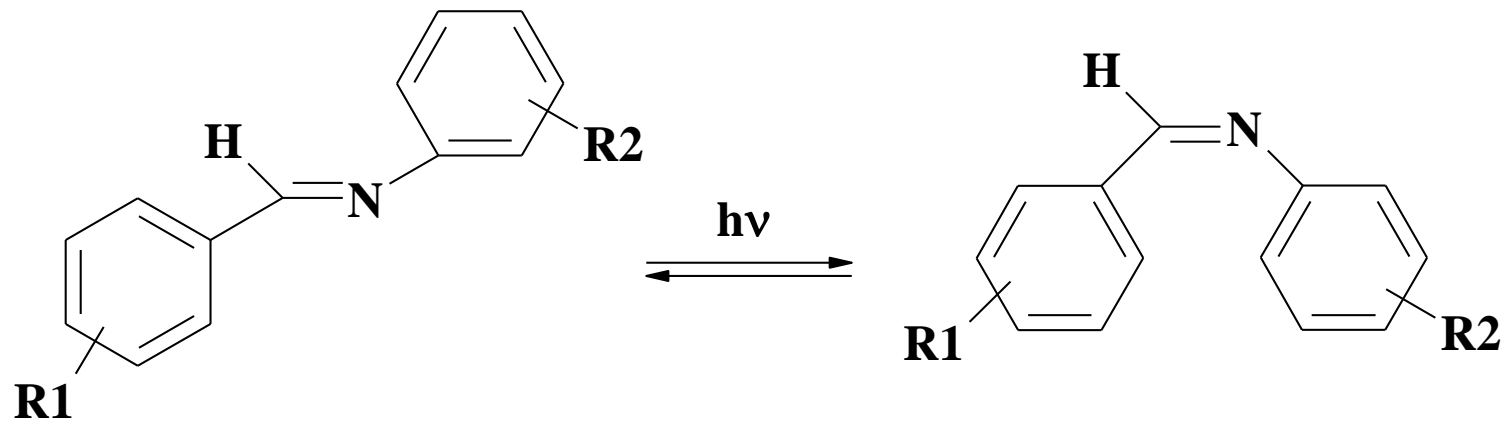


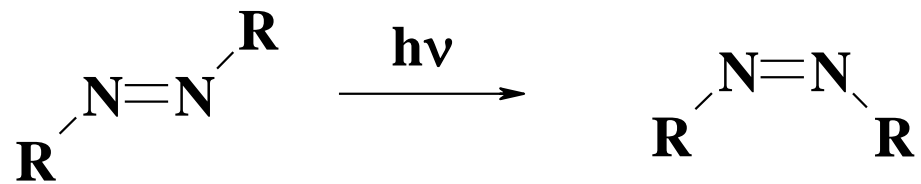


oxaaziridine





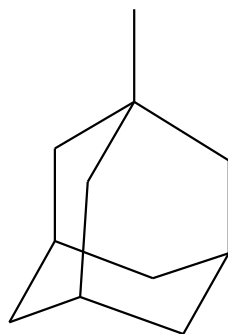




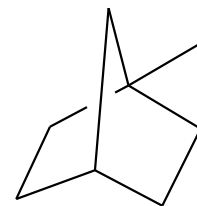
R = Me

R = CHMe

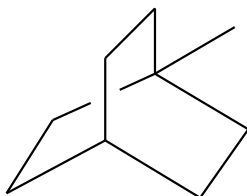
R =



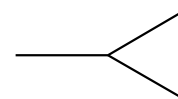
R =

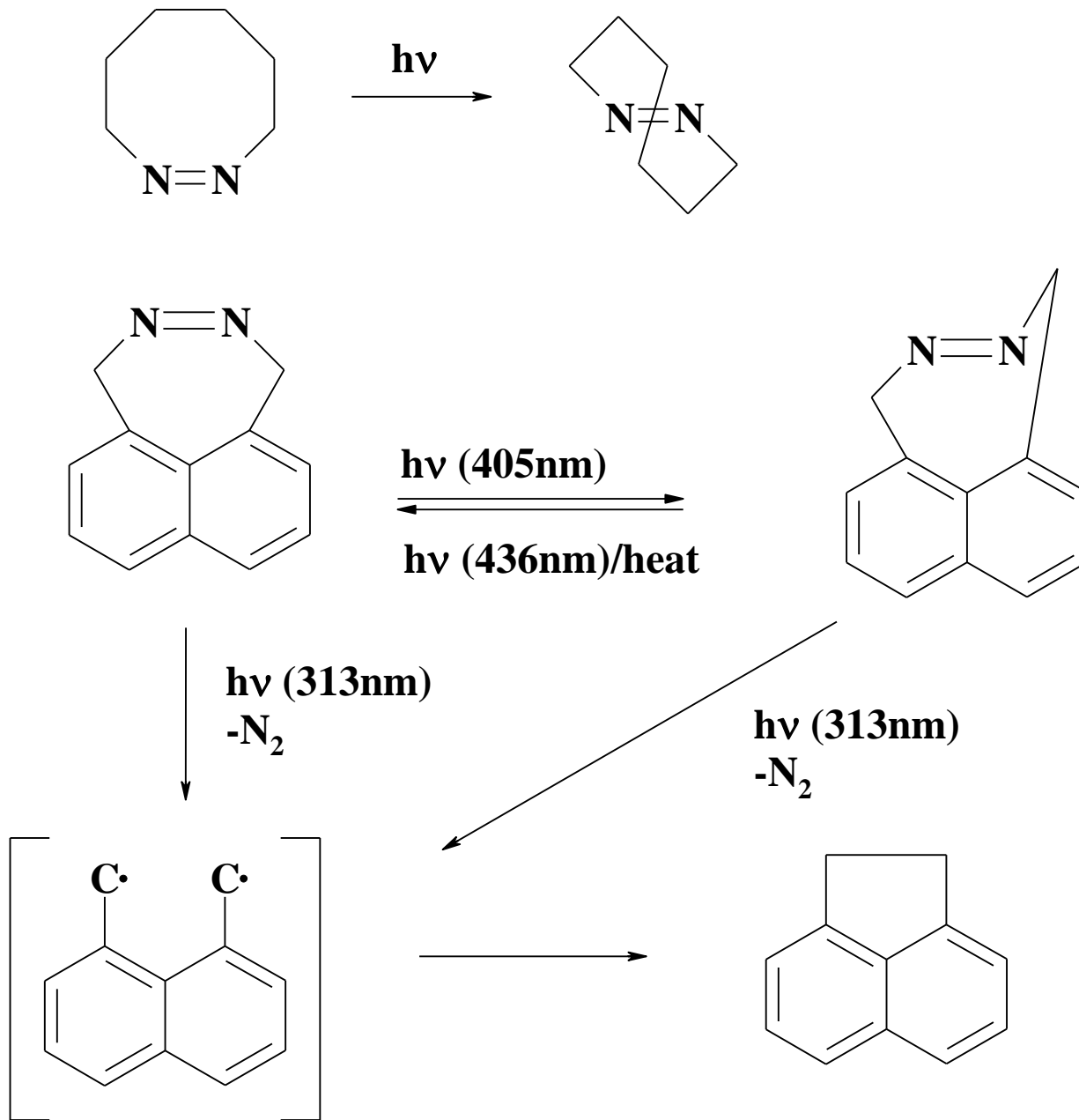


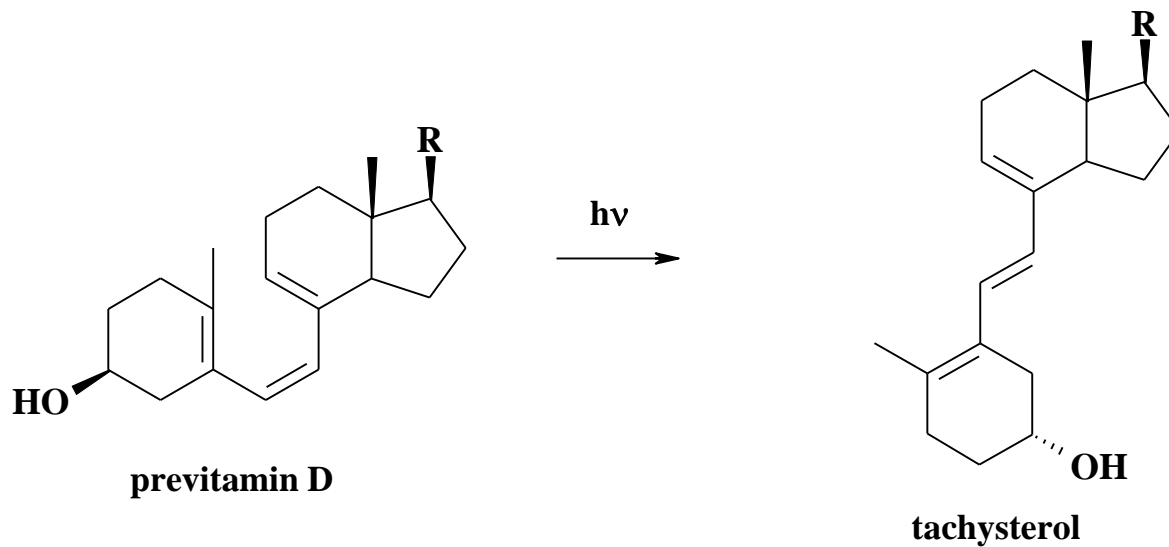
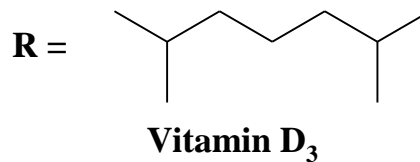
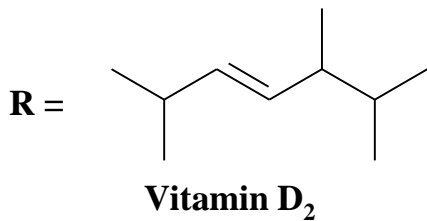
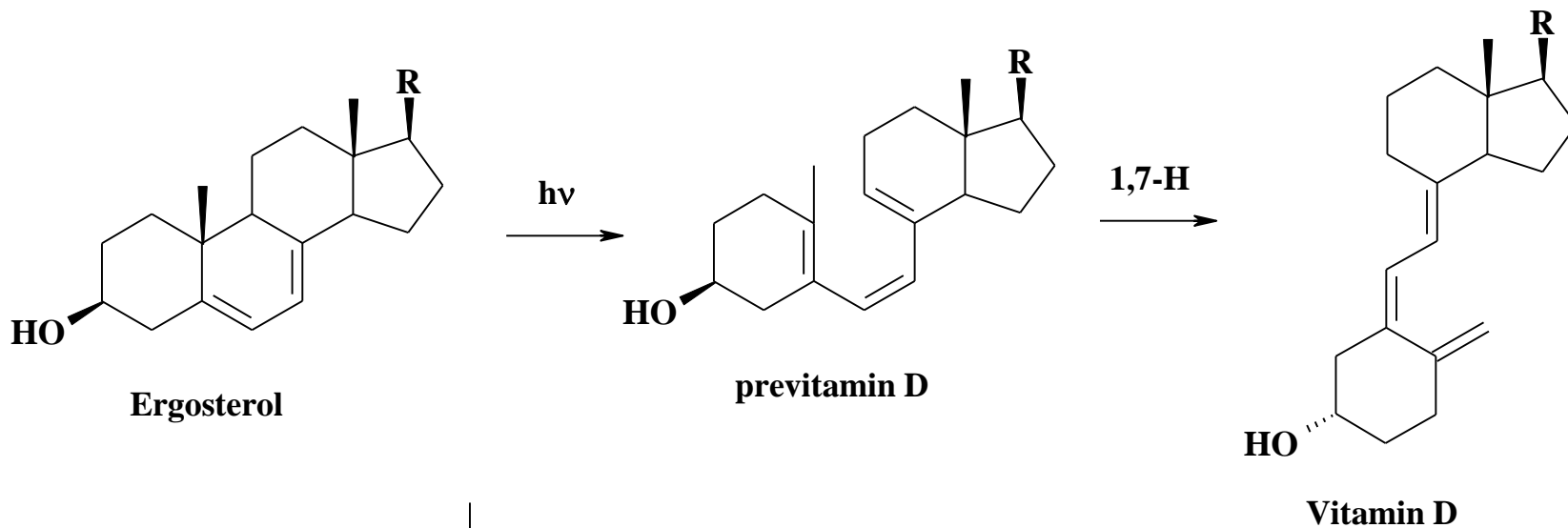
R =



R =







Thank You



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