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

III. Photochemistry

11. The Aza-Di-π-Methane Rearrangement, Photorearrangement of Cyclohexenone

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III Photochemistry 10 Hrs

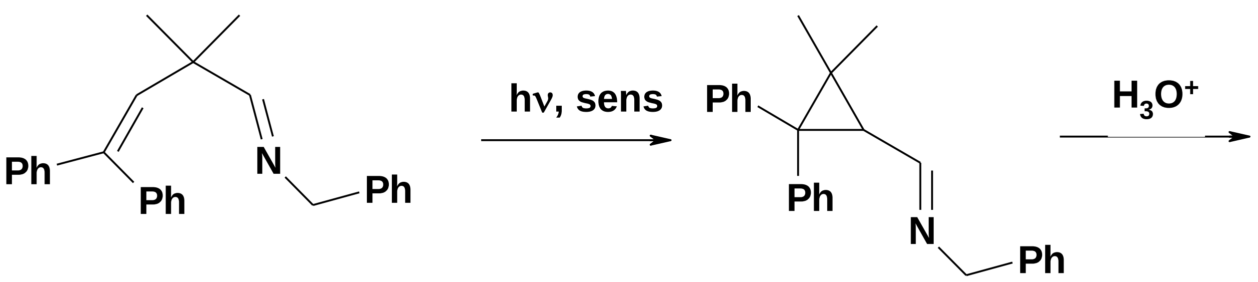
Thermal versus photochemical reactions, Electronic excitations: n–π* and π–π* transitions. Singlet and Triplet energy states: Comparison of energies, Lifetimes and Reactivity. Jablonski diagram, Allowed and forbidden transitions: Fluorescence, Phosphorescence and Internal conversion and Intersystem crossing.

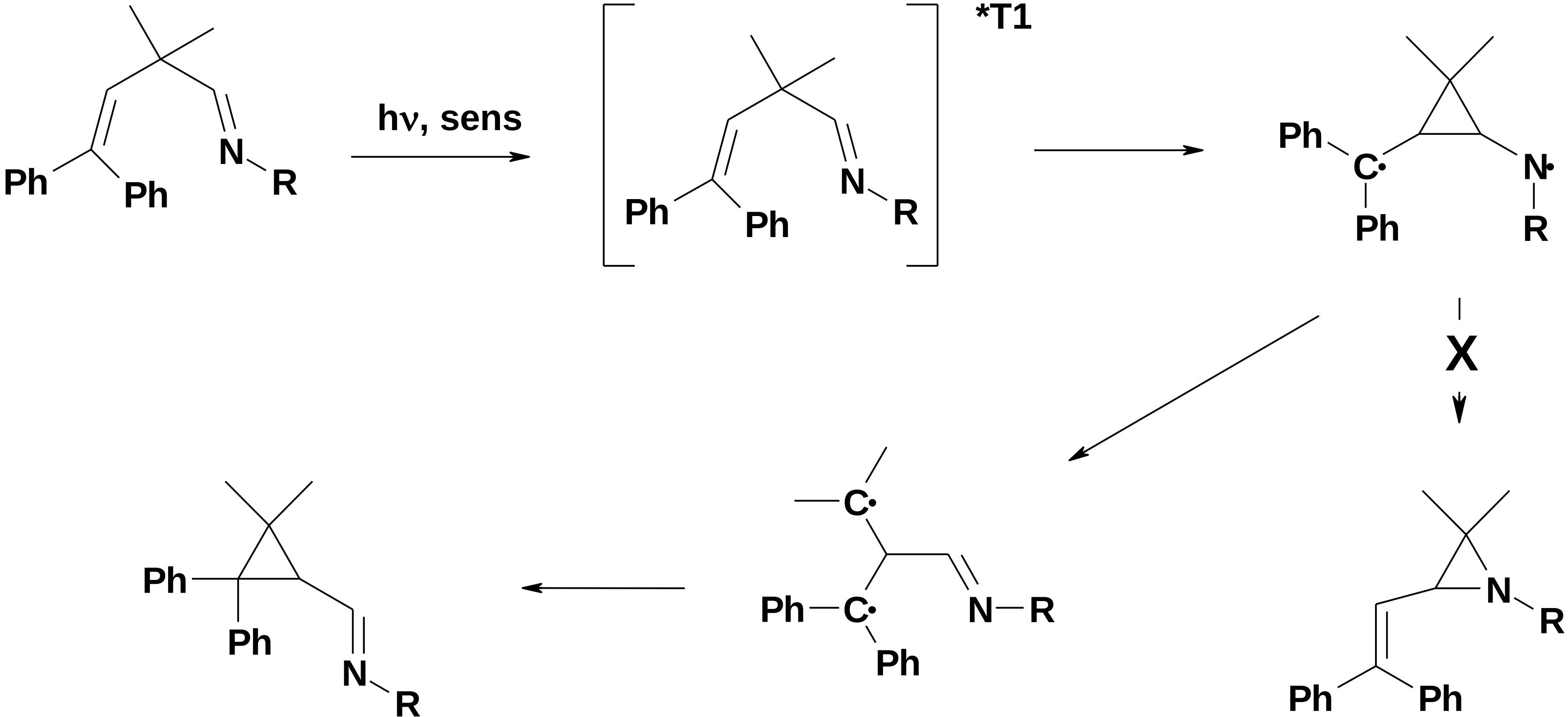
Photochemical reactions of saturated ketones : Norrish Type I and Norrish Type II reaction, Photoreduction of ketone, Photoaddition reactions, Paterno Buchi reaction. Photochemistry of simple olefins : Cis-trans isomerization, Di-pi methane rearrangement. Photooxidation : Formation of peroxy compounds,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

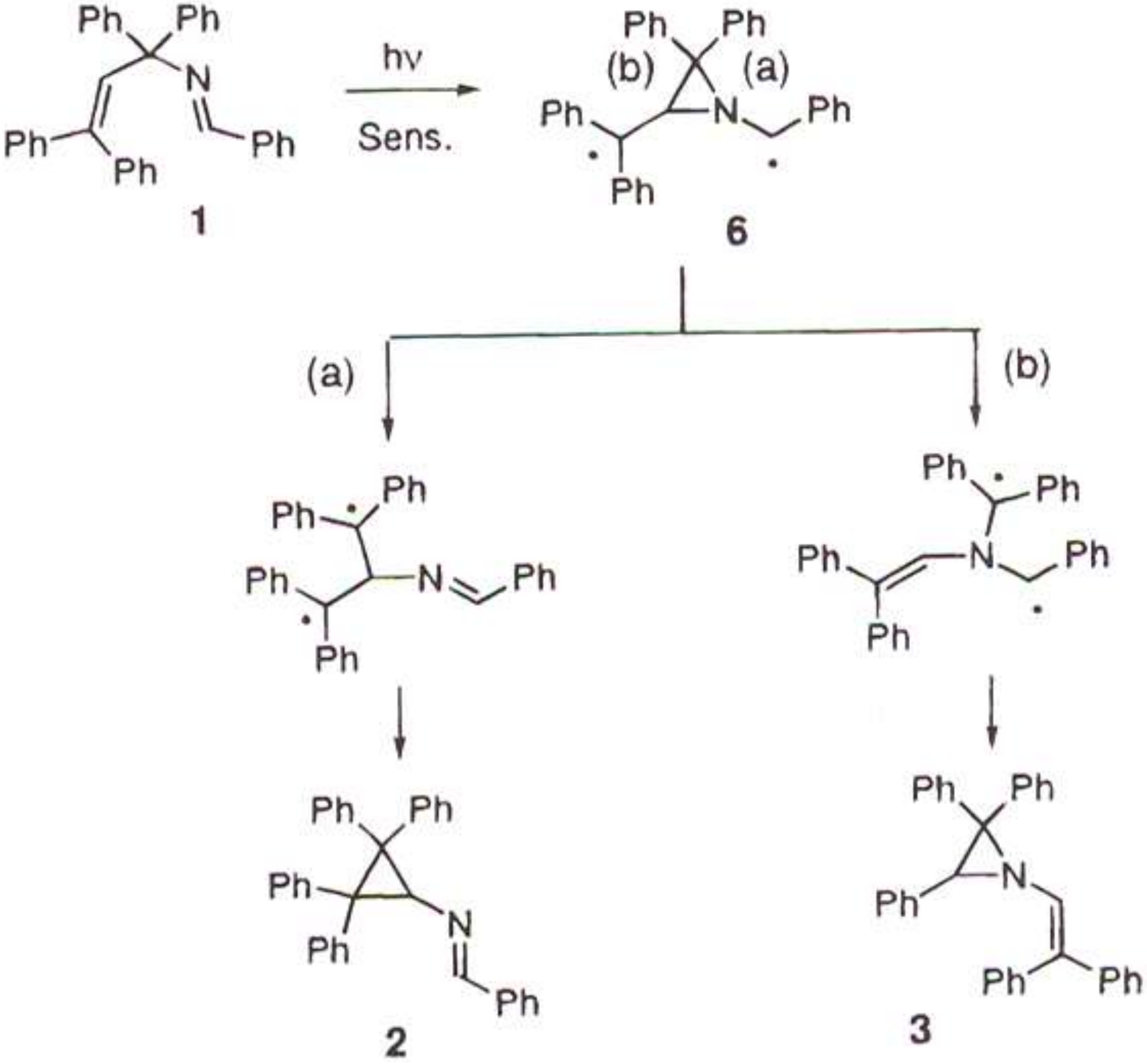
Coverage:

1. The Aza-Di-π-Methane Rearrangement
2. Photorearrangement of Cyclohexenone

The Aza-di-π-methane (ADPM) Rearrangement



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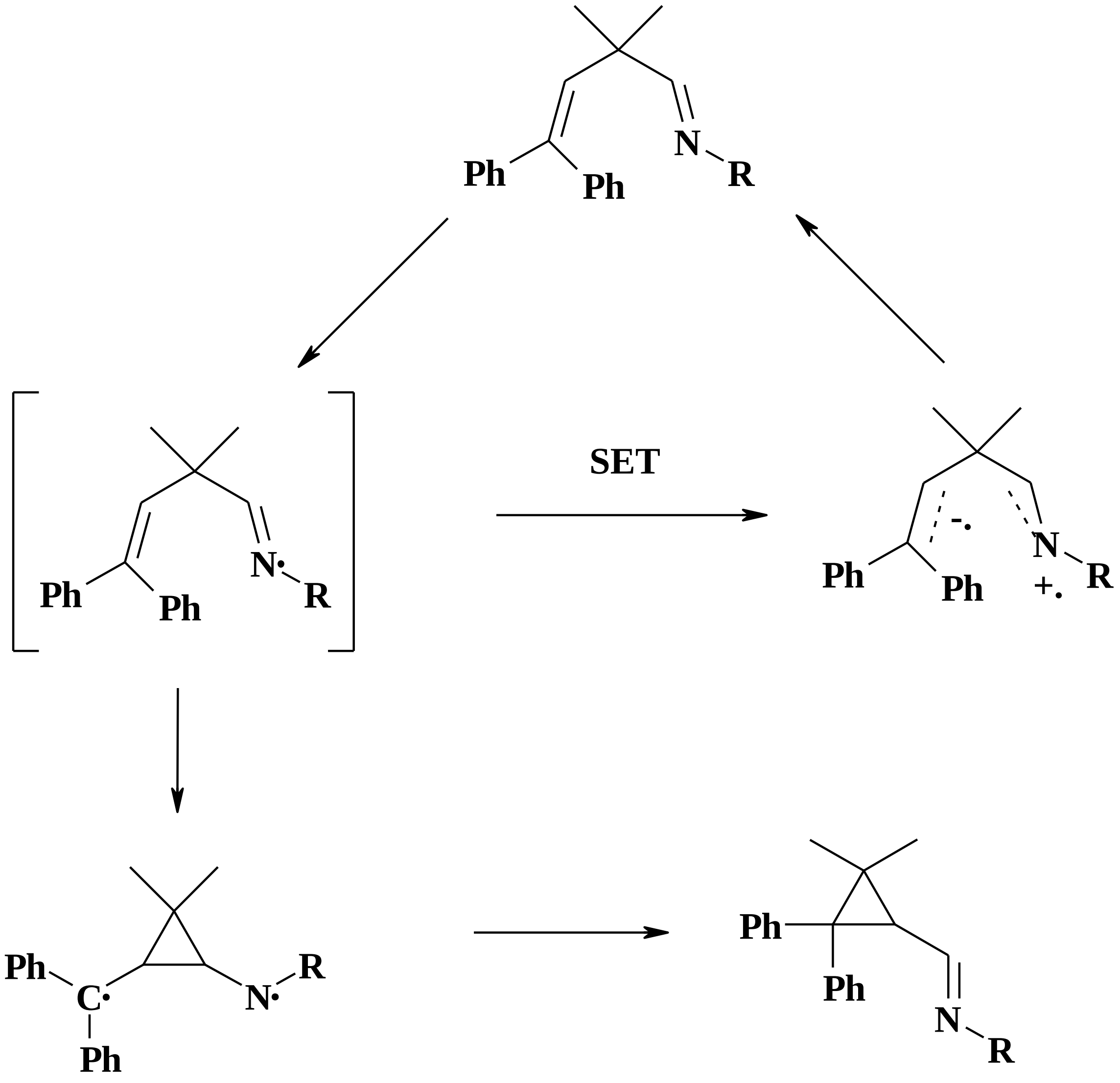
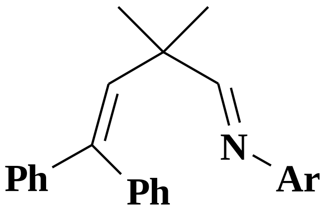
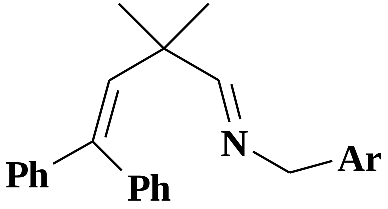
6
(a)
(b)
2
3

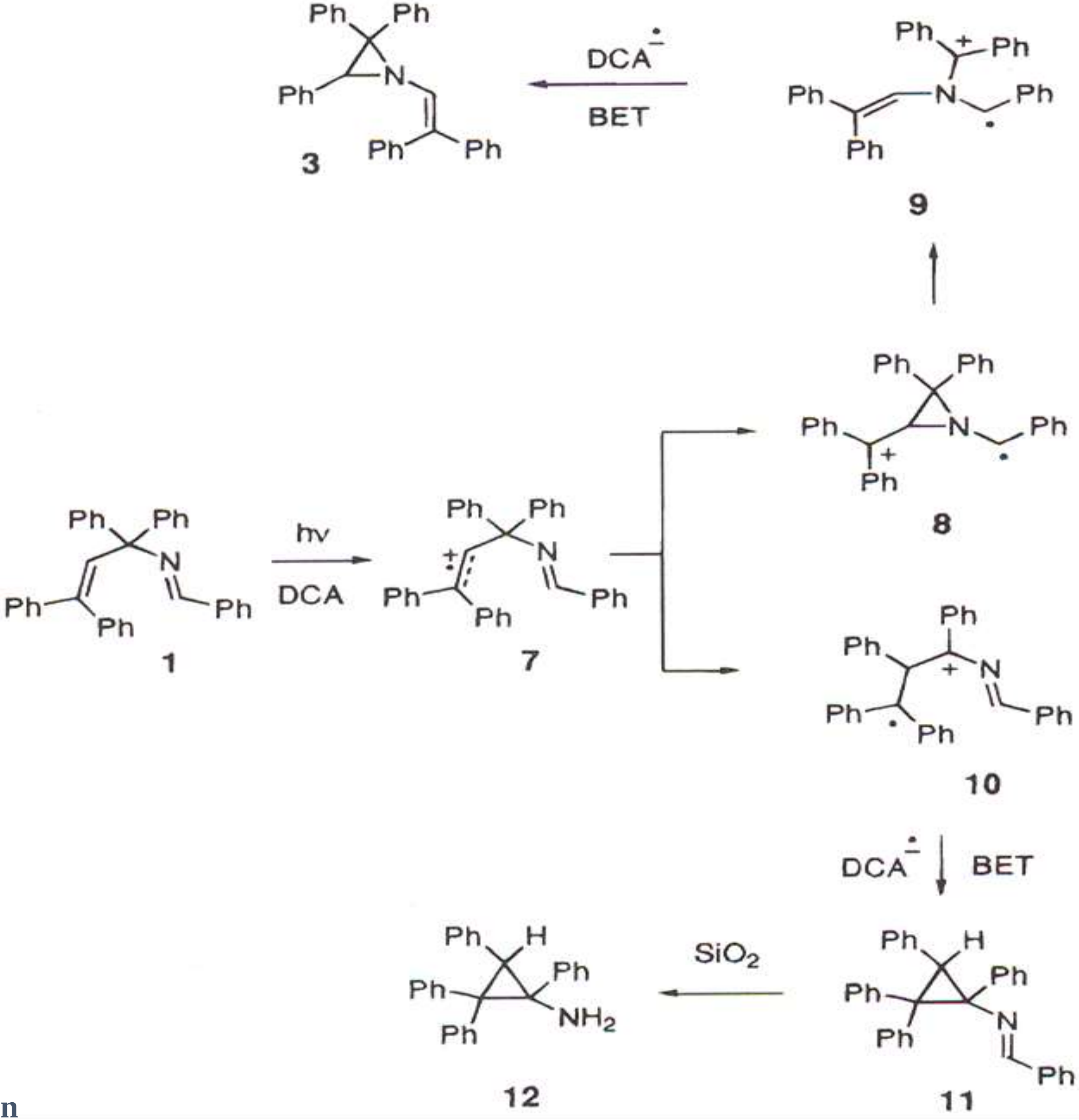




Ar = Ph
Ar = 4-OMe
Ar = 4 Cl
Ar = 3 Me
Ar = 4 CN



Ar = Ph
Ar = 4 Me
Ar = 4 Cl
Ar = 3 F
Ar = 4 CF_3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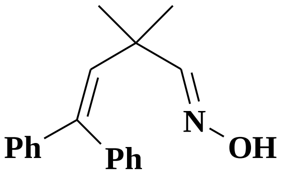
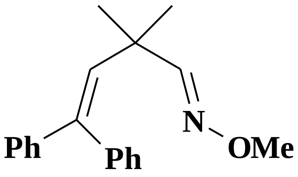
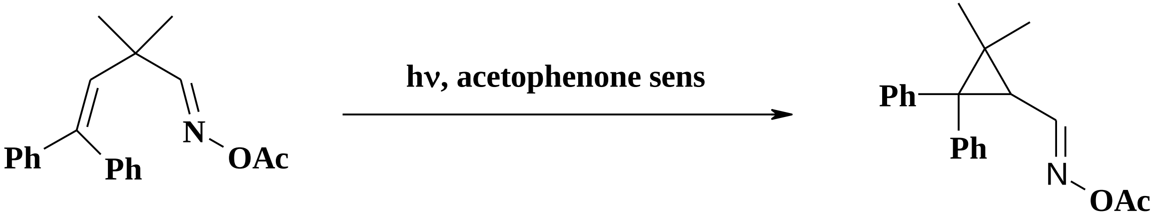
$DCA^{\dot{-}}$
BET
SiO_2
NH_2

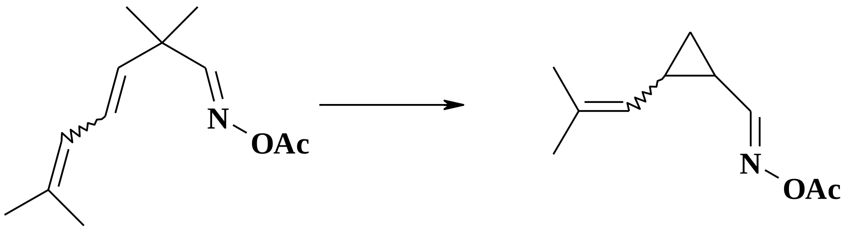


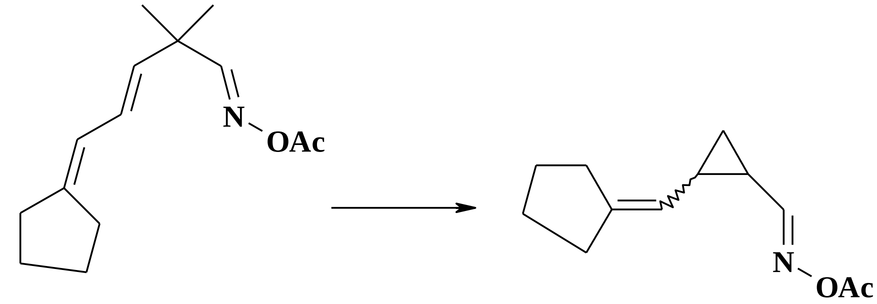


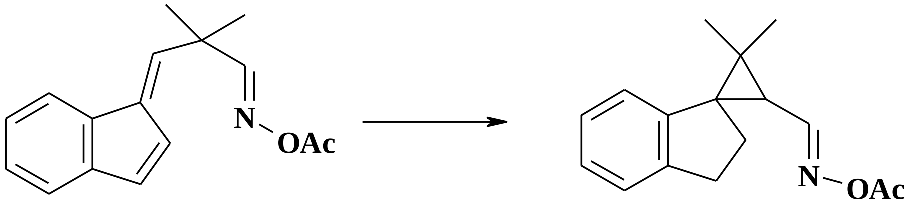
SET from "N" lone pair to the alkene moiety is restricted due to low IP of oxime and oxime ether

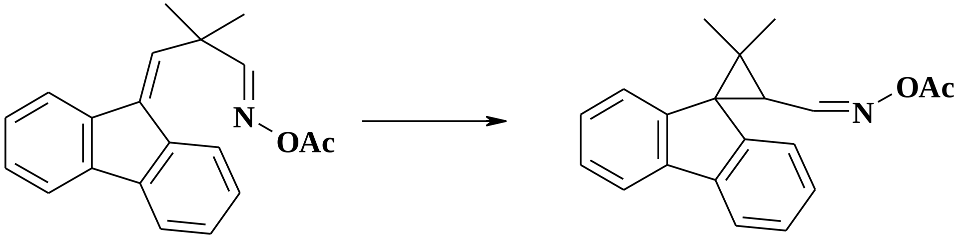


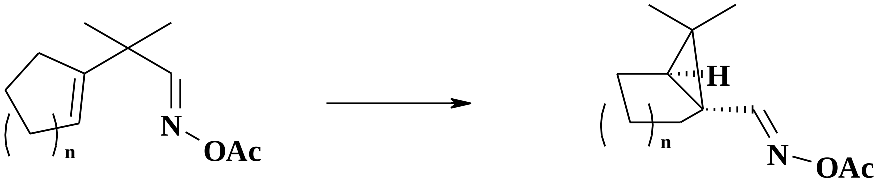
IP of the oxime can be raised by incorporating Ac group





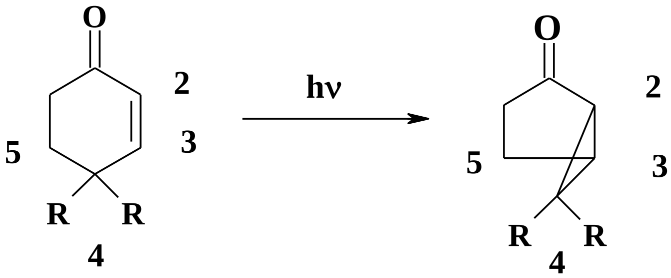




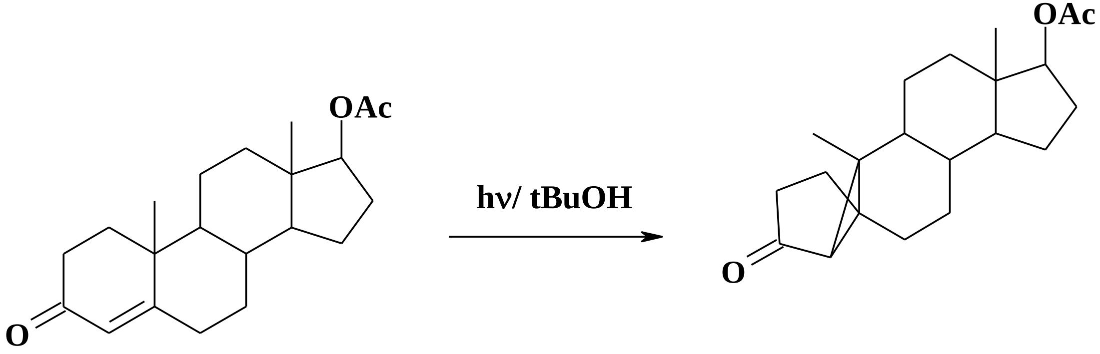


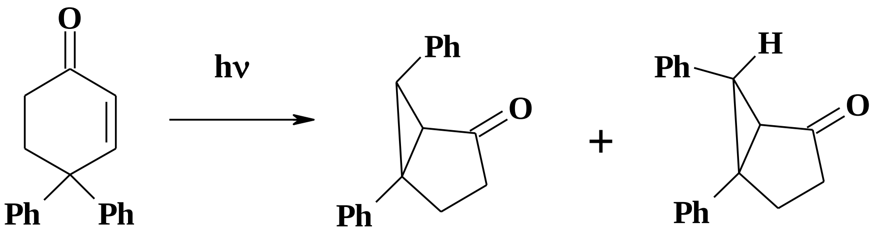
n = 1, 2, 3

Photorearrangement of cyclohexenones

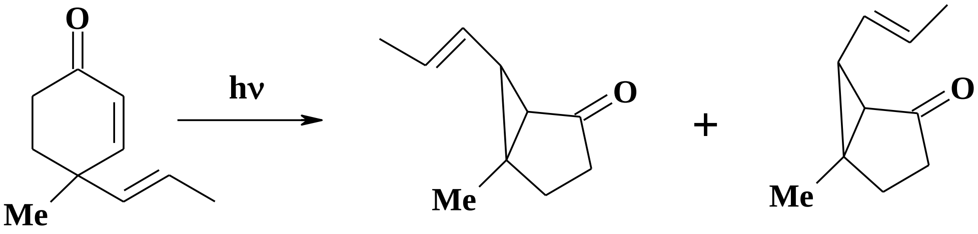


Type A

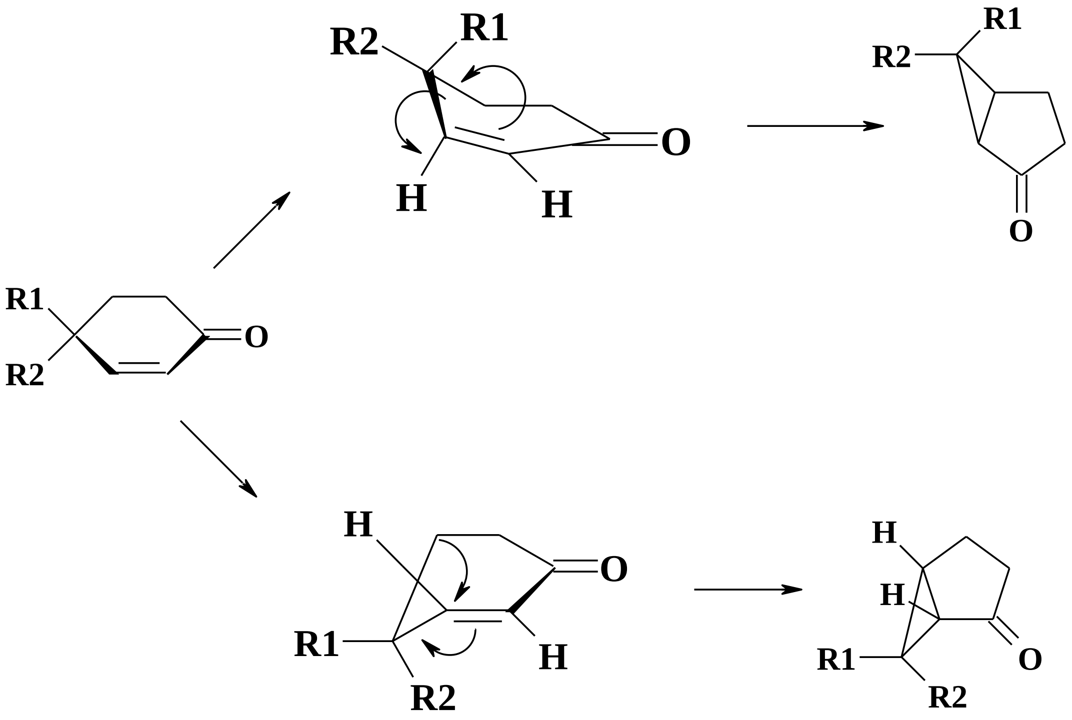


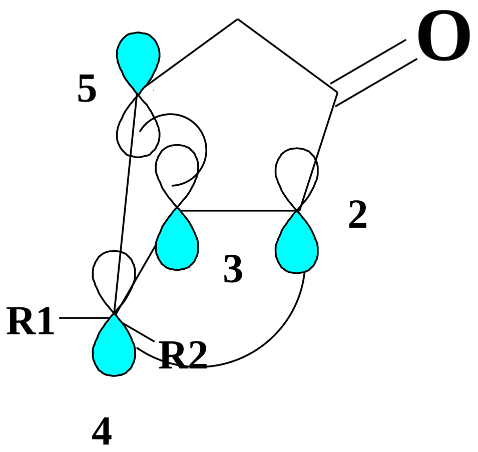


Type B

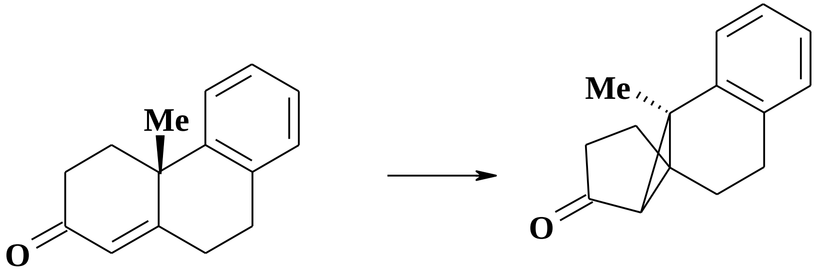


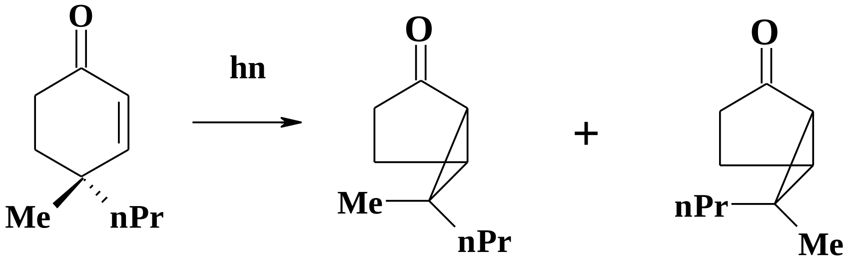
Mechanism and stereochemistry of Type A rearrangement





Inversion occurs at C-4



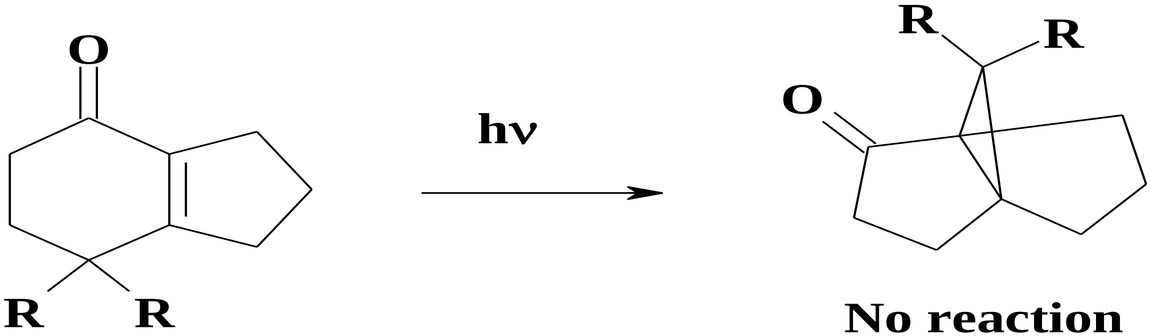


Inversion occurs at C-4

 # Cleavage of the bond between C4 and C5 of the enone is concerted with dformation of bond between C3 and C5 and C2-C4.

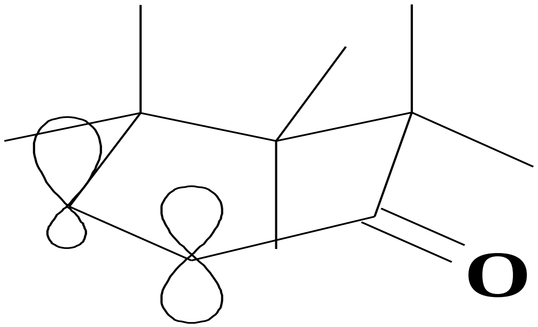
 # In a formal sense the reaction occurs with inversion at C4 and retention at C5

 # In a fuse ketone the rearrangement occurs on only one face of the enonebcause of steric constraints (i.e, the necessary of cis-fusion of the cyclopropaneto both five and six membered ring), hence yielding one product.



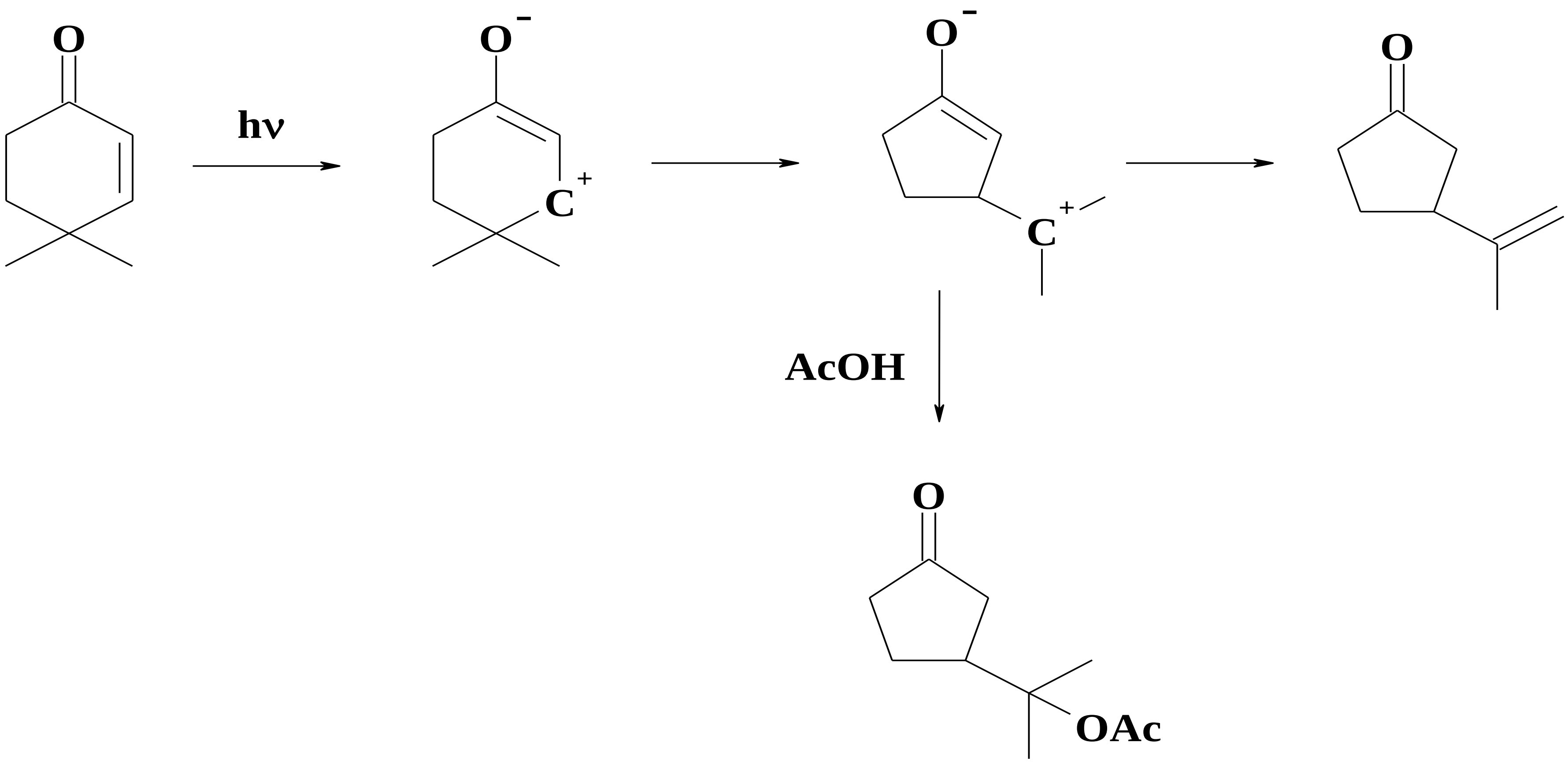
No reaction

R = Me
R = H

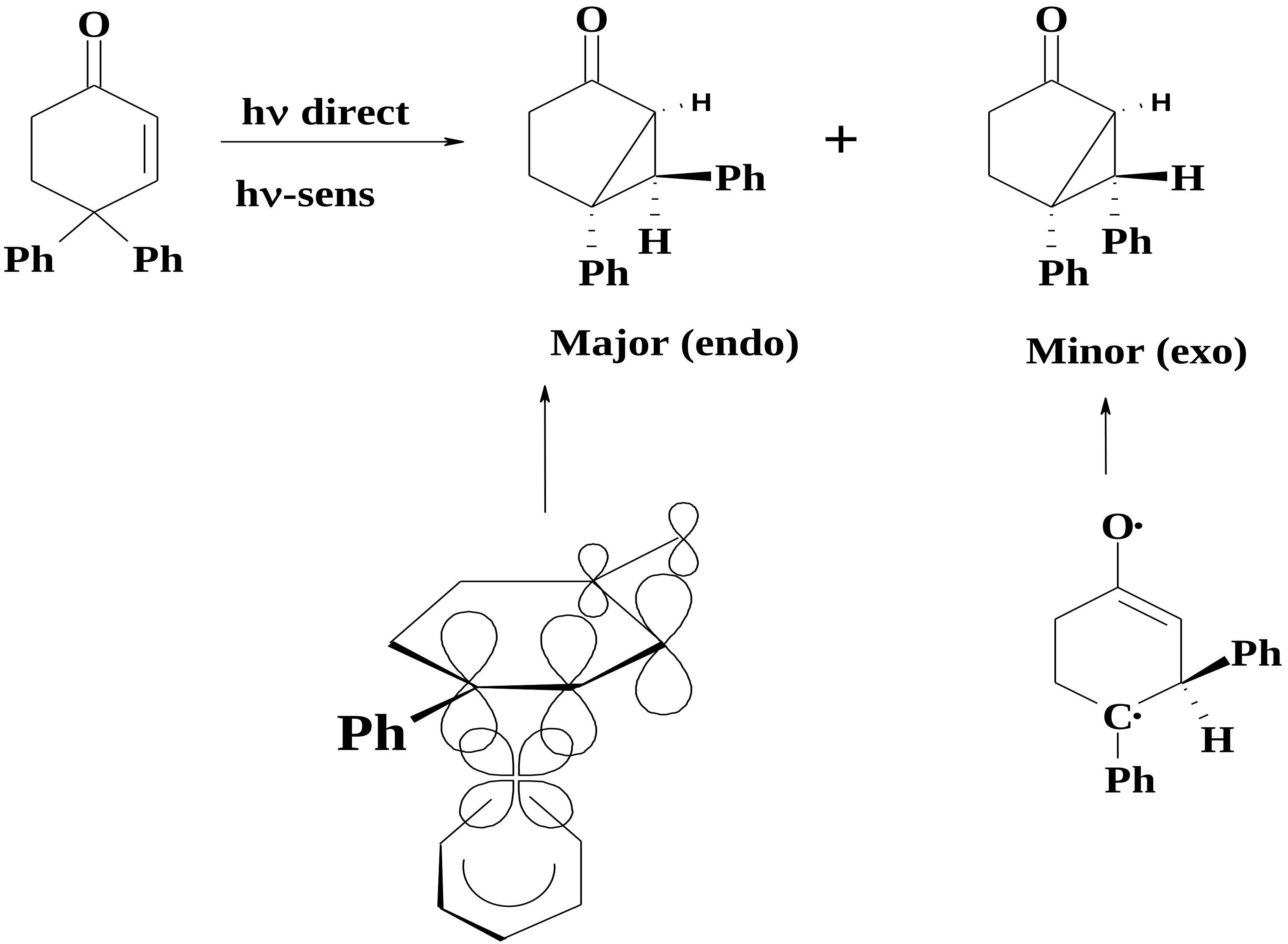


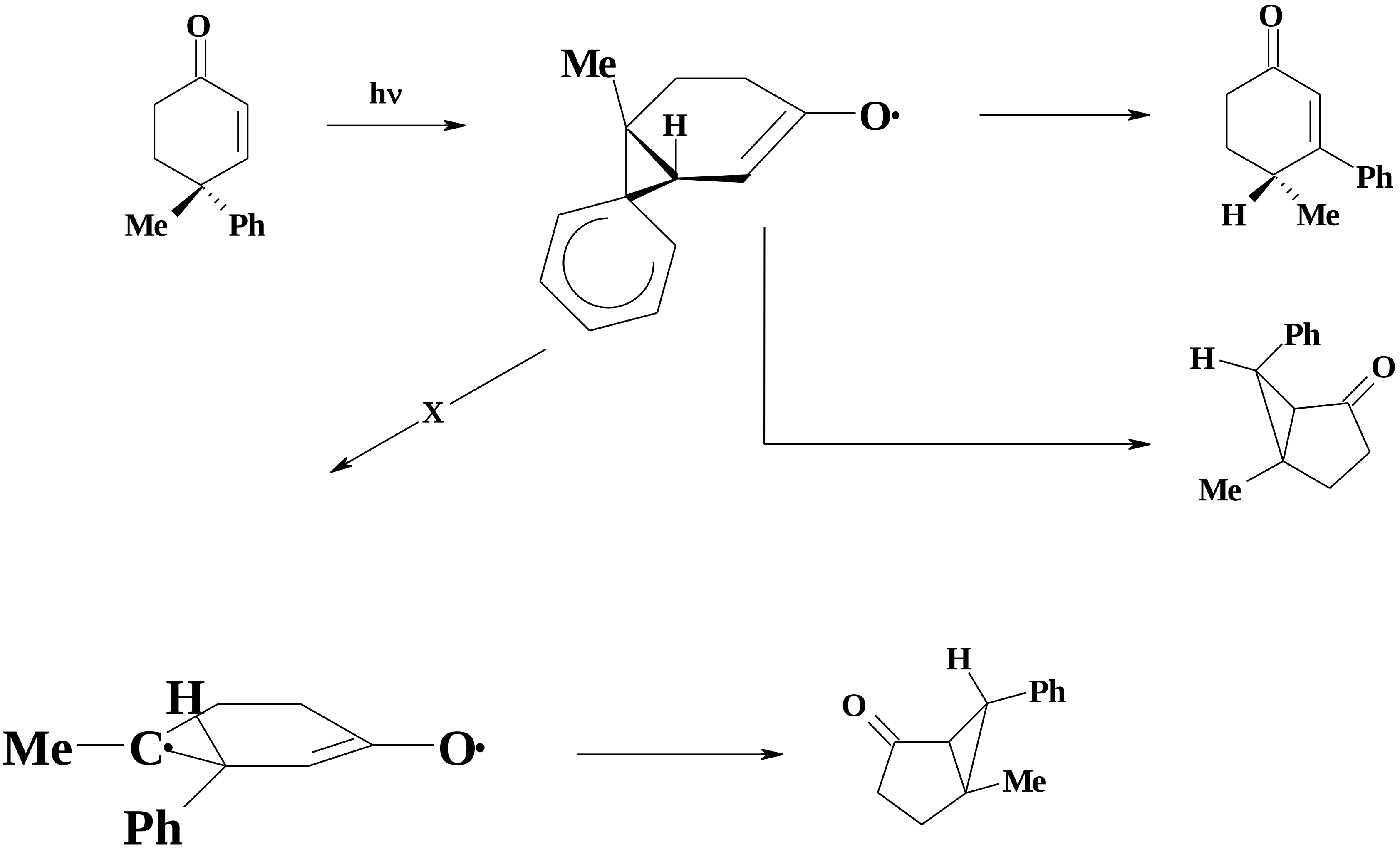
Twisted (around C=C bond) relaxed excited triplet state of ketone

Competititing reactions



Mechanism and stereochemistry of Type B rearrangement: Aryl and vinyl migration

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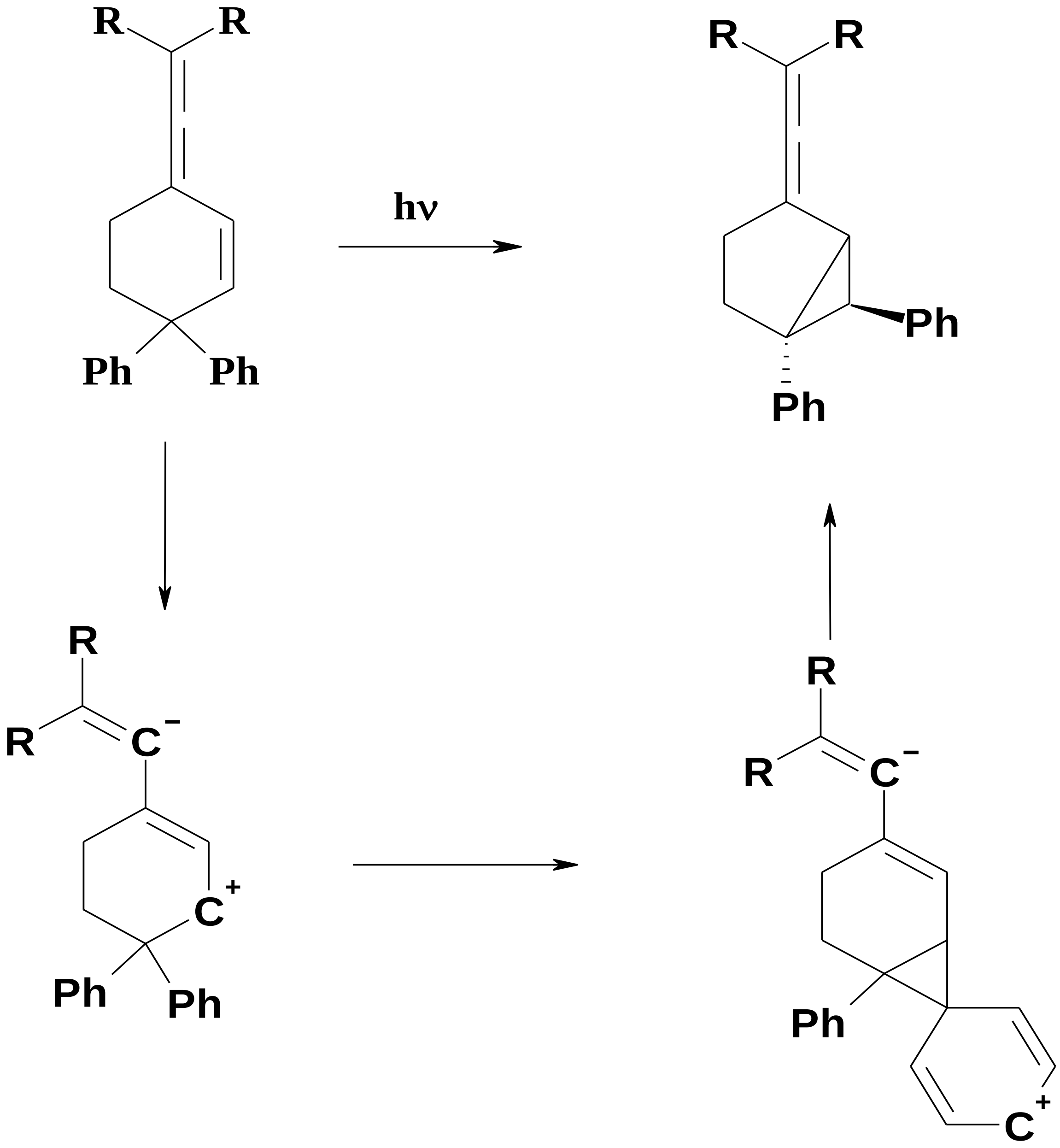
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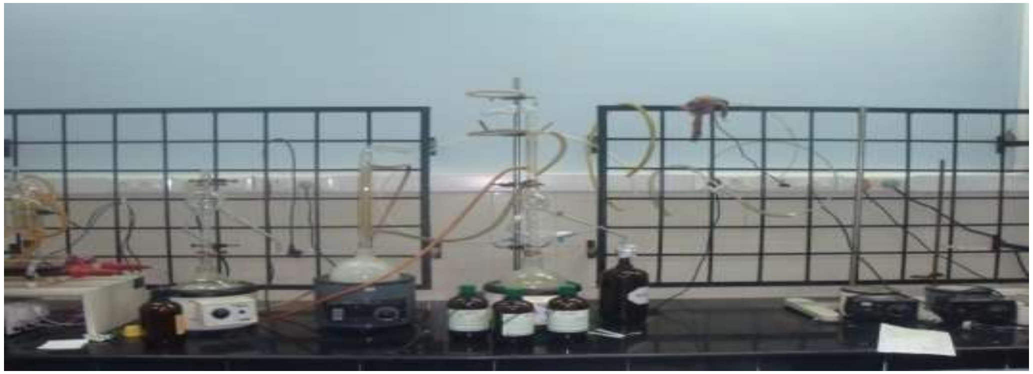
Thank You



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