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

III. Photochemistry

10. The Oxa-Di-π-Methane Rearrangement

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III Photochemistry 10 Hrs

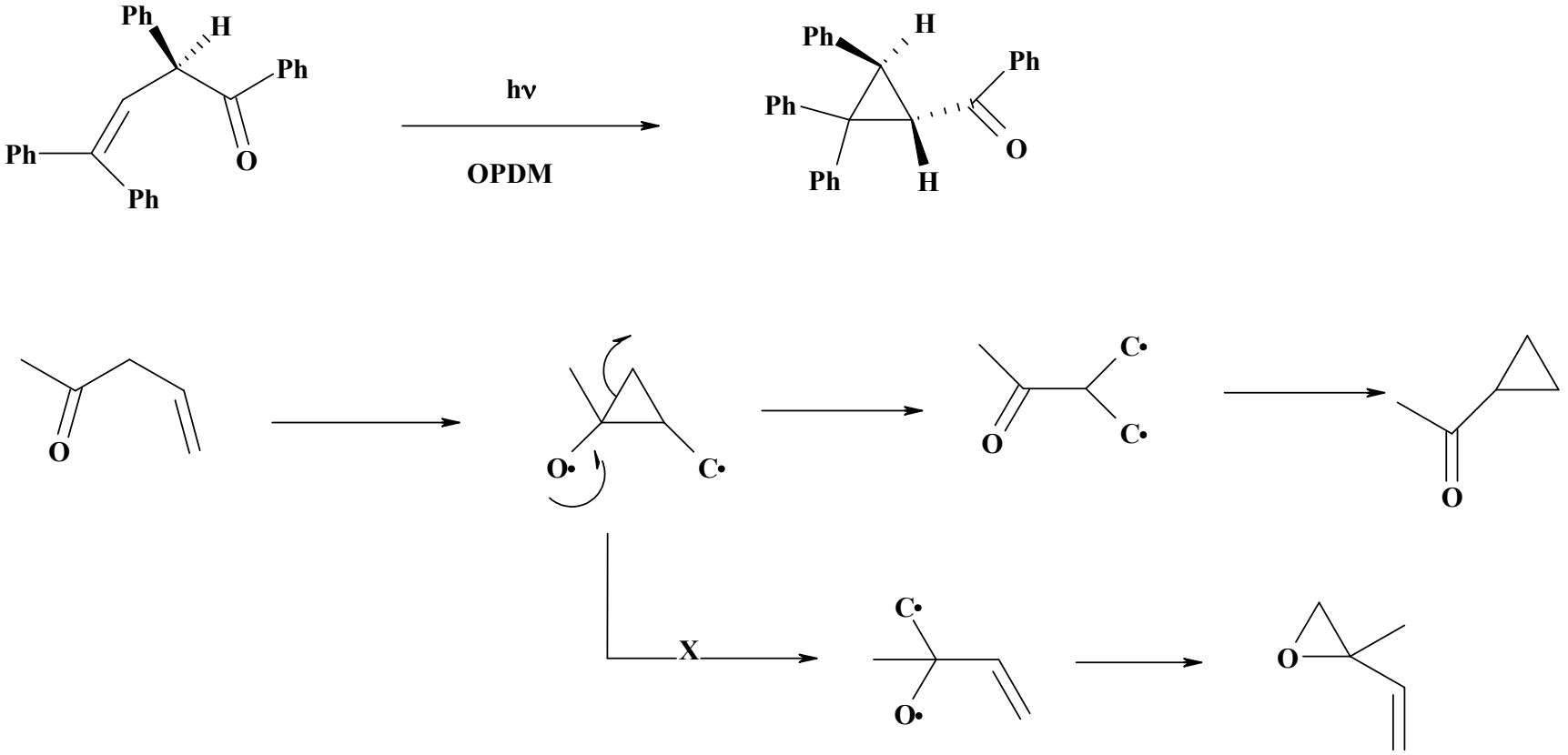
Thermal versus photochemical reactions, Electronic excitations: n–π* and π–π* transitions. Singlet and Triplet energy states: Comparison of energies, Lifetimes and Reactivity. Jablonski diagram, Allowed and forbidden transitions: Fluorescence, Phosphorescence and Internal conversion and Intersystem crossing.

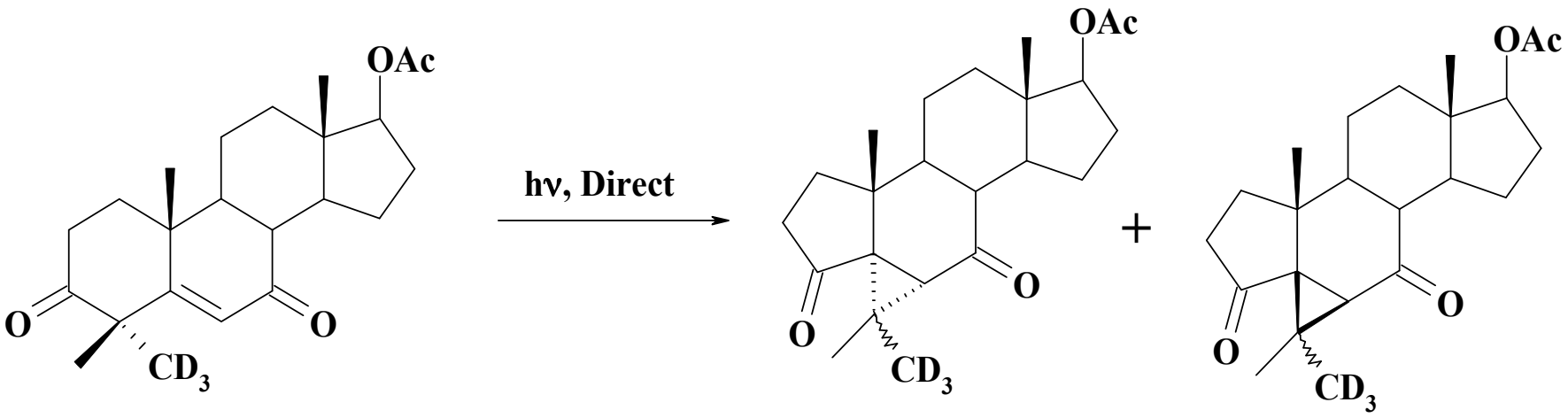
Photochemical reactions of saturated ketones : Norrish Type I and Norrish Type II reaction, Photoreduction of ketone, Photoaddition reactions, Paterno Buchi reaction. Photochemistry of simple olefins : Cis-trans isomerization, Di-pi methane rearrangement. Photooxidation : Formation of peroxy compounds,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

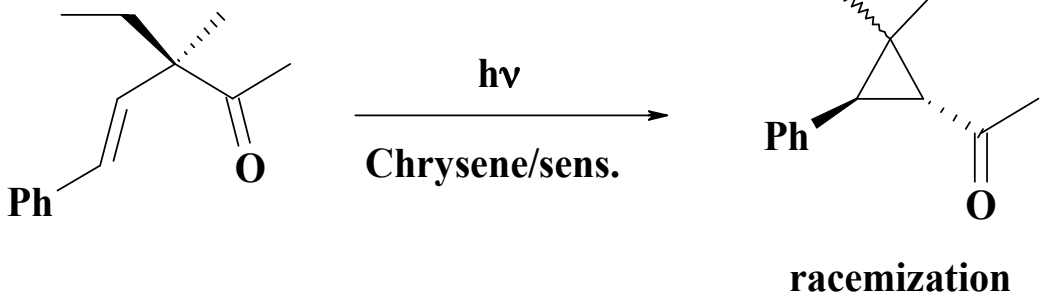
Coverage:

The Oxa-Di-π-Methane Rearrangement

The Oxa-di-π-methane rearrangement

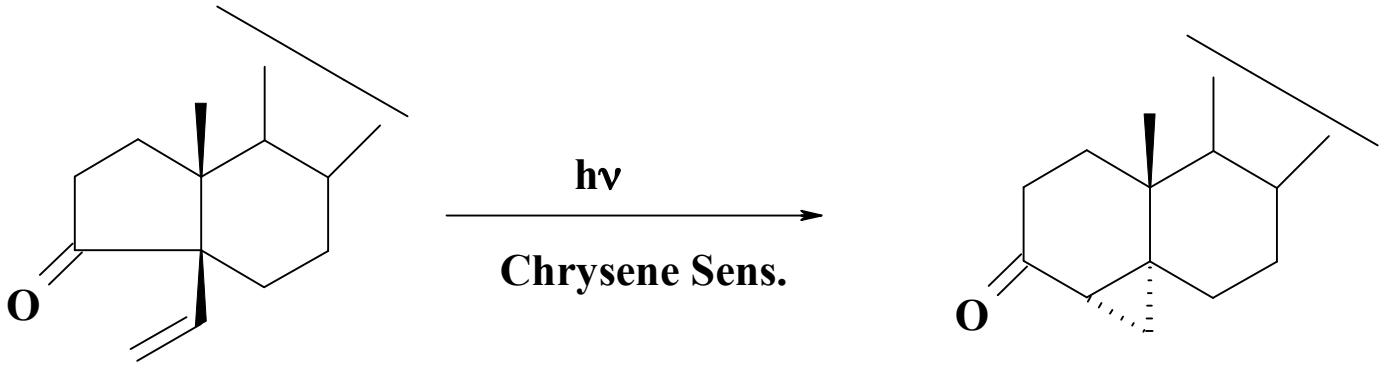


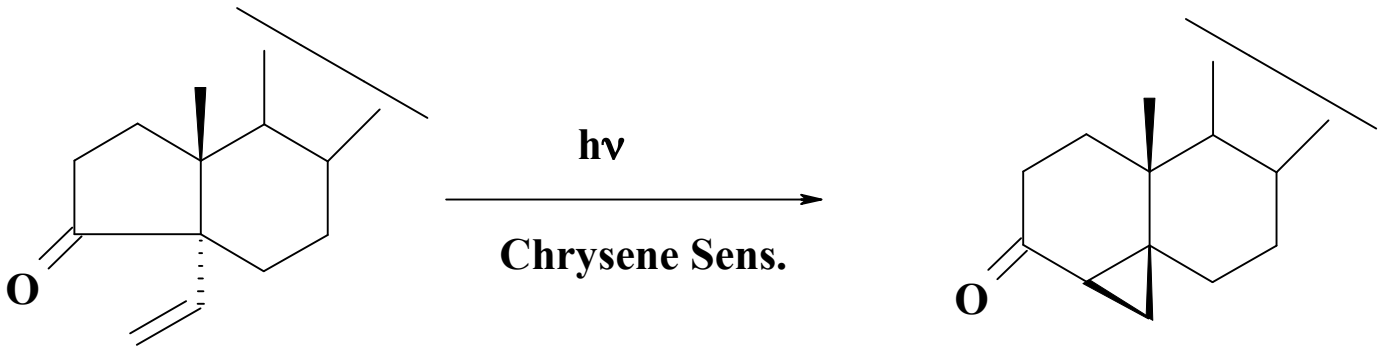




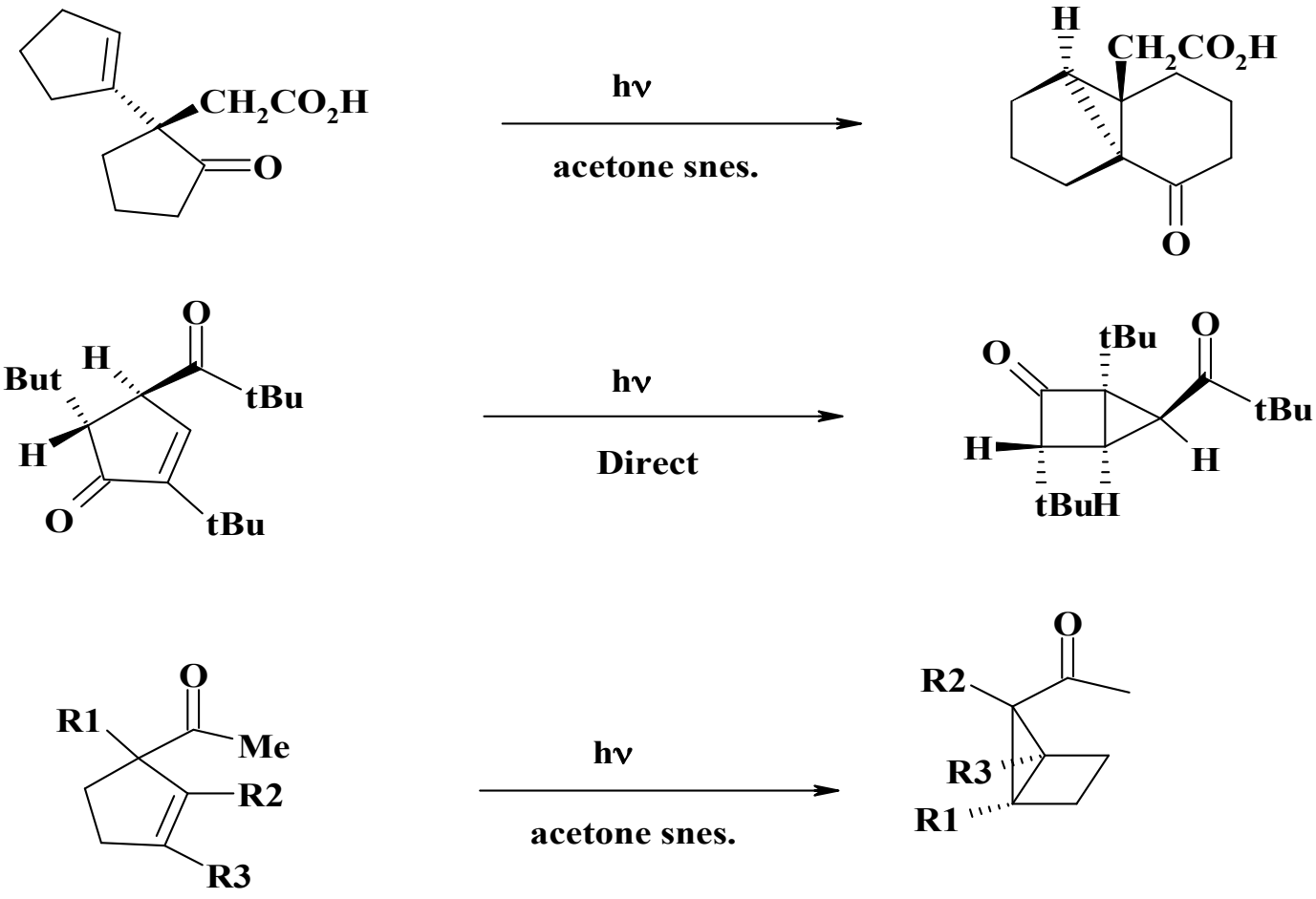
racemization

Retention of Configuration



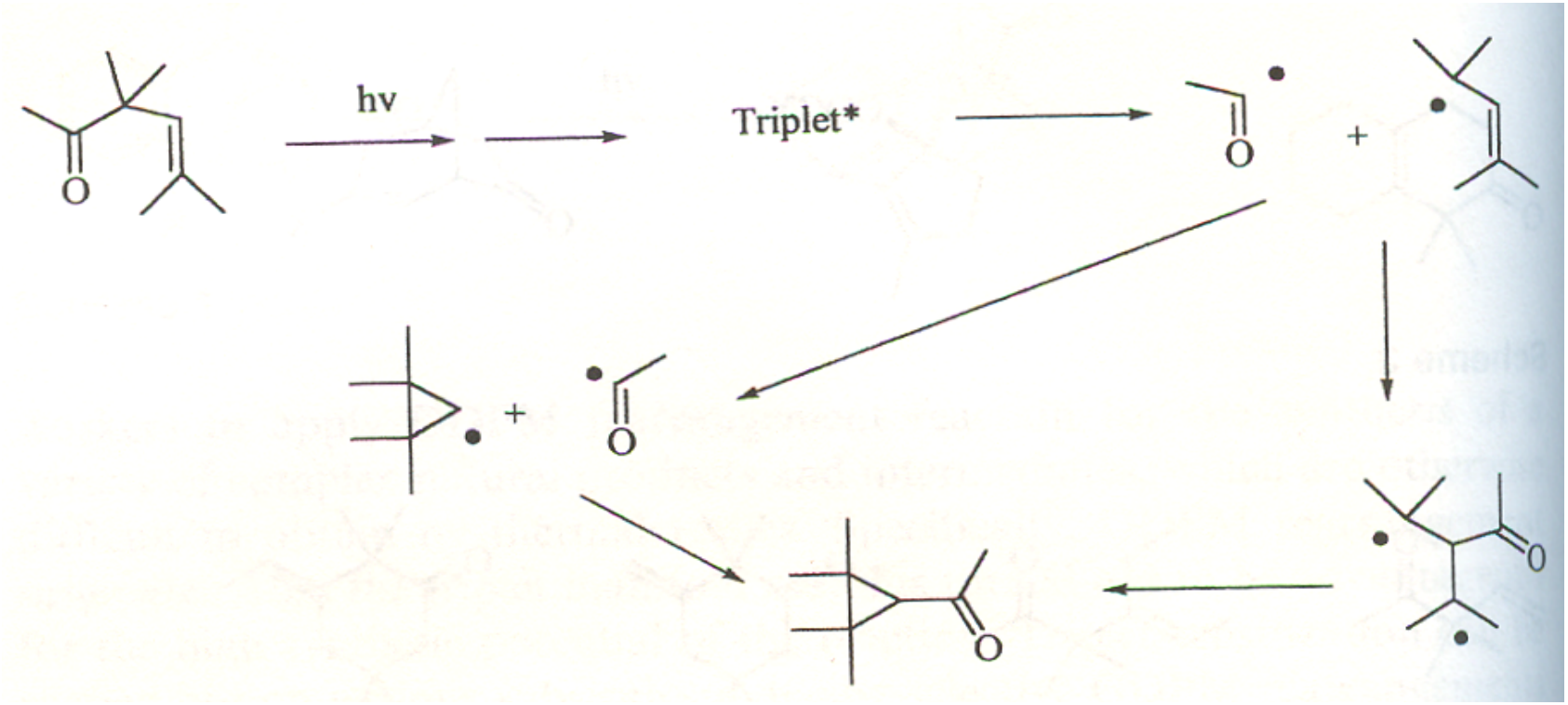


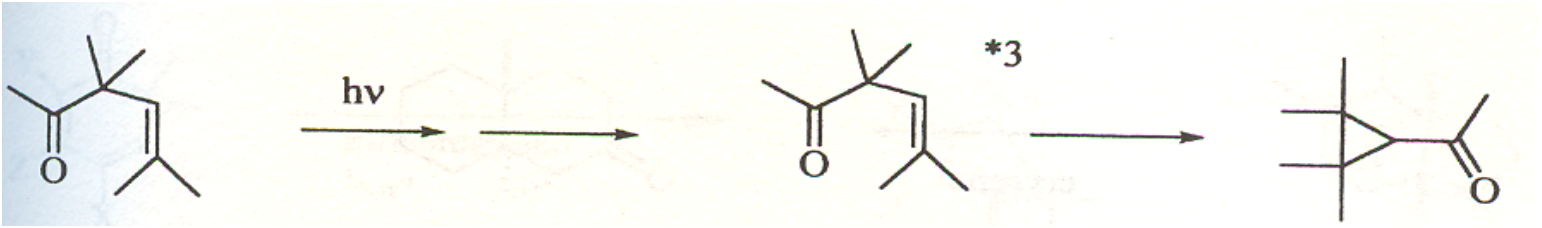
Inversion of conviguration



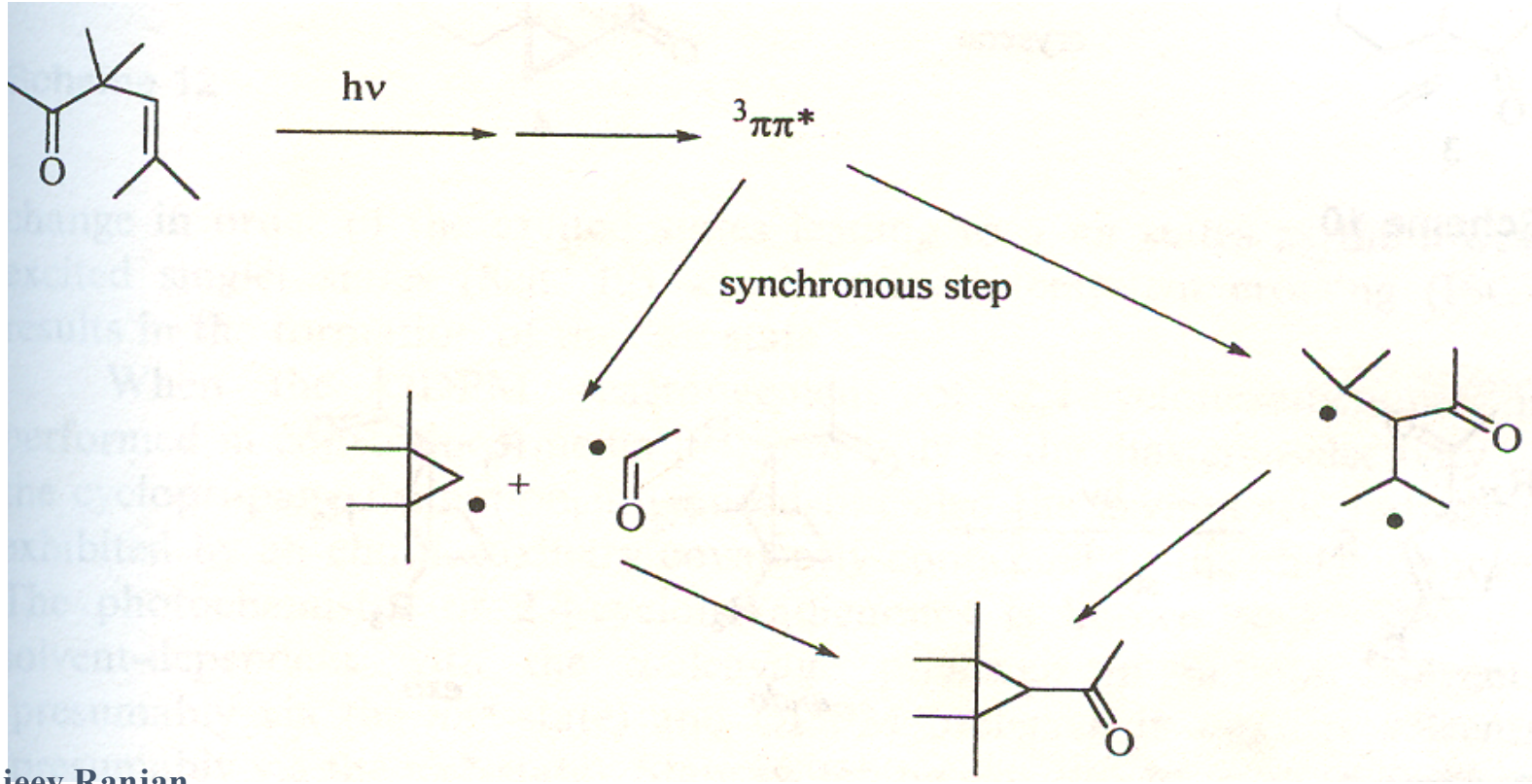
The Oxa-di-π-methane Rearrangement

Mechanism I





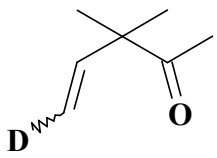
Mechanism II

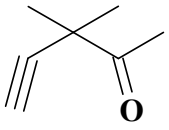


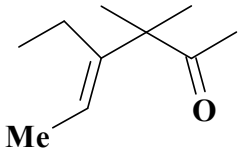
The OPDM rearrangement of acyclic β,γ-unsaturated ketones

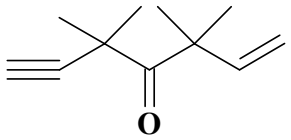
Key structural features favoring OPDM

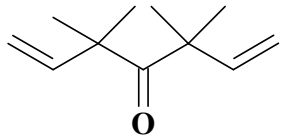
 # Conjugation of the alkene moiety with phenyl, vinyl or oxo groups (efficient triplet energy transfer, biradical stabilization)
 # disubstitution or alternatively, monosubstitution by bulky groups at the central carbon

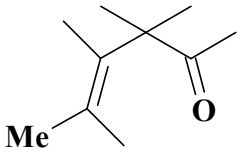


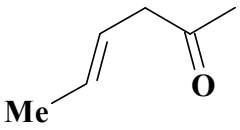


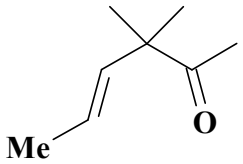


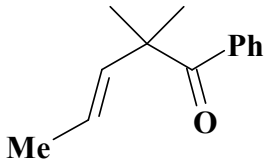


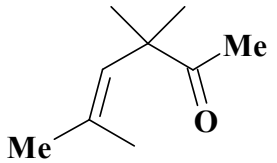


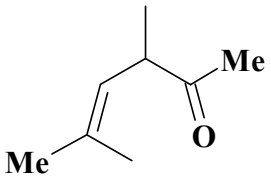


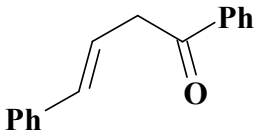


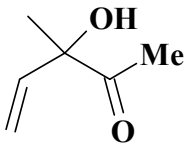


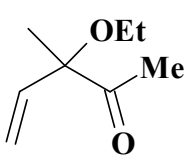


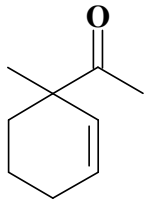


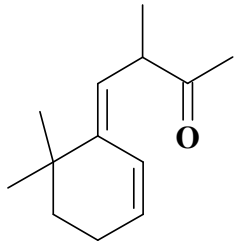


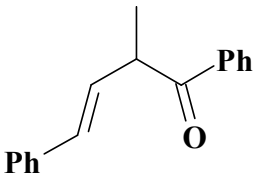


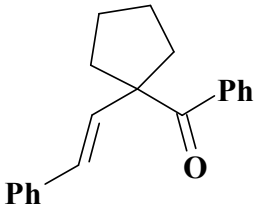


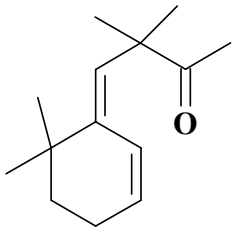


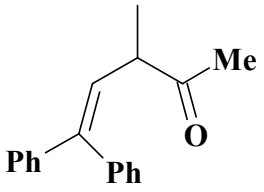


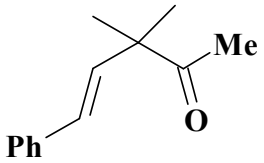




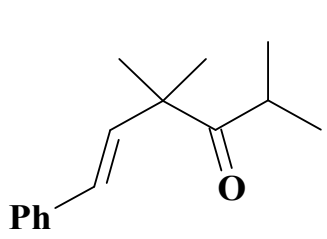


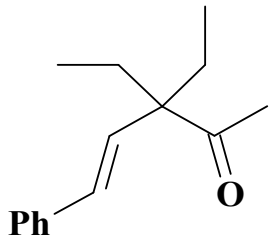


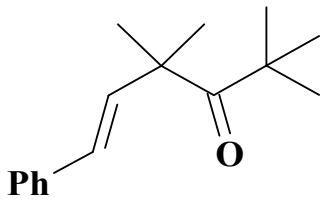


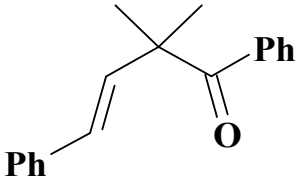


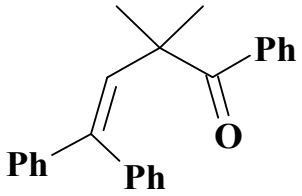
Unreactive towards OPDM

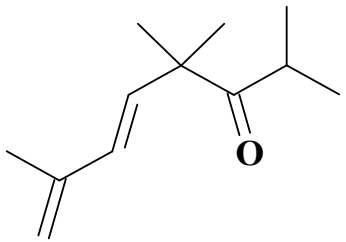


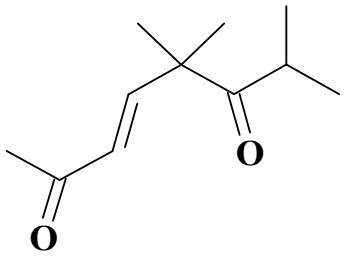


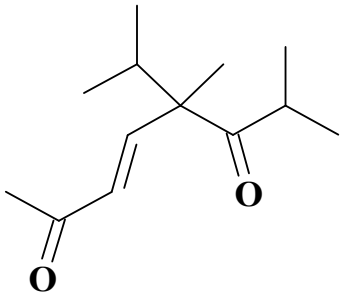


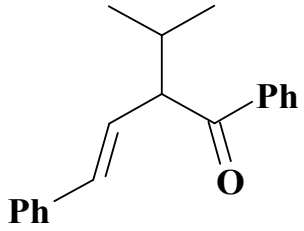






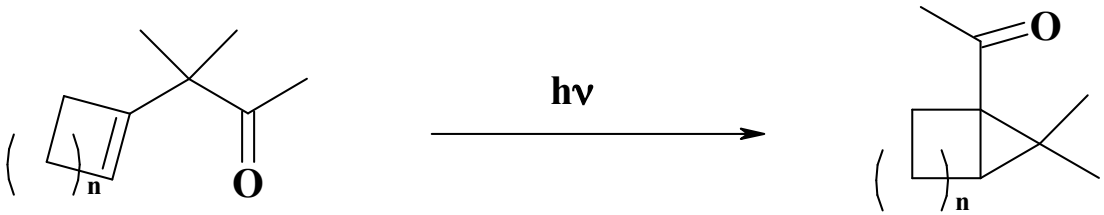




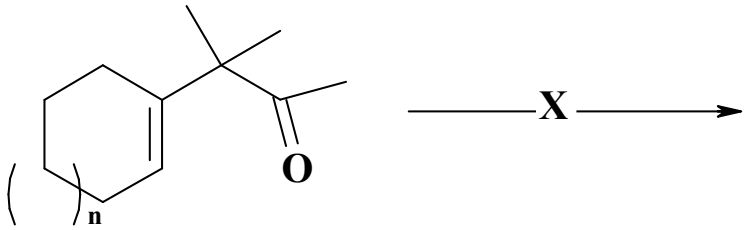


 # The cental methylene carbon is di-substituted or having bulky mono substitution
 # Conjugation with vinyl, phenyl or carbonyl groups

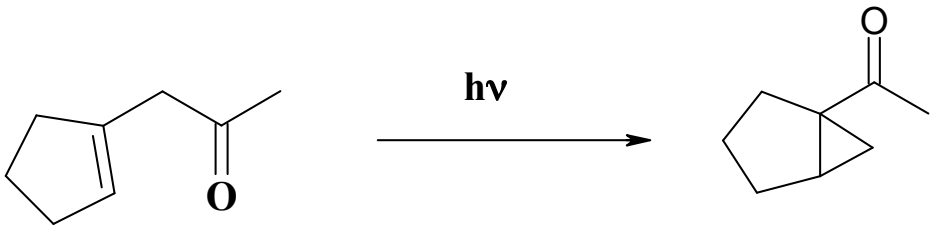
The OPDM Rearrangement of cycloalkenyl β.γ-unsaturated ketones



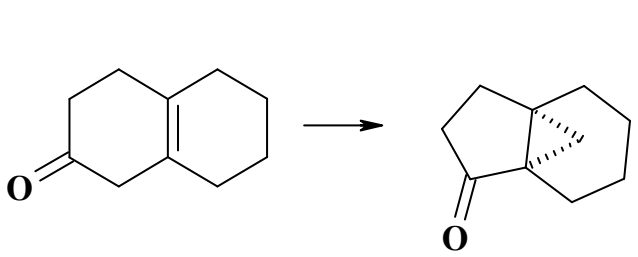
n = 1, 2 n = 1, 2

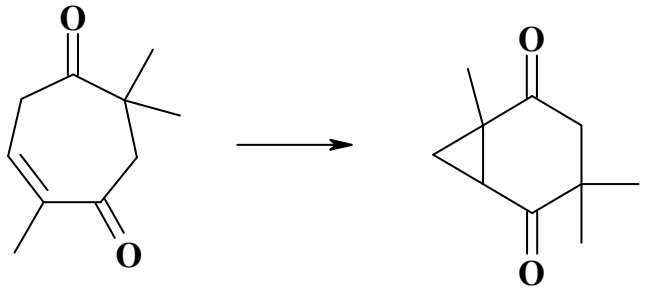


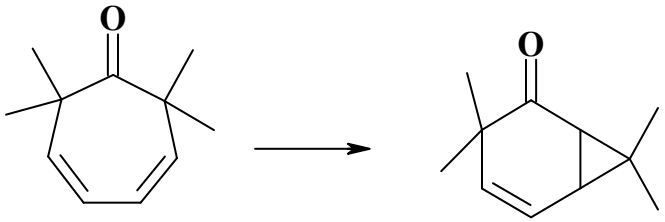
n = 1, 2, 3

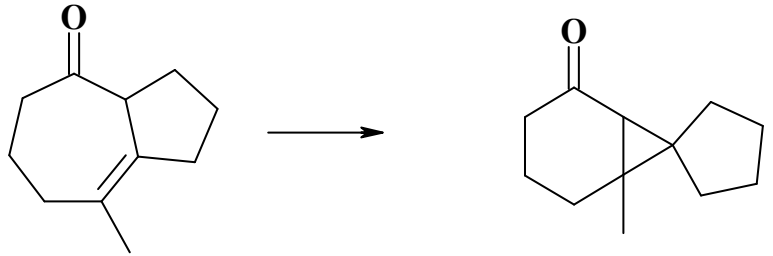


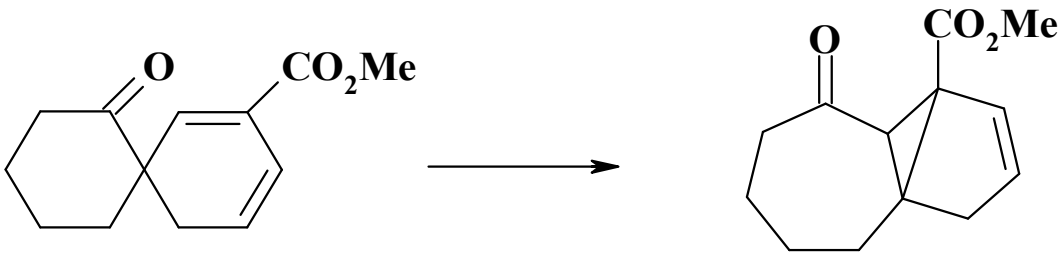
The OPDM rearrangement s of monocyclic and condensed polycyclic β,γ-unsaturated ketones

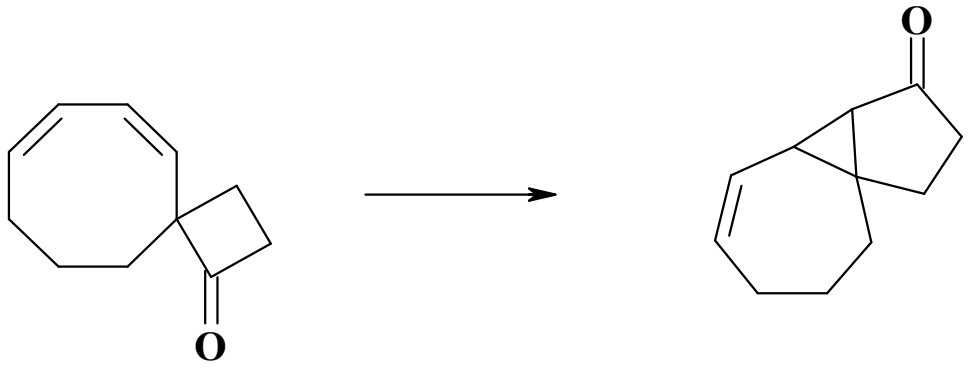


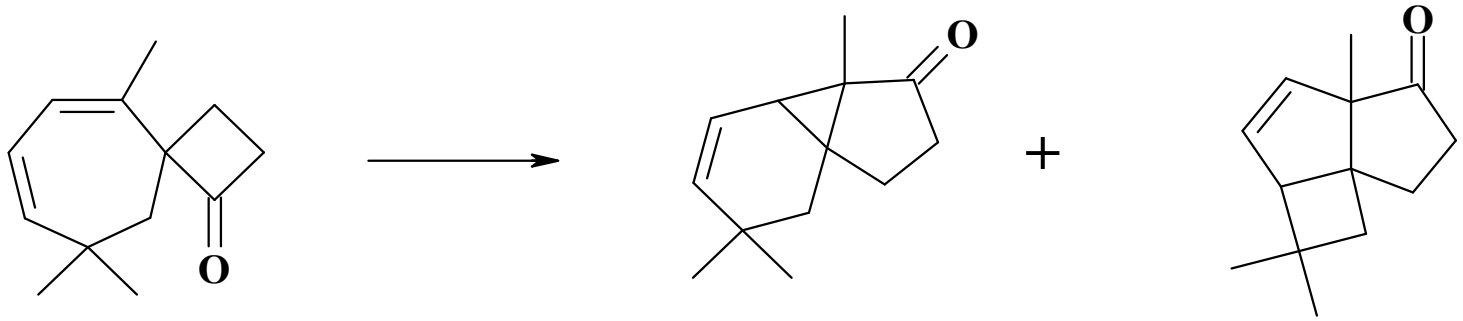




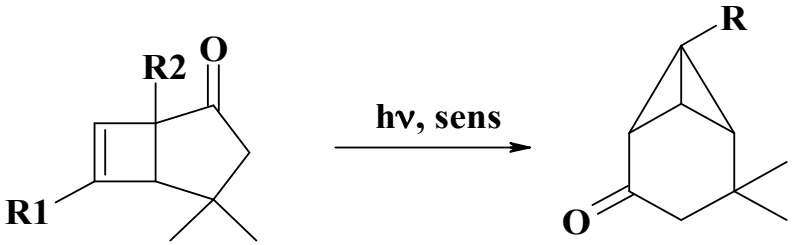



O
CO2Me
O
CO2Me

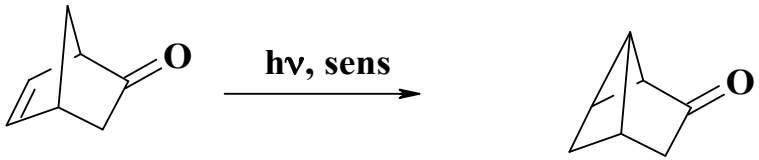

O
O

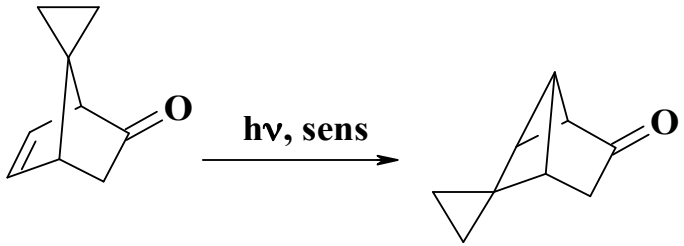

O
O
O
+
O

The OPDM rearrangement of Bridged cyclic β,γ-unsaturated ketones



R1 = Me, R2 = H
R1 = H, R2 = Me
R1 = R2 = H





Thank You

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