**B.Sc. Semester-VI**
**Group-A / DSE-4**
**Organic Synthesis**

# III. Photochemistry

## 6. Norrish Type I Reaction

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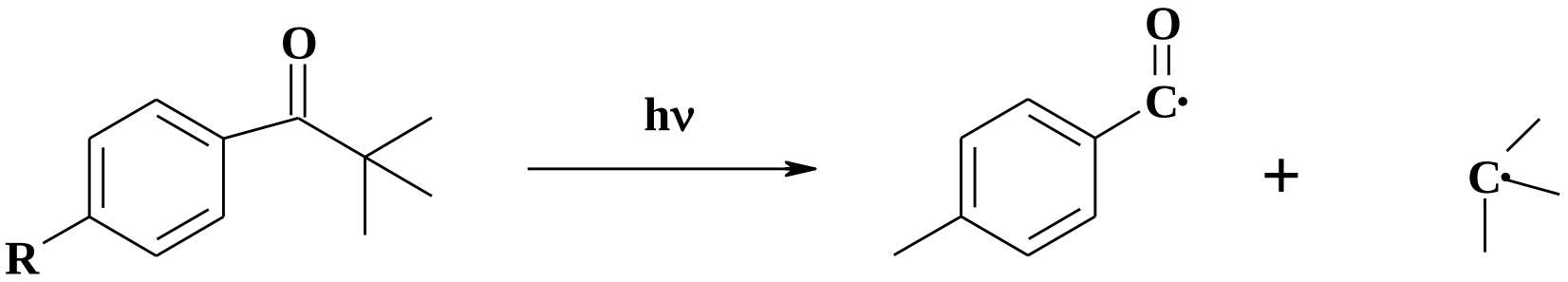
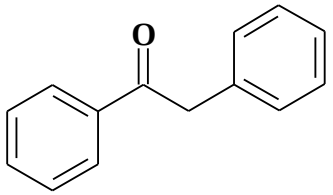
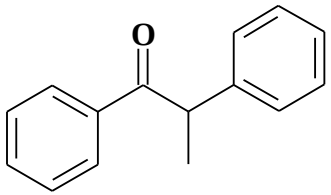
**University Department of Chemistry**
**Dr. Shyama Prasad Mukherjee University, Ranchi**

# Norrish Type I Reaction

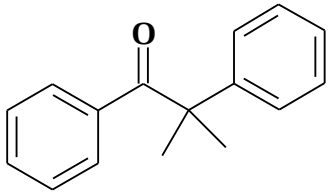




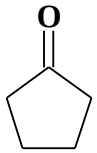
**2 X $10^6$**



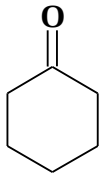
**3 X $10^7$**



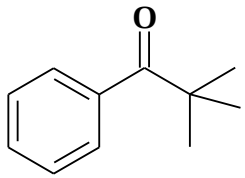
**1 X $10^8$**



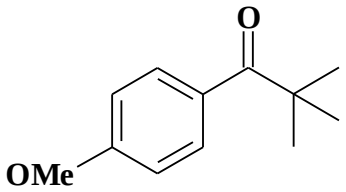
**2 X $10^8$**



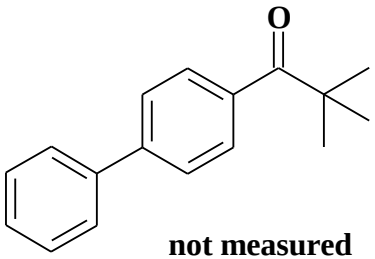
**2 X $10^7$**



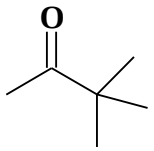
**1 X $10^7$**



**7 X $10^5$**



**not measured**



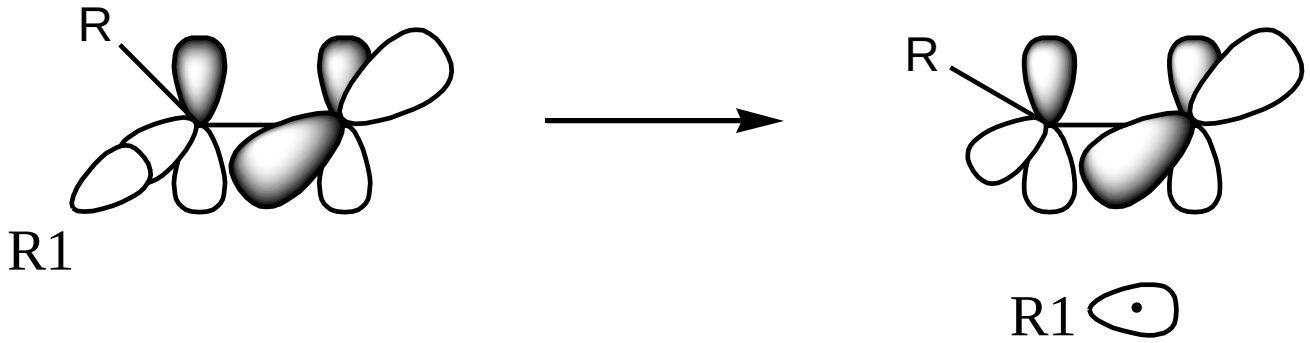
**>$10^9$**

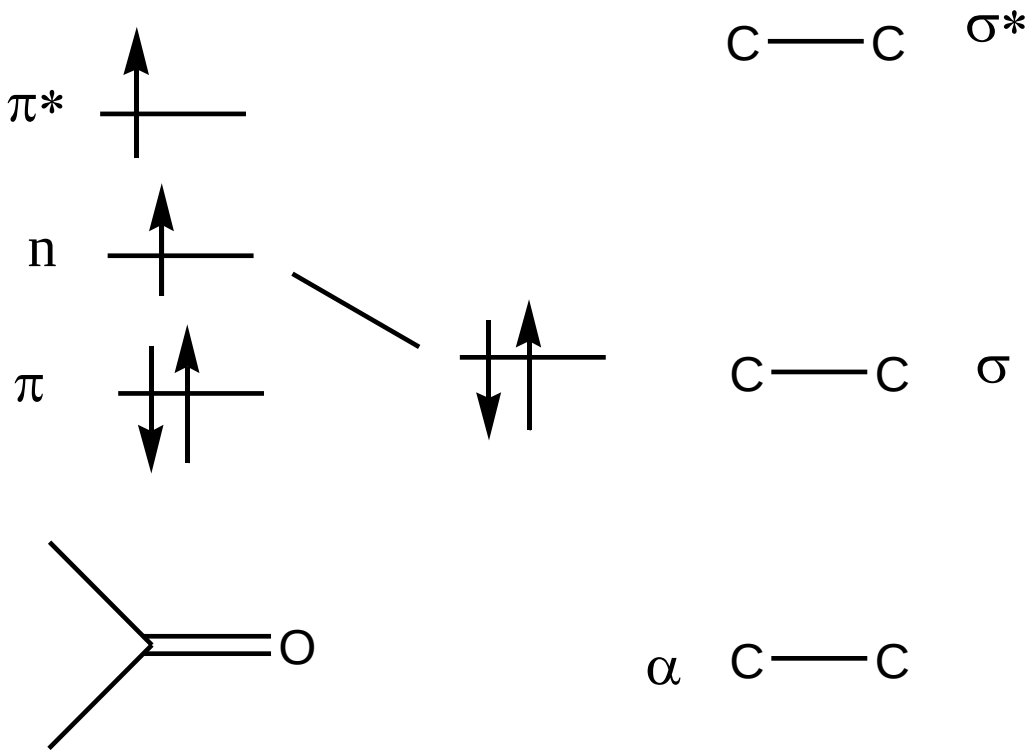
**# Norish type I reaction is much faster for n-π* compared to π–π* excited states**

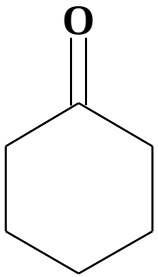
**# n-π* reactivity is due to the weakening of the α-bond by overlap of this bond with the half vaccant n-orbital of oxygen.**

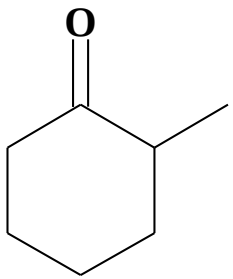
**# This overlap is not possible for π–π* excited states**

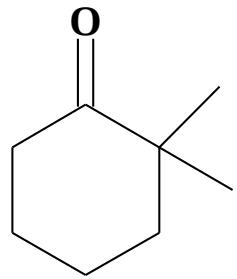
**# Electron releasing group at para position lead to stabilization of π–π* excited states hence decrease in reactivity**


R
R1
R
R1

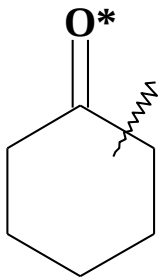

π*
n
π
C—C
σ*
C—C
σ
O
α
C—C







| | | | |
|---|---|---|---|
| $K_\alpha$ | 3.3 x $10^7$/s | 4.7 x $10^8$/s | 1.8 X $10^9$/S |



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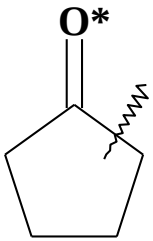

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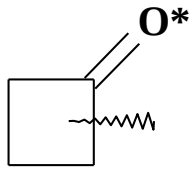
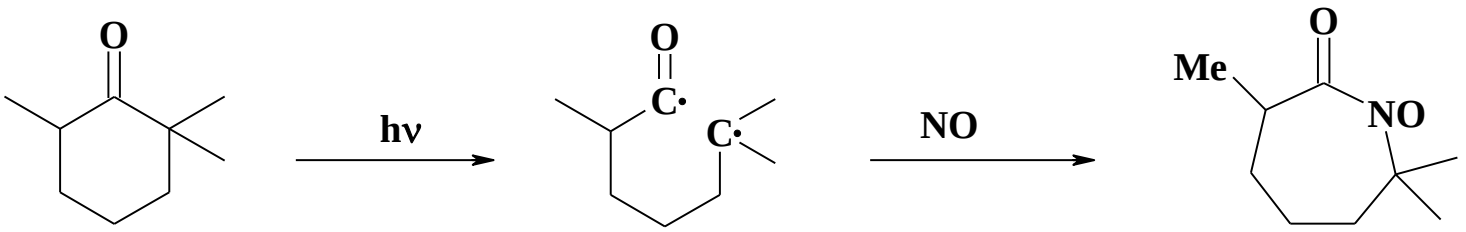
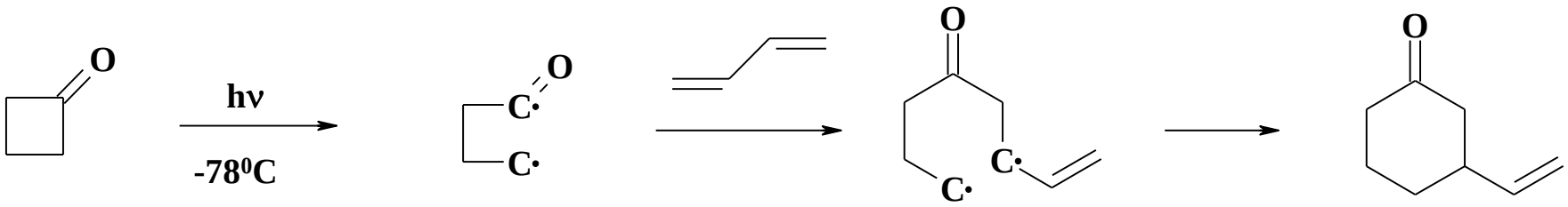


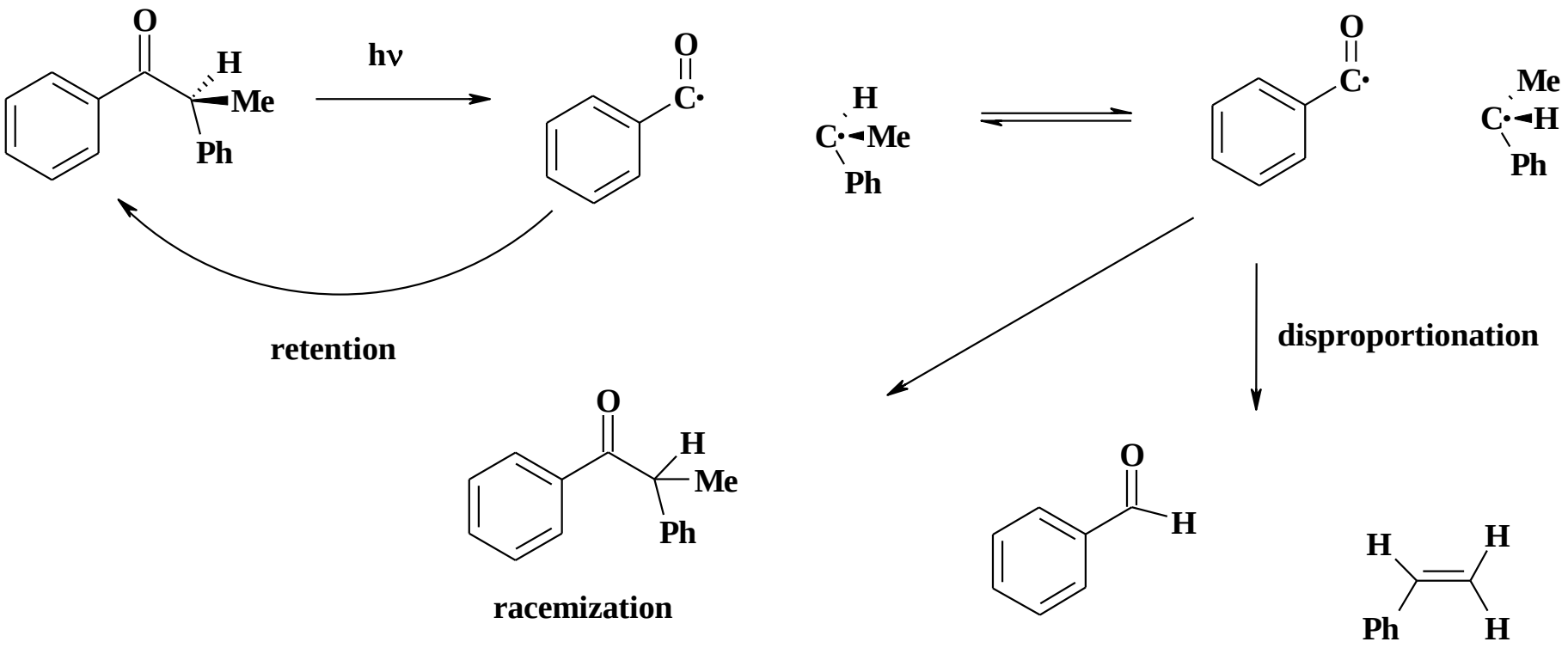
**Rate of α cleavage increasing ring strain**

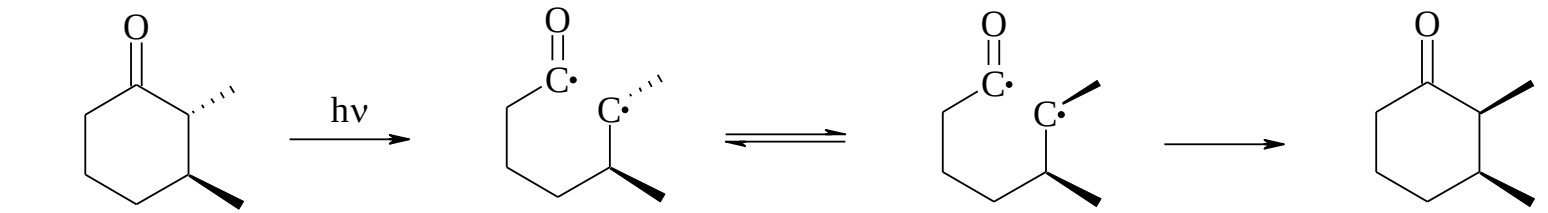
# Intermediate trapping experiment

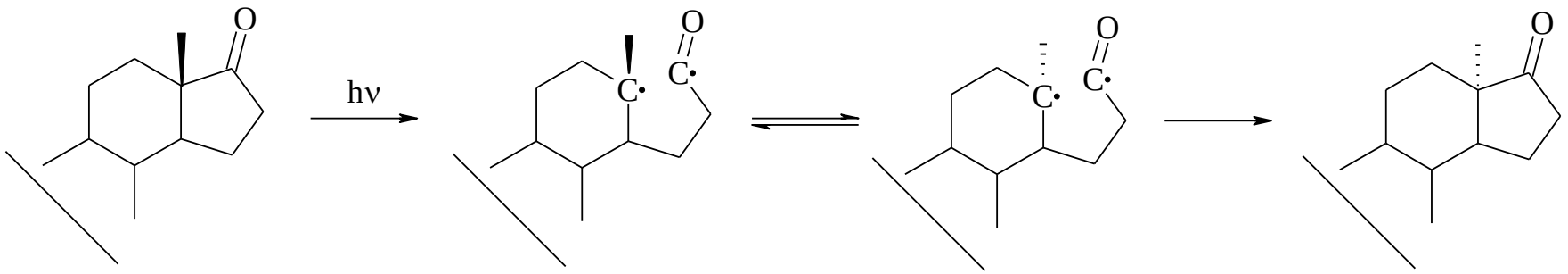


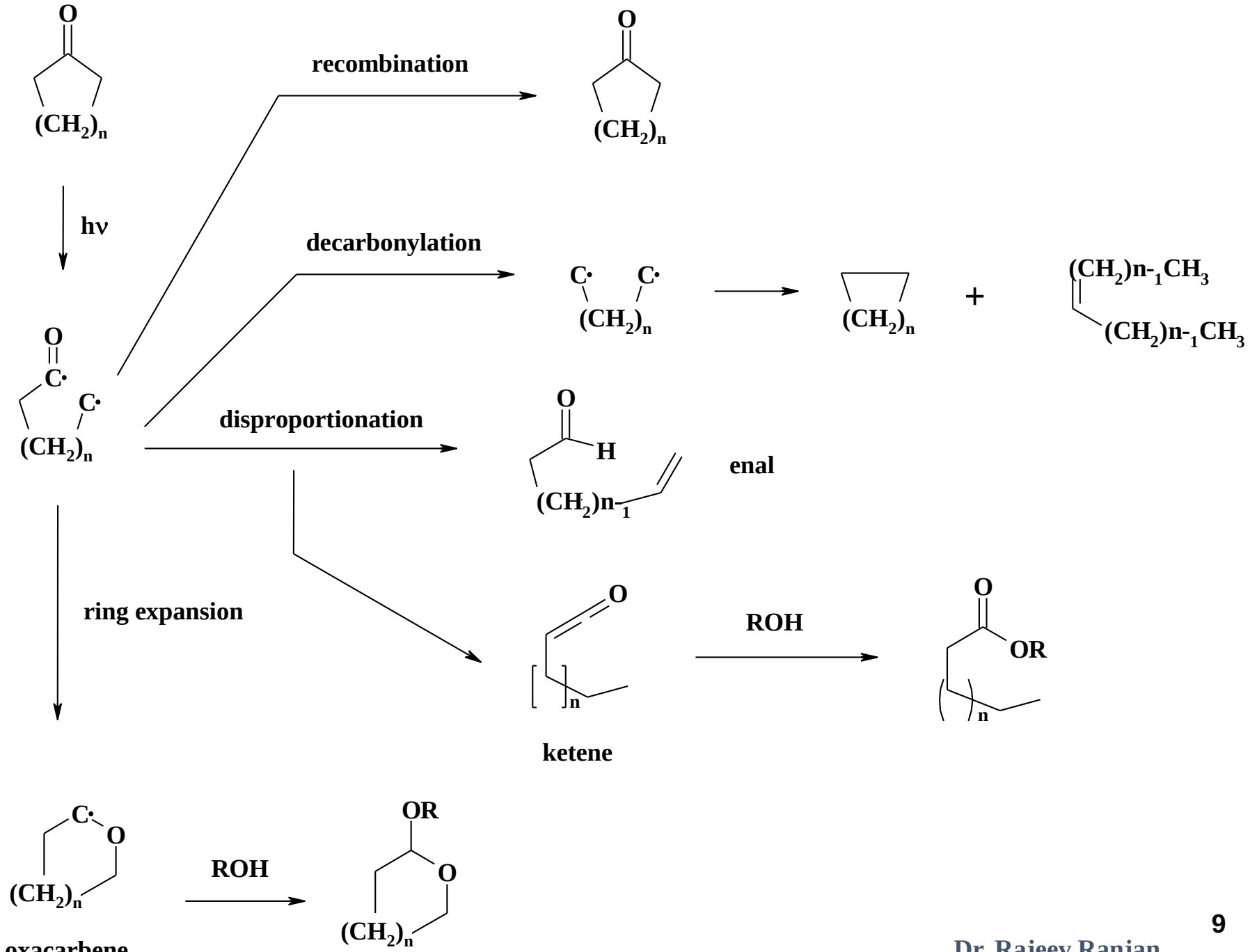

acyl-alkyl diradical

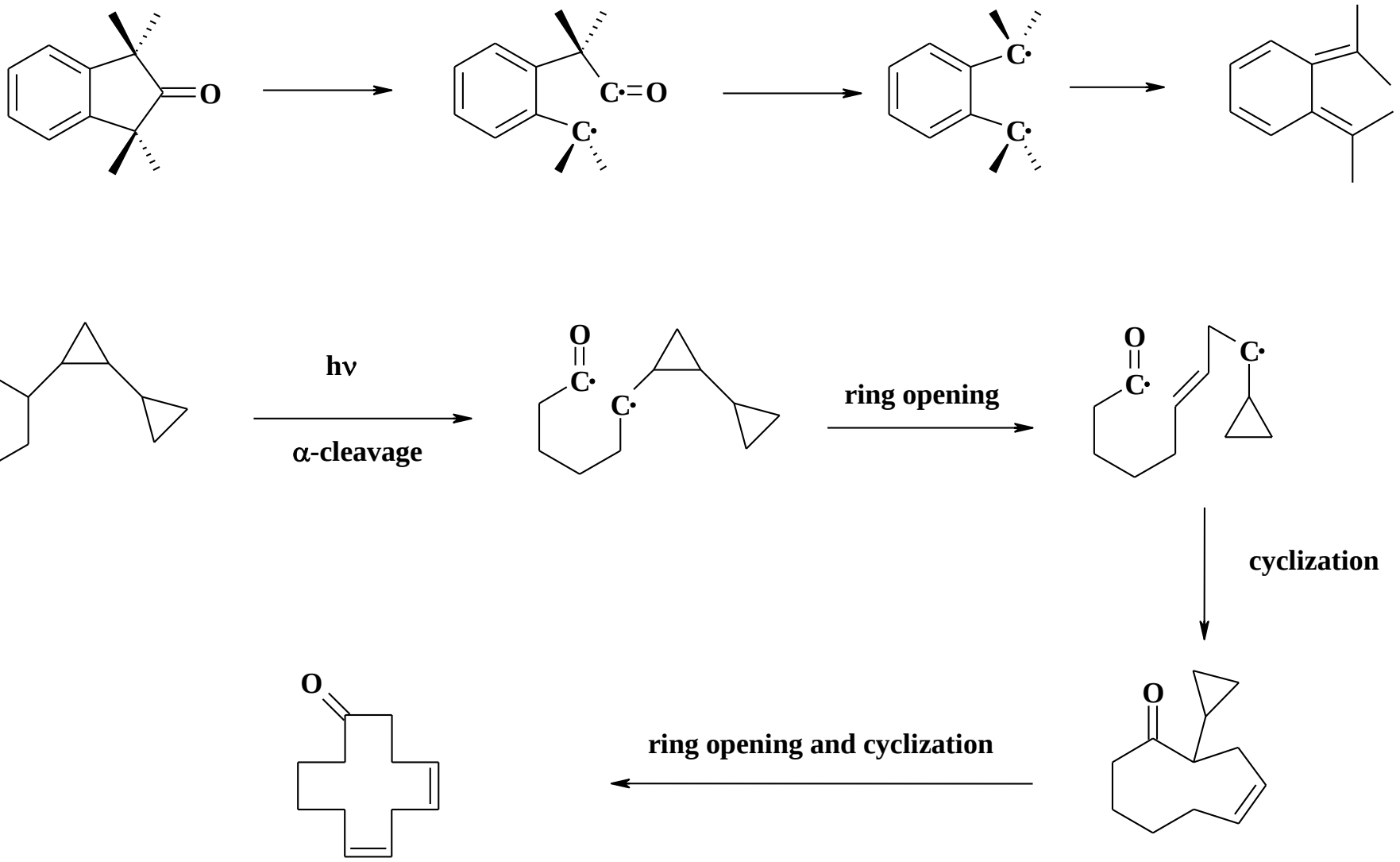


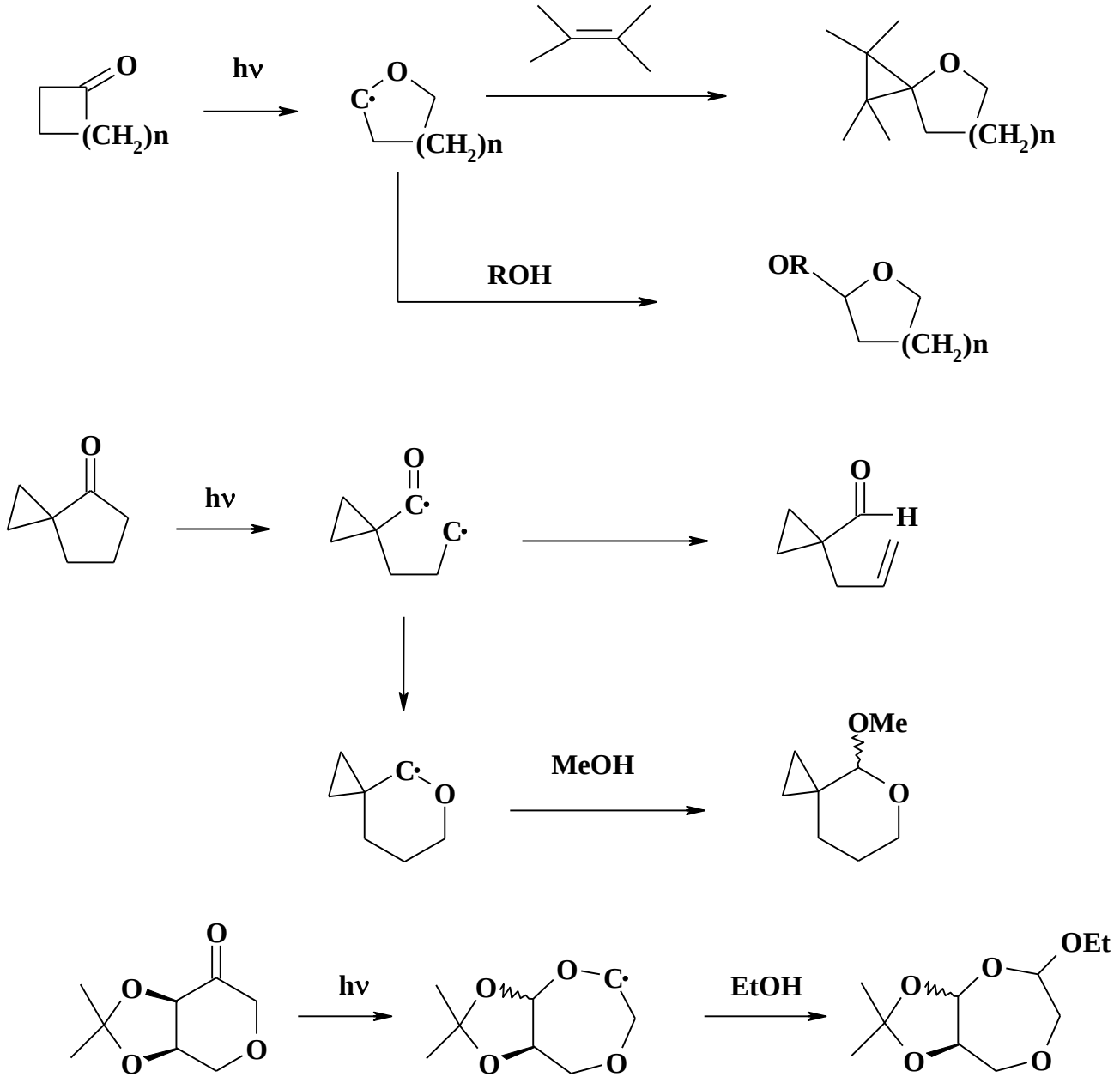

O
H
Me
Ph
hν
O
C·
H
C·
Me
Ph
O
C·
Me
C·
H
Ph
retention
disproportionation
O
H
Me
Ph
racemization
O
H
H
H
Ph
H

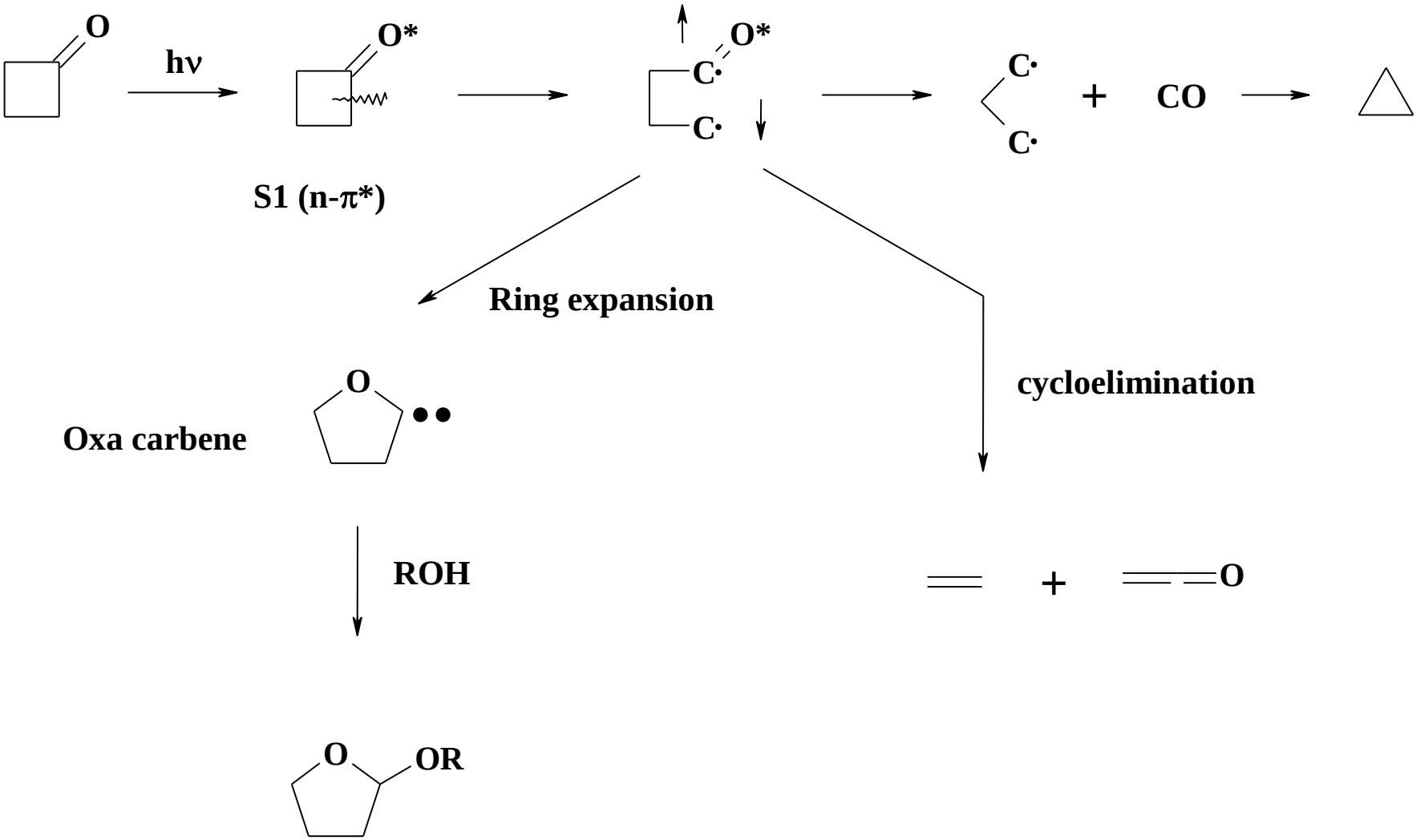

O
hν
O
C•
C•
O
C•
C•
O

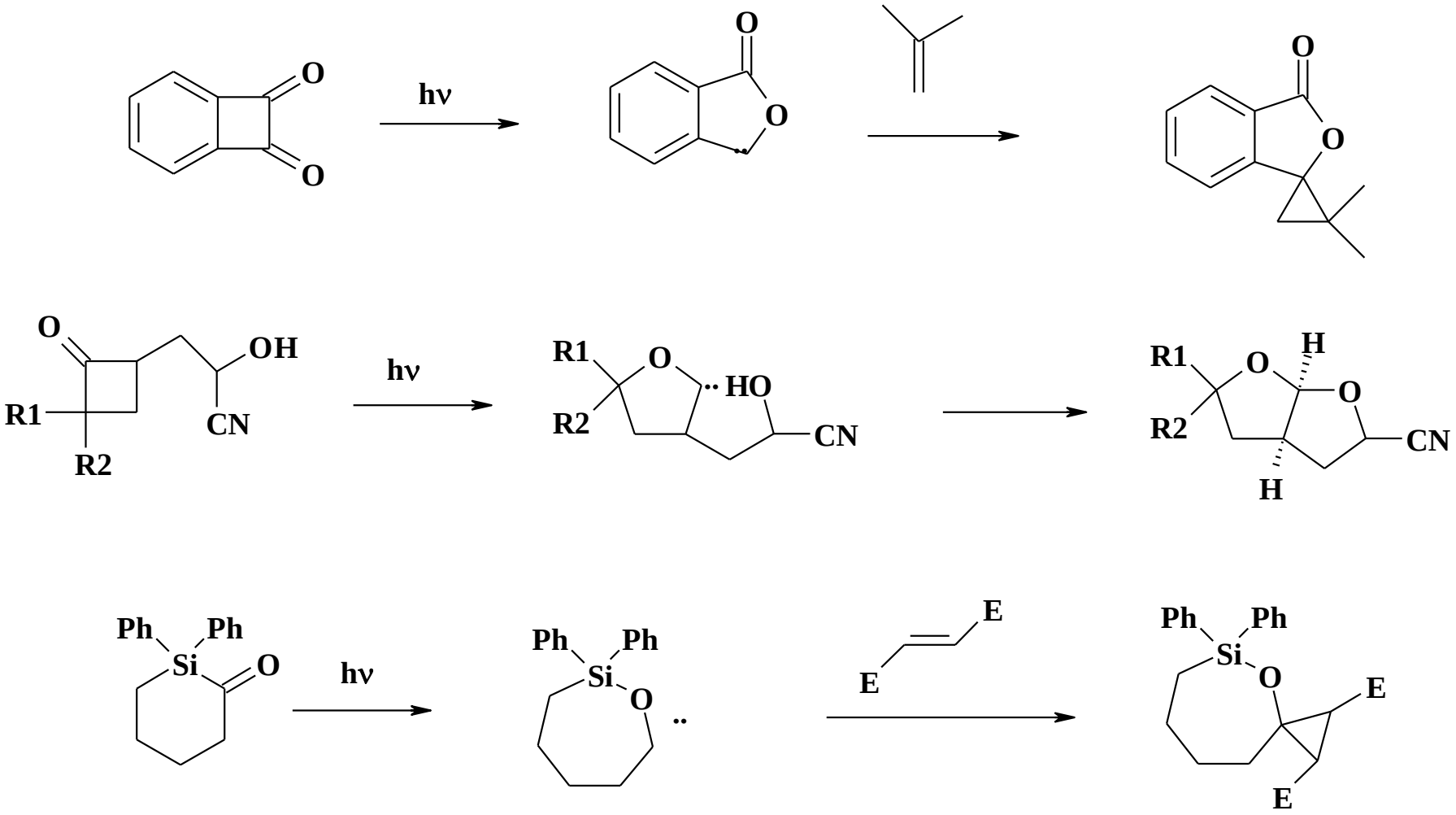

O
hν
O
C•
C•
O
C•
C•
O

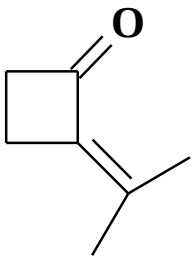

O
(CH2)n
recombination
O
(CH2)n
hν
decarbonylation
C·
C·
(CH2)n
(CH2)n
+
(CH2)n-1CH3
(CH2)n-1CH3
O
C·
C·
(CH2)n
disproportionation
O
H
(CH2)n-1
enal
ring expansion
O
n
ROH
O
OR
n
ketene
C·
O
(CH2)n
ROH
OR
O
(CH2)n
oxacarbene


O
C·=O
C·
C·
C·
O
hν
α-cleavage
O
C·
C·
ring opening
O
C·
C·
cyclization
O
ring opening and cyclization
O


O
hν
(CH2)n
C·
O
(CH2)n
O
(CH2)n
ROH
OR
O
(CH2)n
O
hν
O
C·
C·
O
H
C·
O
MeOH
OMe
O
O
O
hν
O
O
O
O
C·
O
O
EtOH
OEt
O
O
O
O

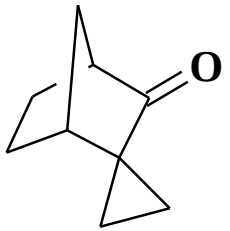

O
hν
O*
O*
C·
C·
C·
C·
+
CO
S1 (n-π*)
Ring expansion
cycloelimination
Oxa carbene
O
ROH
+
O
O
OR


O
O
hν
O
O
O
O
O
R1
R2
OH
CN
hν
R1
R2
O
HO
CN
R1
R2
O
H
O
H
CN
Ph
Ph
Si
O
hν
Ph
Ph
Si
O
E
E
Ph
Ph
Si
O
E
E



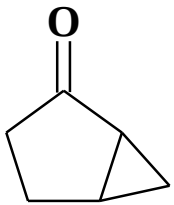

$h\nu$

MeOH



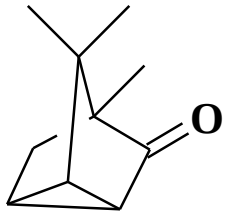

$h\nu$

ROH



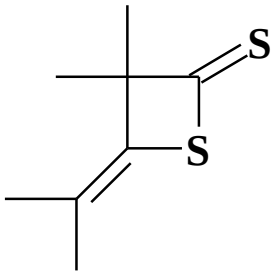

$h\nu$

tBuOH



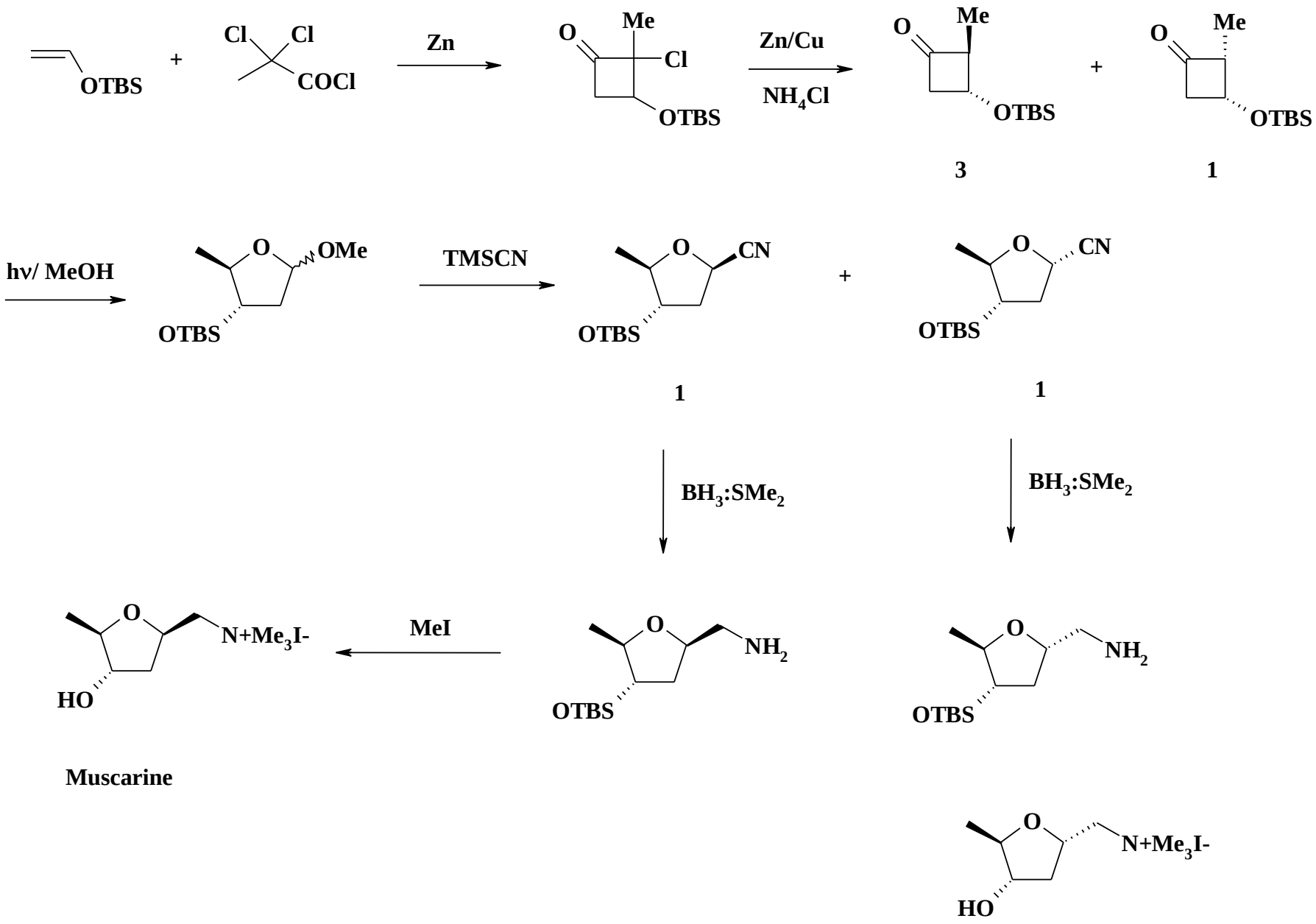

$h\nu$

ROH

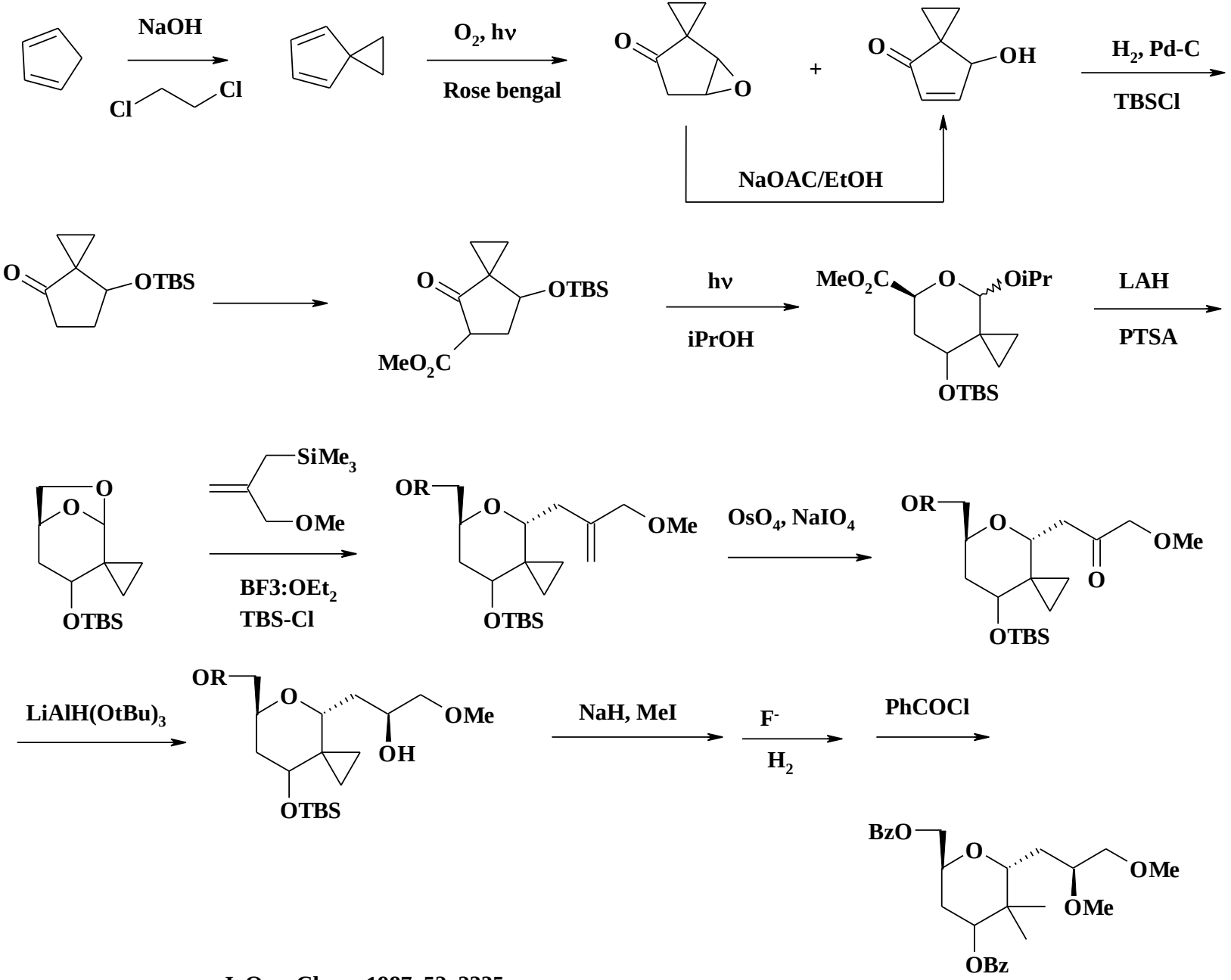



$h\nu$

MeOH



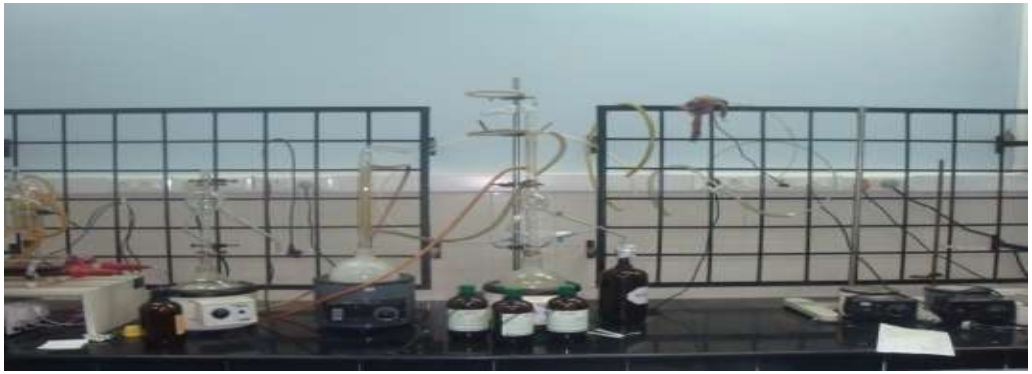

Tet.Lett, 1988, 29, 159




J. Org. Chem. 1987, 52, 2335

Pederol dibenzoate

# Thank You



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