SATHYABAMA
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SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

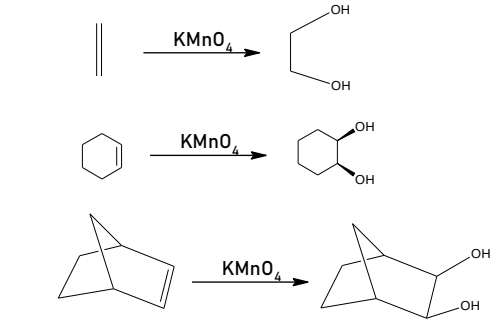
UNIT – 1 ORGANIC REAGENTS - I – SCY1620

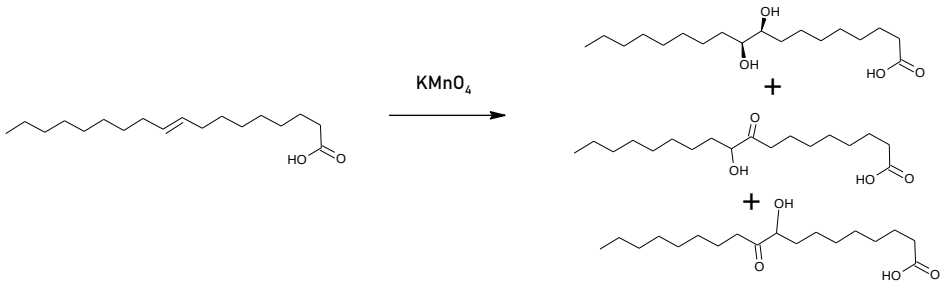
1. ORGANIC REAGENTS – I

Introduction to Organic Reagents, Types of Reagents, Oxidation Reagents, DDQ, SeO_2, $KMnO_4$,OsO_4 , Epoxidation of Olefins ,Jones Reagent, Oppenauer Oxidation, HIO4.

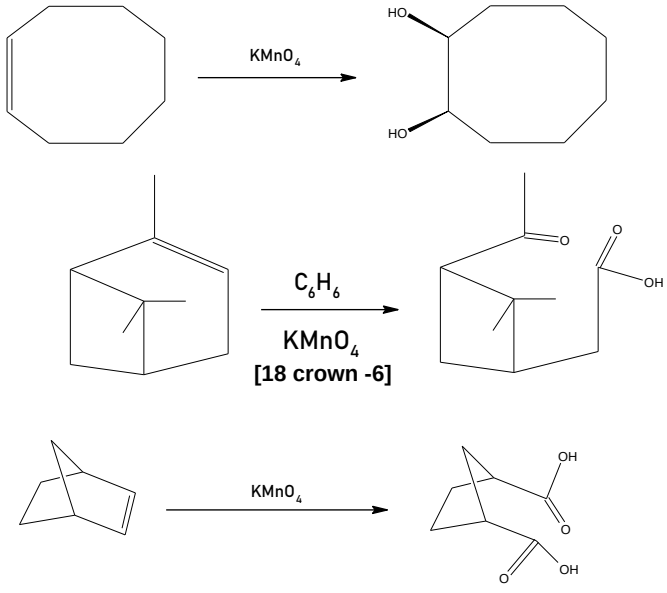
$KMnO_4$

1. cis Hydroxylating agent

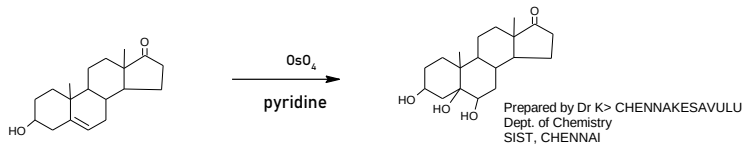


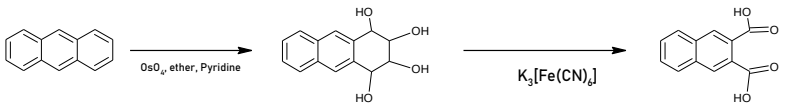


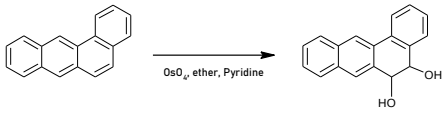
Potassium permanganate will attack on double bond which is having less steric hinderance.

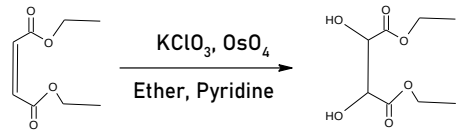


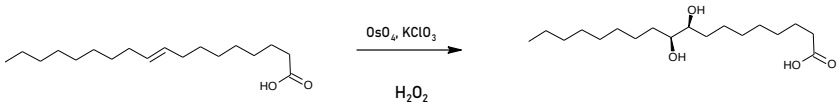
OsO_4

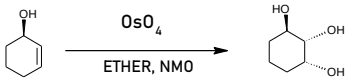

OsO4
pyridine
Prepared by Dr K> CHENNAKESAVULU
Dept. of Chemistry
SIST, CHENNAI

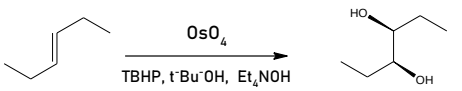

OsO4, ether, Pyridine
K3[Fe(CN)6]

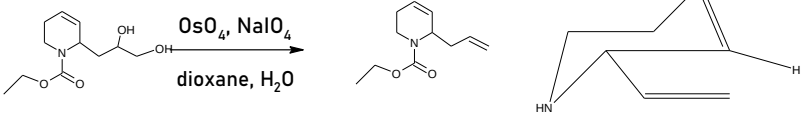

OsO4, ether, Pyridine

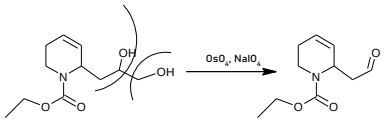

KClO3, OsO4
Ether, Pyridine

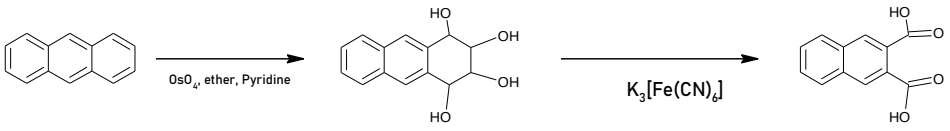

OsO4, KClO3
H2O2

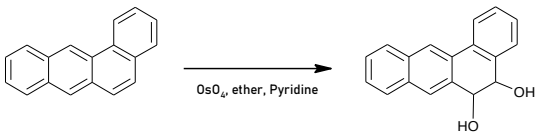

OsO4
ETHER, NMO


OsO4
TBHP, t-Bu-OH, Et4NOH

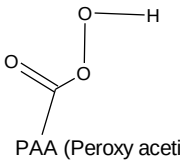

OsO4, NaIO4
dioxane, H2O


OsO4, NaIO4

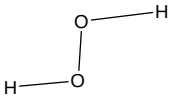

OsO4, ether, Pyridine
K3[Fe(CN)6]


OsO4, ether, Pyridine

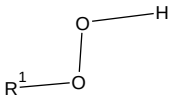
Epoxidation of olefins



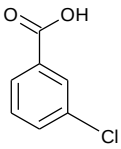
PAA (Peroxy acetic acid)



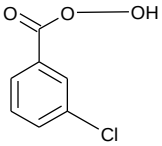
H_2O_2



Alkyl peroxide



m-chloro benzoic acid



m-chloro perbenzoic acid
(mcPBA)

Epoxides and their nomenclature

EPOXY ETHANE

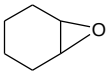
oxirane

1,2 EPOXY PROPANE

2-methyloxirane

2,3 EPOXY BUTANE

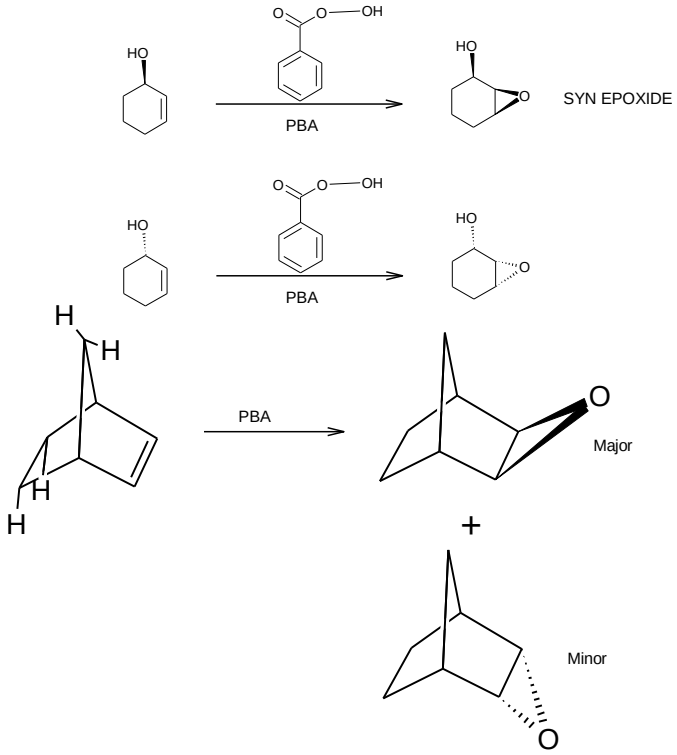
2,3-dimethyloxirane

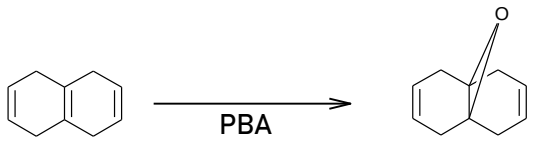


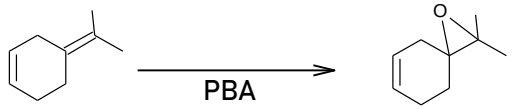
1,2 EPOXY CYCLO HEXANE

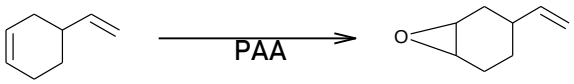
7-oxabicyclo[4.1.0]heptane

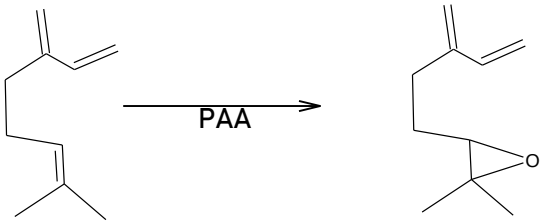
Epoxidation of olefins



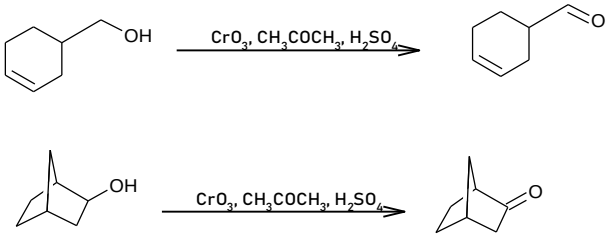




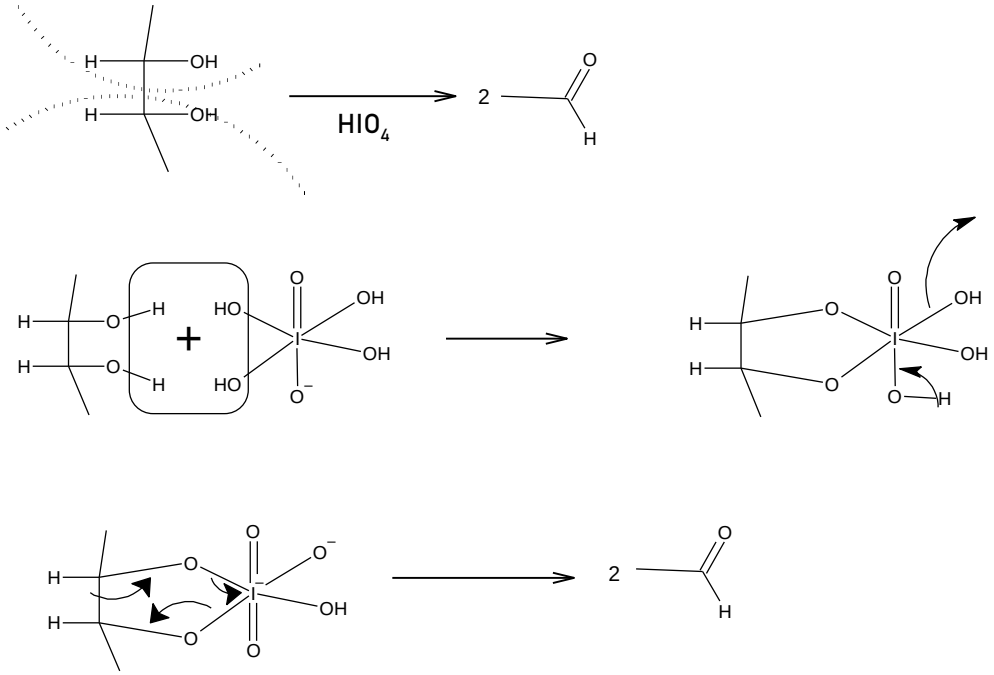




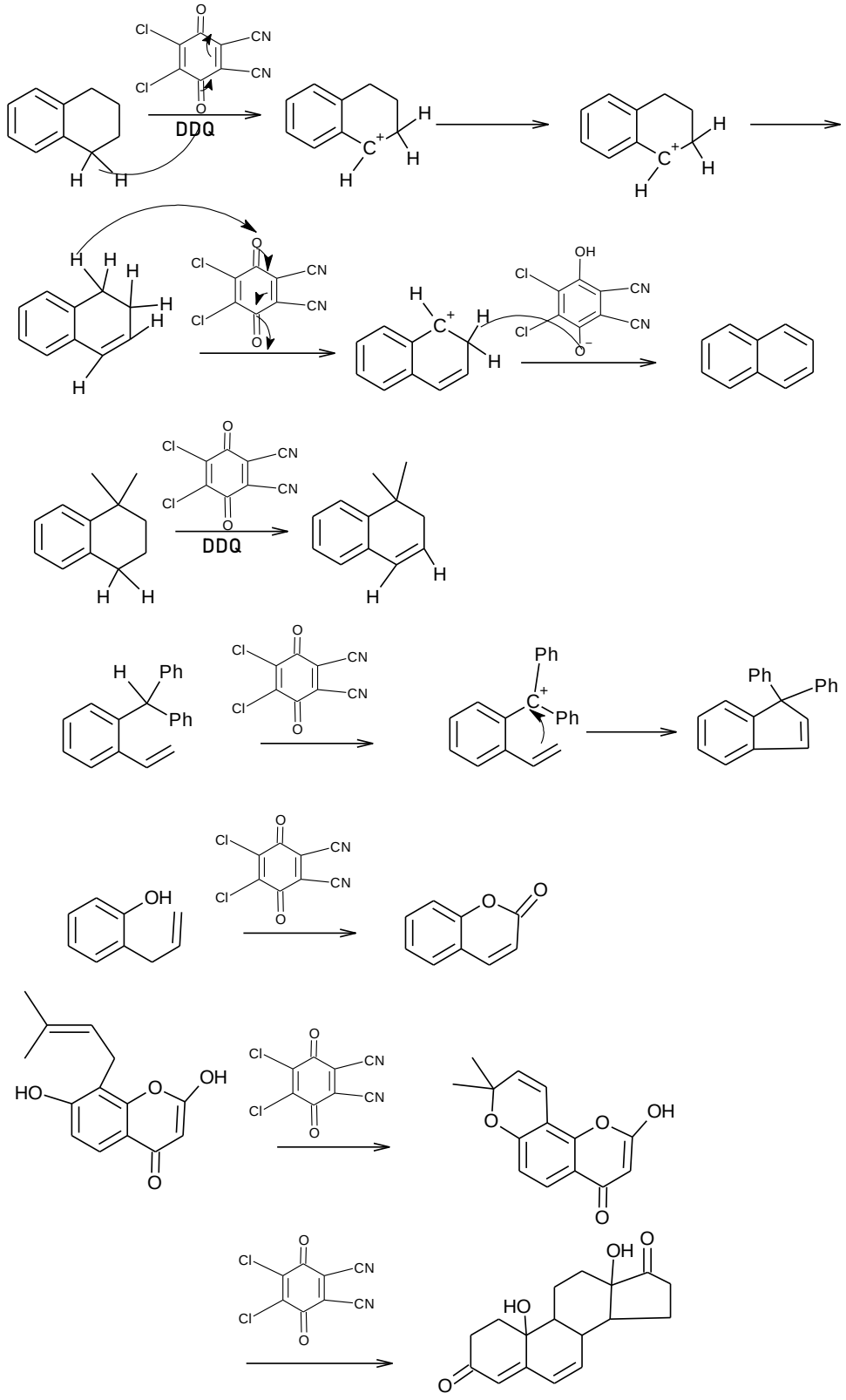
JONES REAGENT

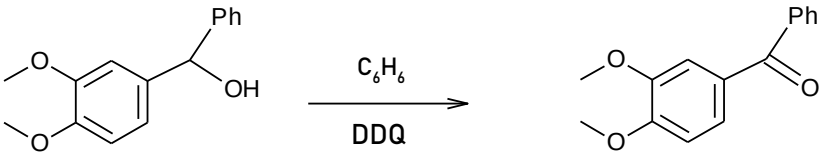


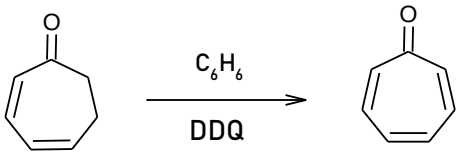
HIO4

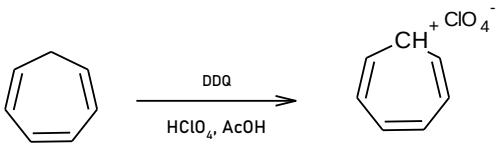


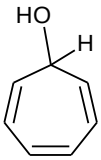
DDQ

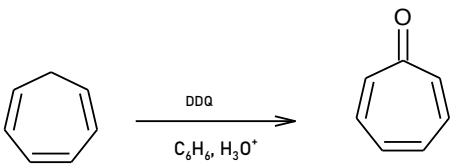


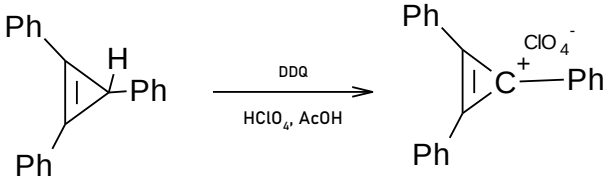

Ph
O
OH
O
C_6H_6
DDQ
Ph
O
O
O

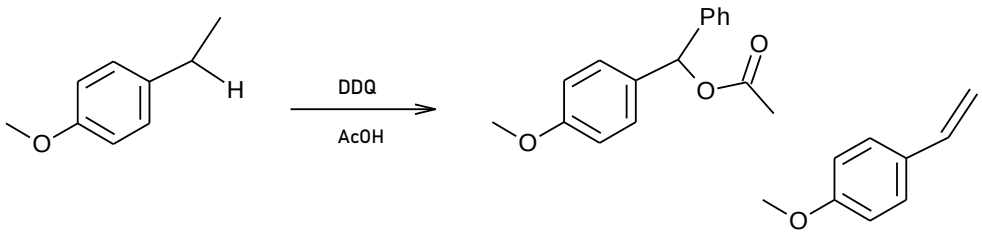

O
C_6H_6
DDQ
O

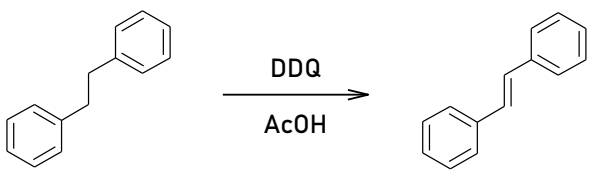

DDQ
$HClO_4$, AcOH
CH
+
ClO_4
-

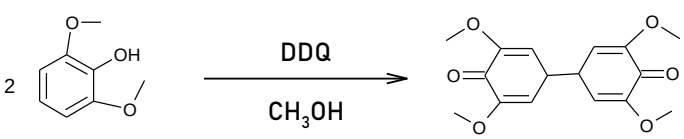

HO
H


DDQ
C_6H_6, H_3O^+
O

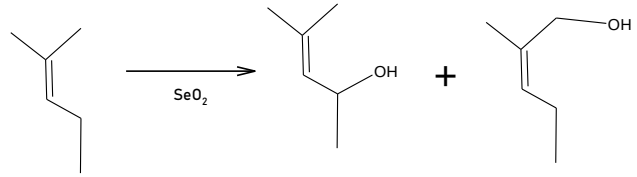

Ph
H
Ph
Ph
DDQ
$HClO_4$, AcOH
Ph
ClO_4
-
+
C
Ph
Ph


H
O
DDQ
AcOH
Ph
O
O
O
O

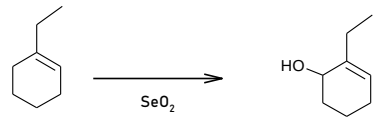

DDQ
AcOH

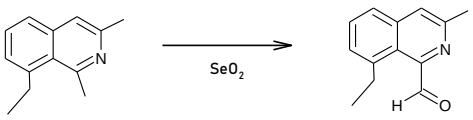

2
O
OH
O
DDQ
CH_3OH
O
O
O
O
O
O

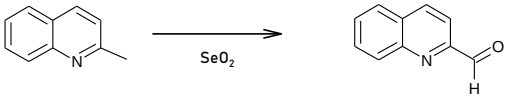
SeO2

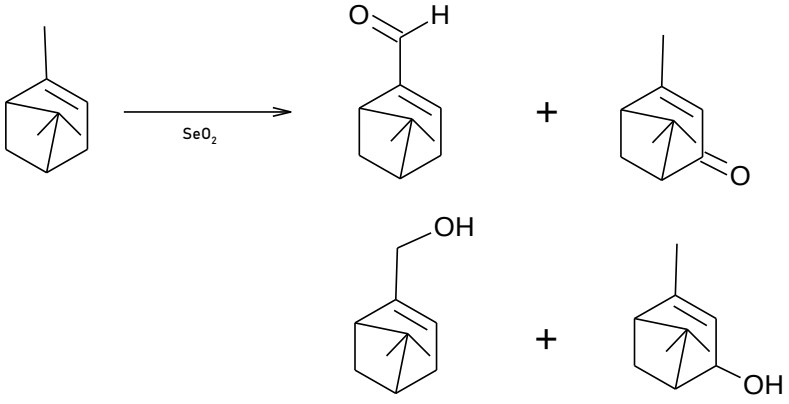


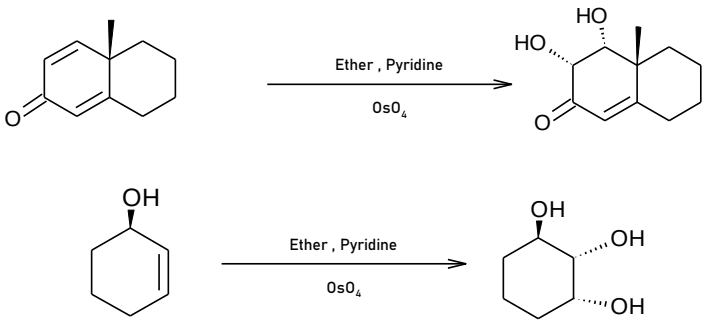
Prepared by Dr K> CHENNAKESAVULU
Dept. of Chemistry
SIST, CHENNAI











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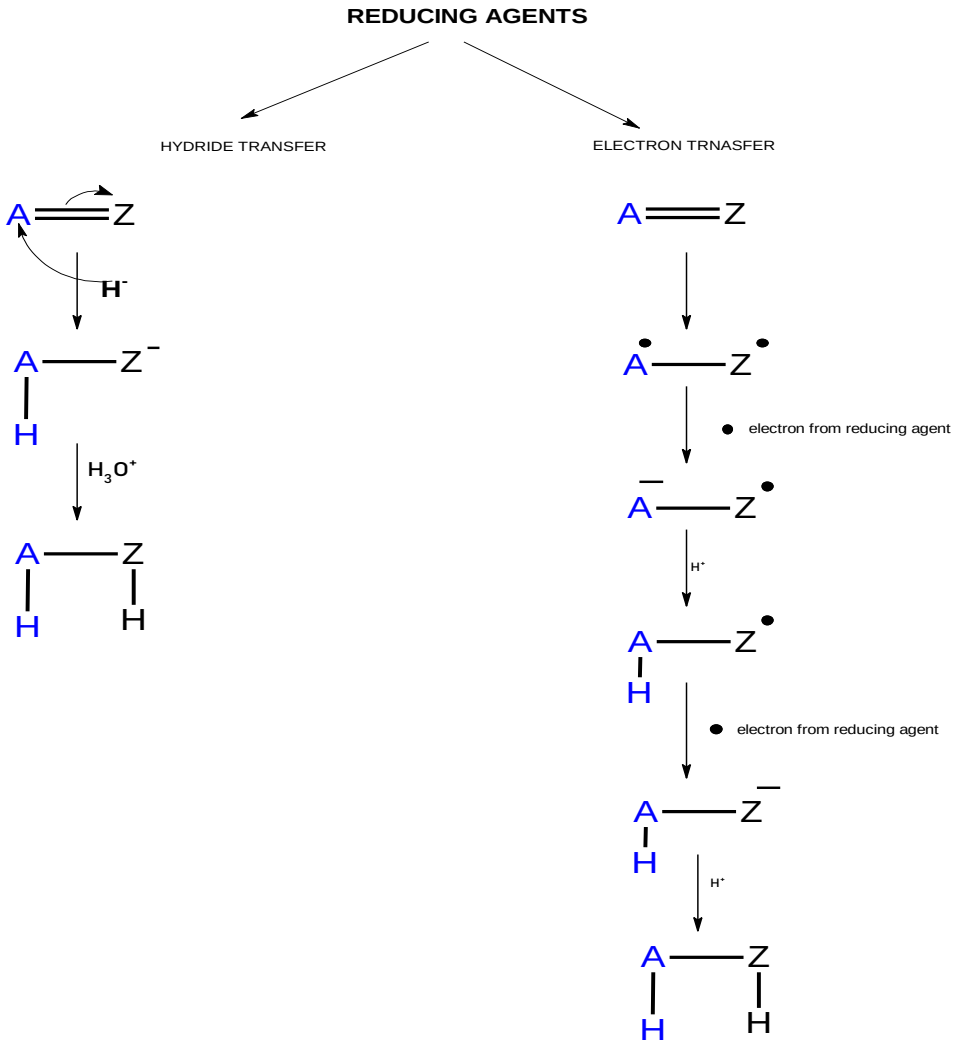
SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

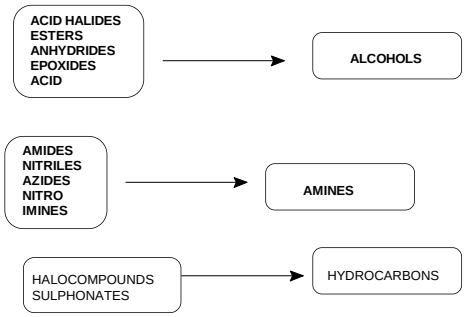
UNIT – 1 ORGANIC REAGENTS - II – SCY1620

1. ORGANIC REAGENTS – II

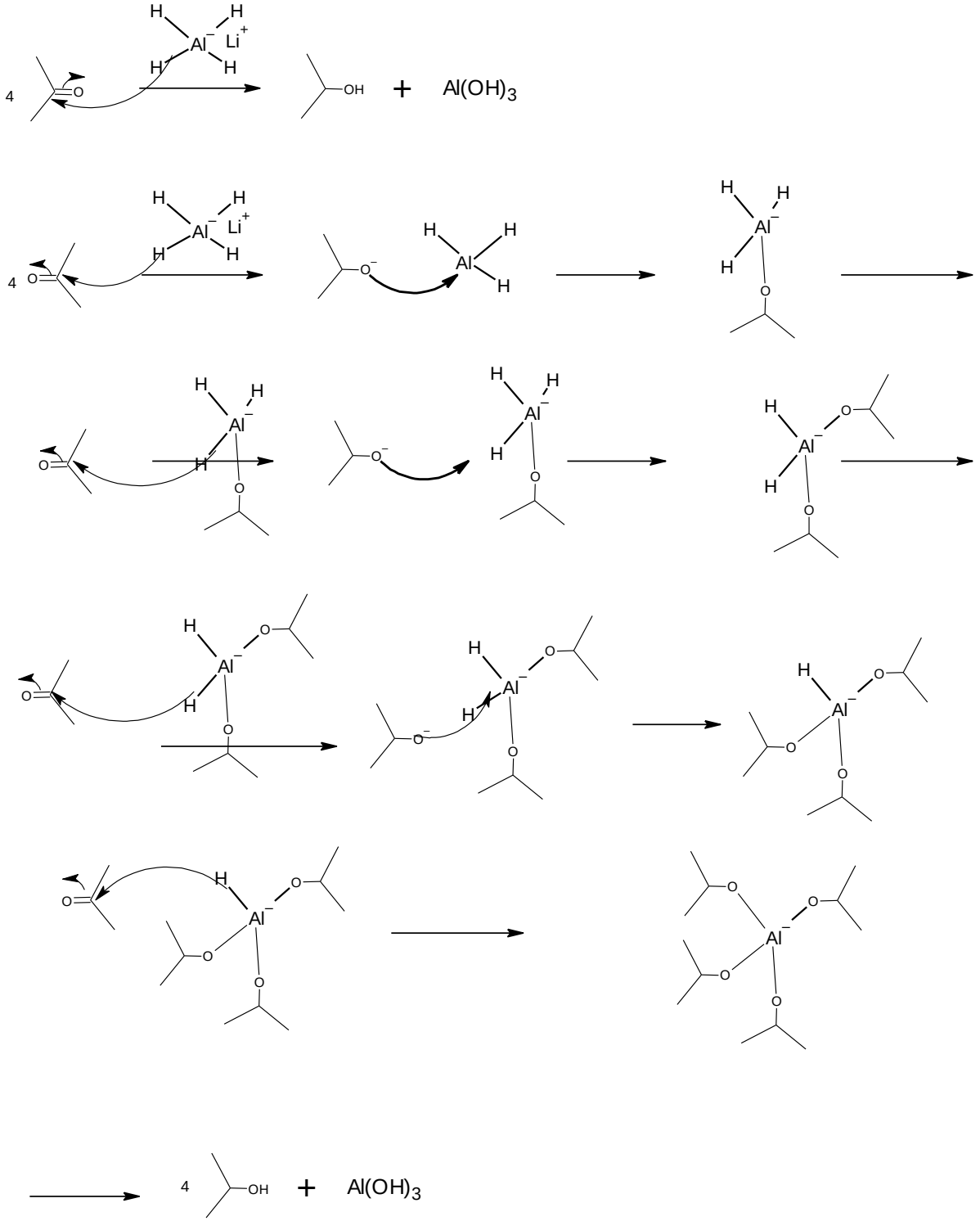
Reducing Agents , Hydride ion transfer mechanism, Electron Transfer mechanism LAH, NaBH4, Electrophilic Reducing Agents, Allanes and Boranes, Hydroboration, Dissolving metal reduction, Birch Reduction, Clemmensen Reduction, Wolf-Kishner Reduction Lindlars Reagent.



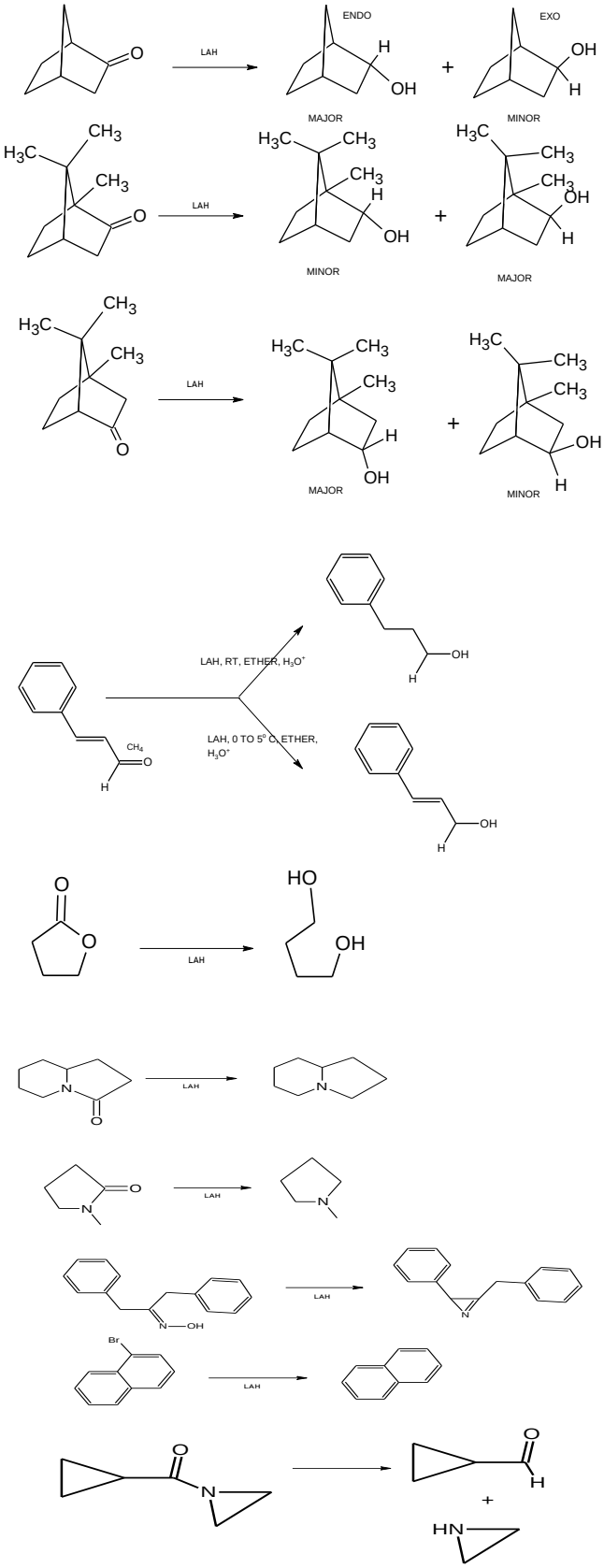
LAH FUNCTIONS



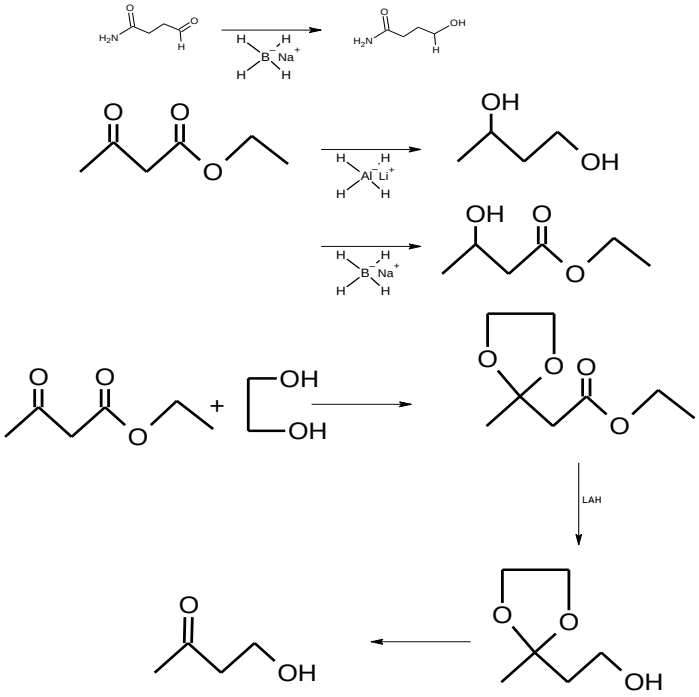
LAH MECHANISM

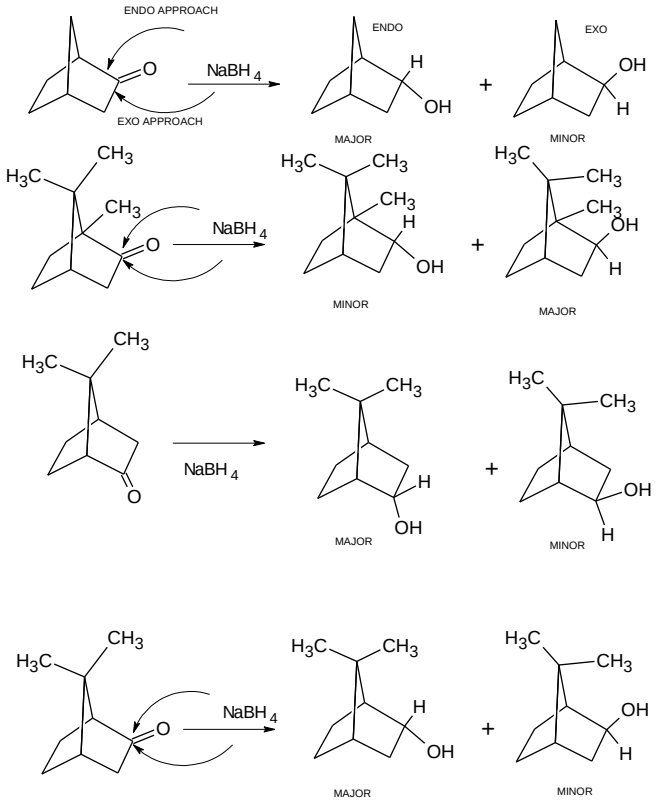


LAH CHEMICAL REACTIONS

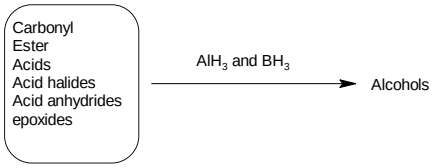


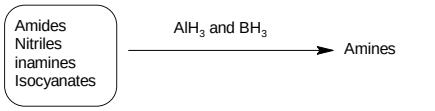
$NaBH_4$

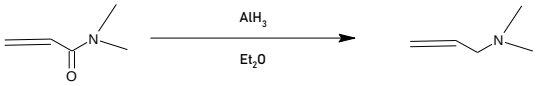

LAH

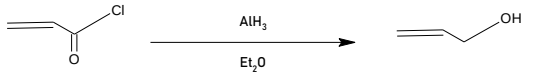

ENDO APPROACH
EXO APPROACH
NaBH 4
ENDO
EXO
MAJOR
MINOR
NaBH 4
MINOR
MAJOR
NaBH 4
MAJOR
MINOR
NaBH 4
MAJOR
MINOR

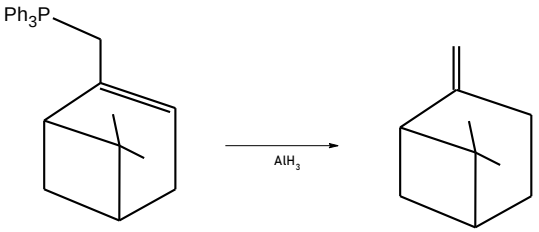
AlH3 and BH3

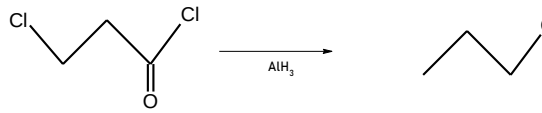

Carbonyl
Ester
Acids
Acid halides
Acid anhydrides
epoxides
AlH3 and BH3
Alcohols

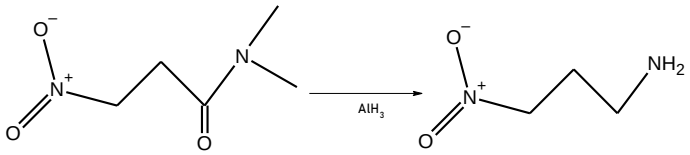

Amides
Nitriles
inamines
Isocyanates
AlH3 and BH3
Amines

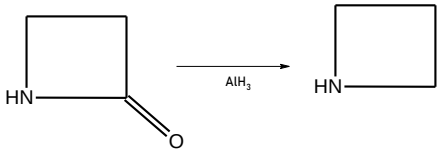

AlH3
Et20
N
O


Cl
AlH3
Et20
O
OH

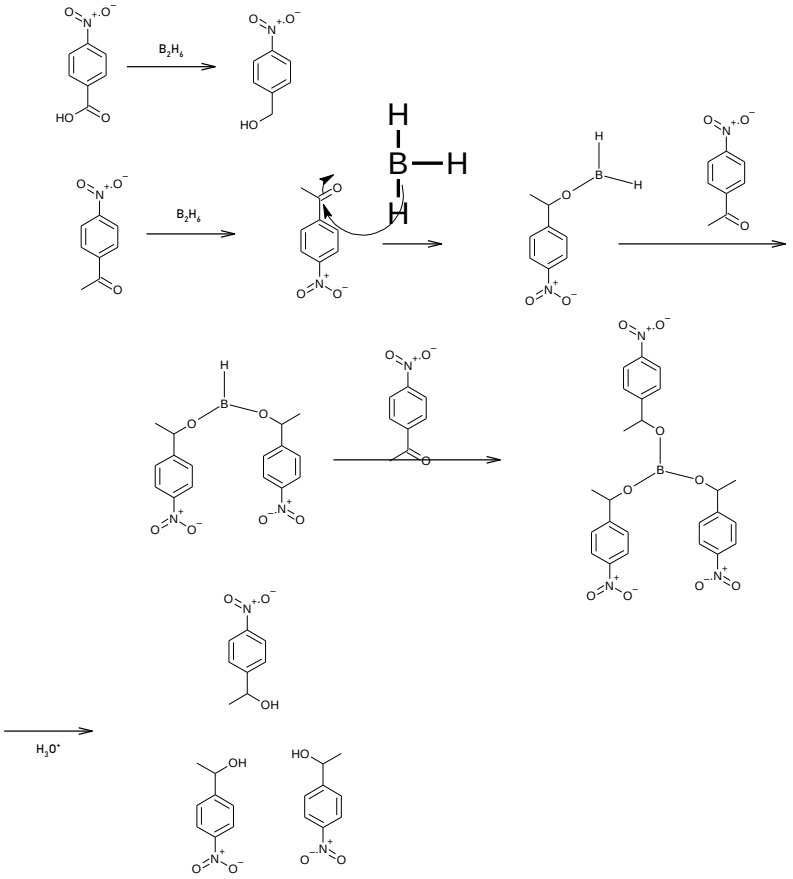

Ph3P
AlH3

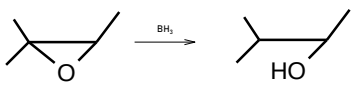

Cl
Cl
O
AlH3
OH

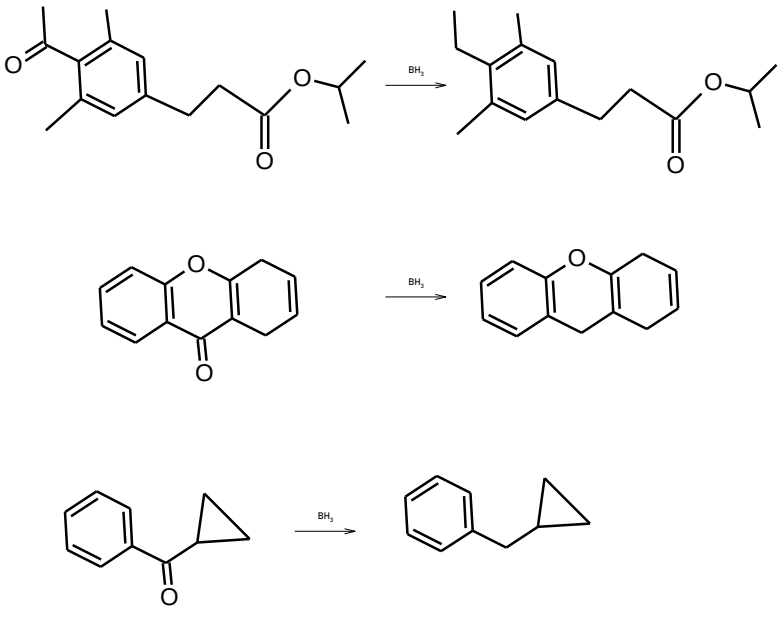

O−
N+
O
N
O
AlH3
O−
N+
O
NH2


HN
O
AlH3
HN

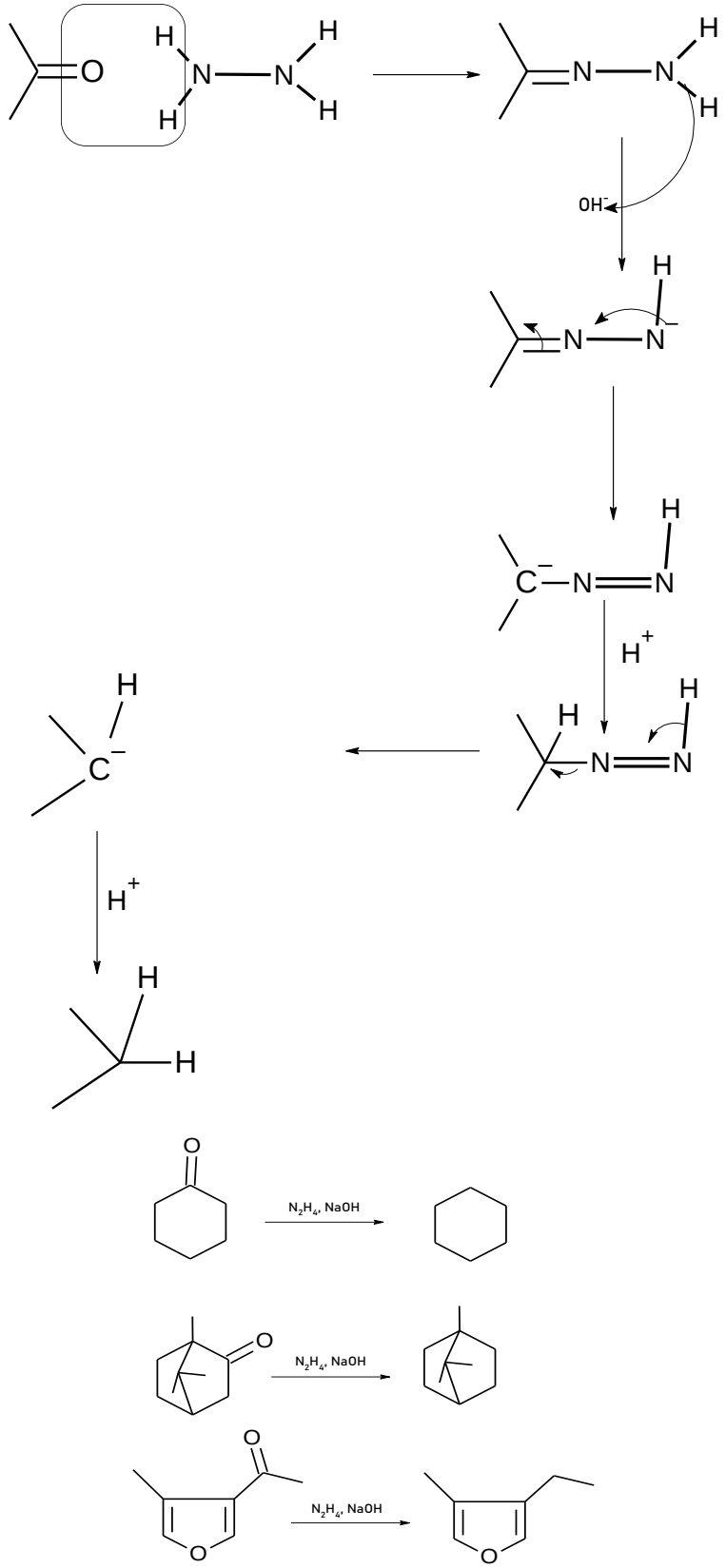
BH_3



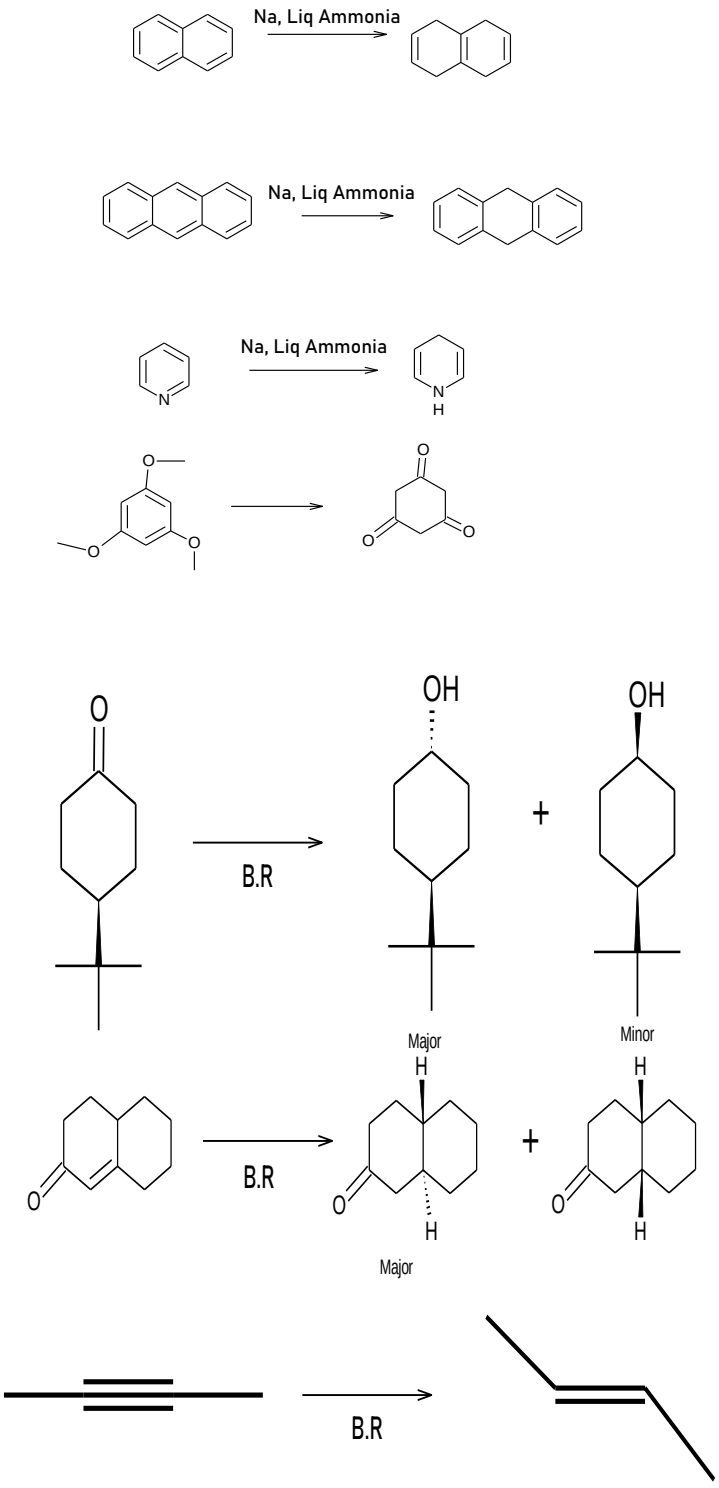




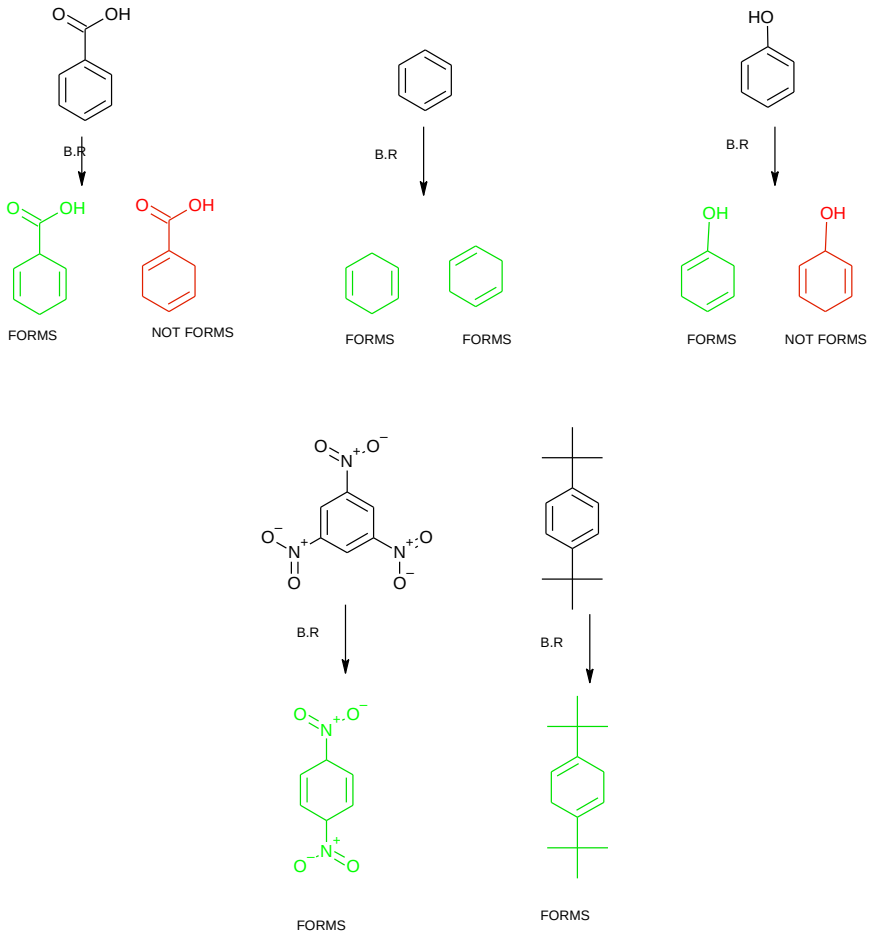
Wolf Kishner Reduction



Birch Reduction



The effect of electron donating and withdrawing groups on Birch Reduction (B.R.)



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SCHOOL OF SCIENCE AND HUMANITIES

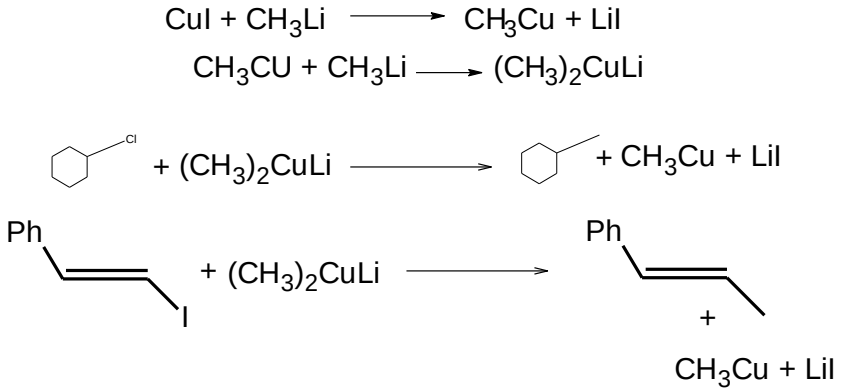
DEPARTMENT OF CHEMISTRY

UNIT – 3 ORGANIC REAGENTS - III – SCY1620

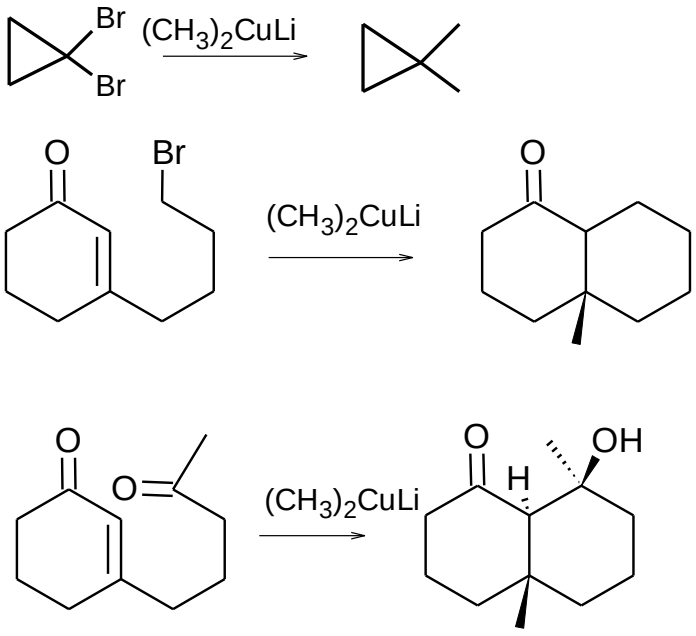
3. ORGANIC REAGENTS - III

Introduction to organo-metallic reagents, Grignard reagent, Gilman's reagent, LDA, 1, 3 dithianes, Wittig Reagent, Peterson olefination

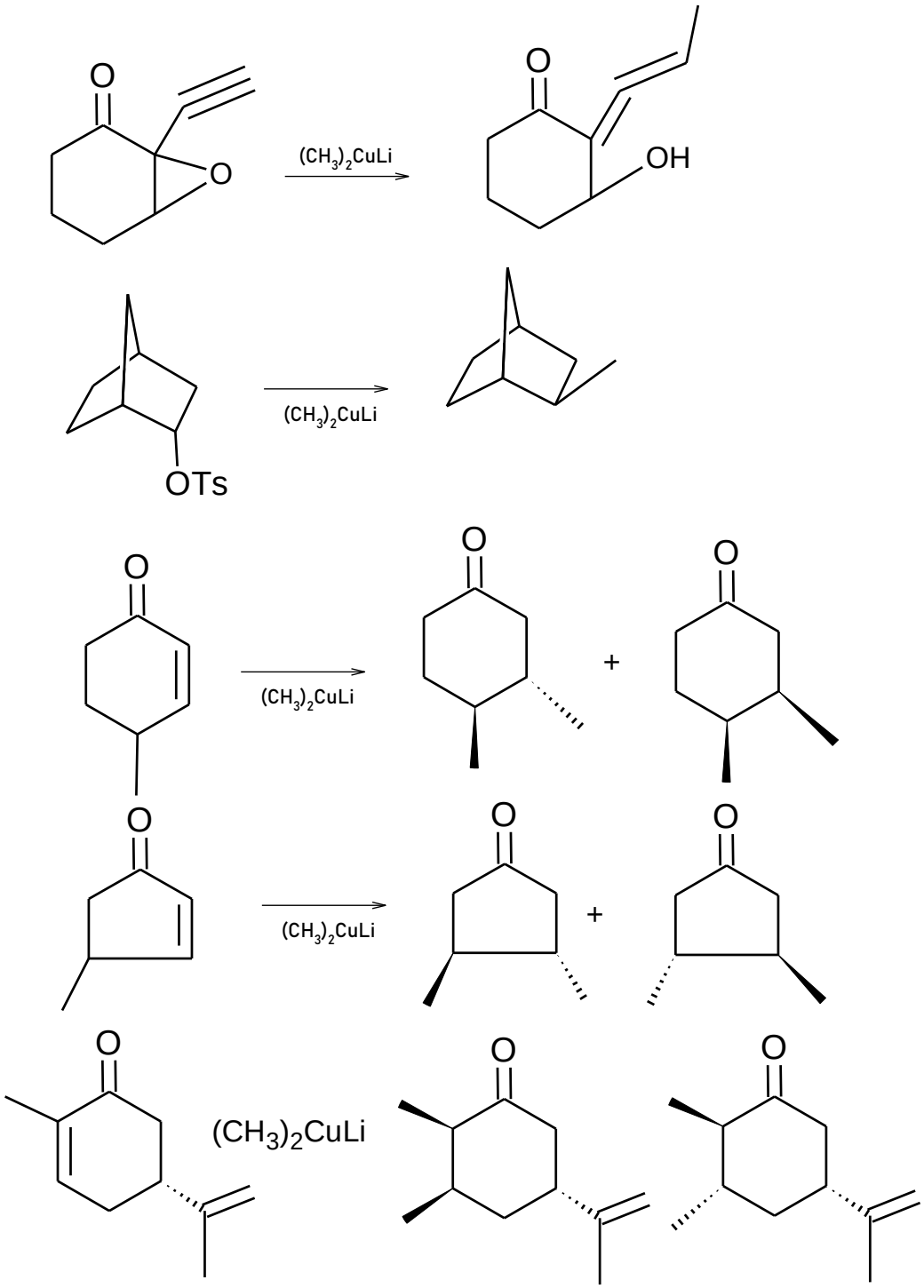
Gilman's Reagent
Preparation:



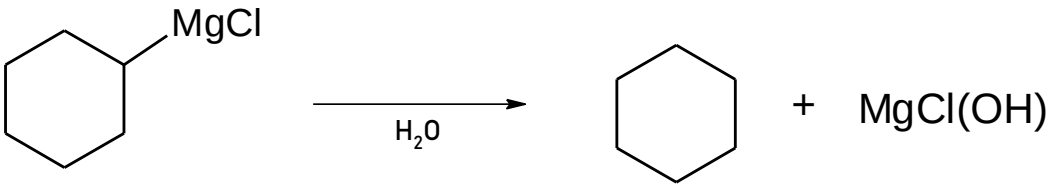
Reactions

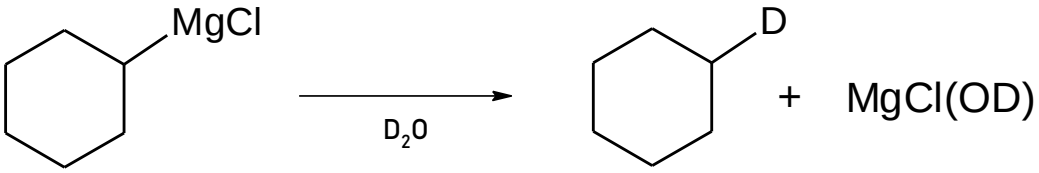


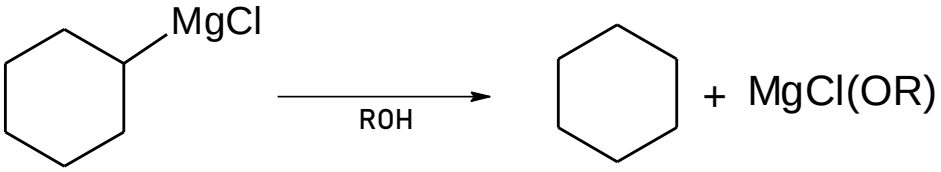
Gilman's Reagent Reactions

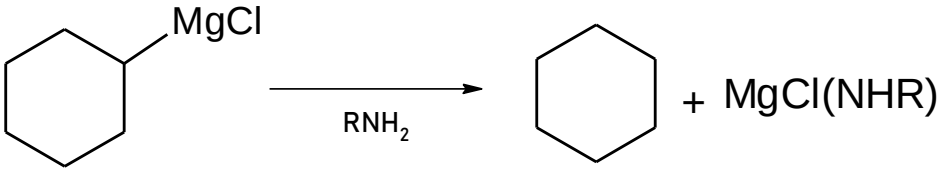


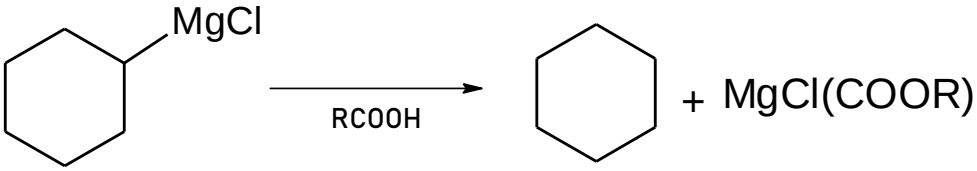
Grignard Reagents

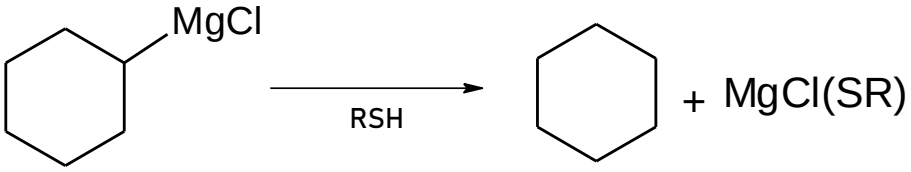


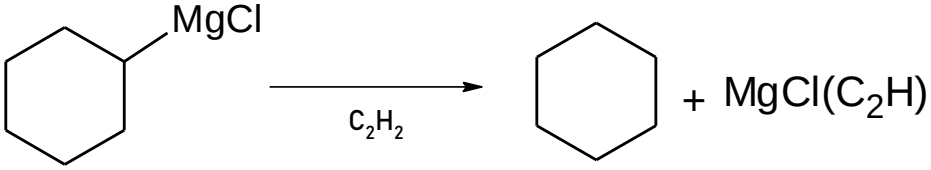


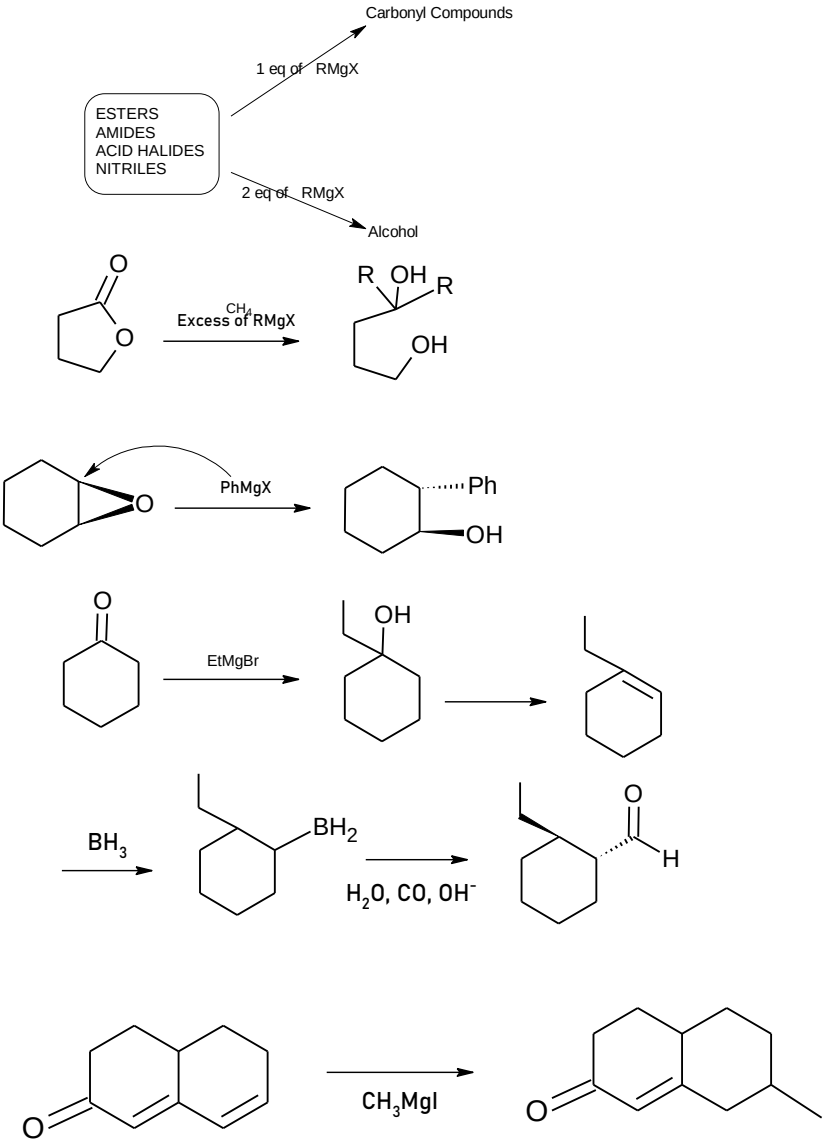




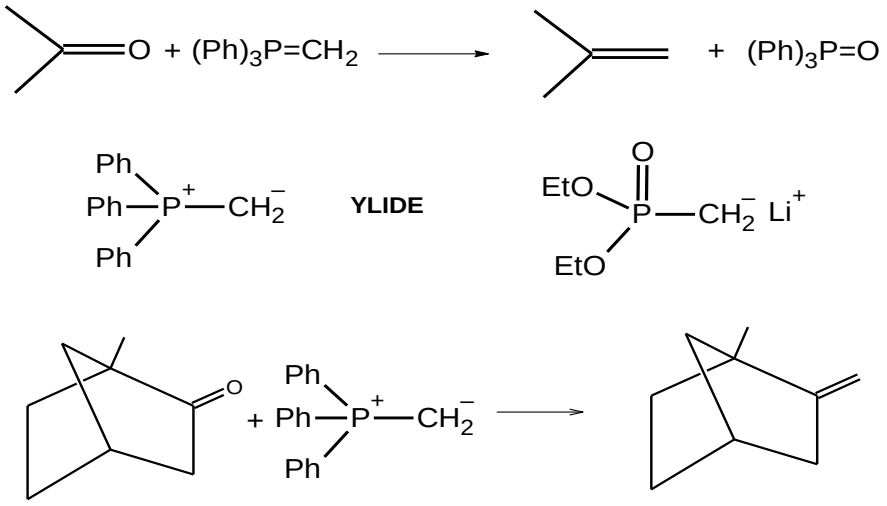


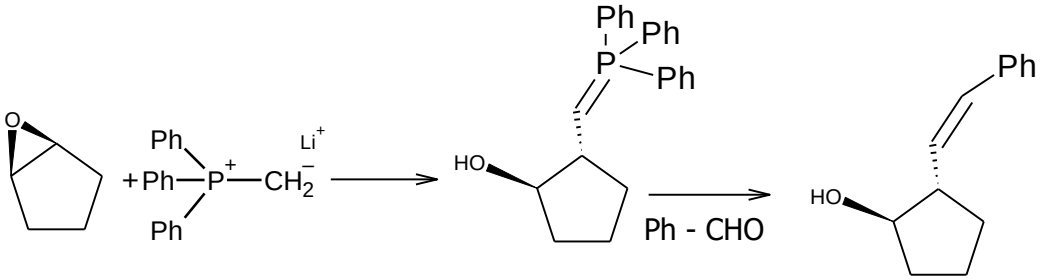


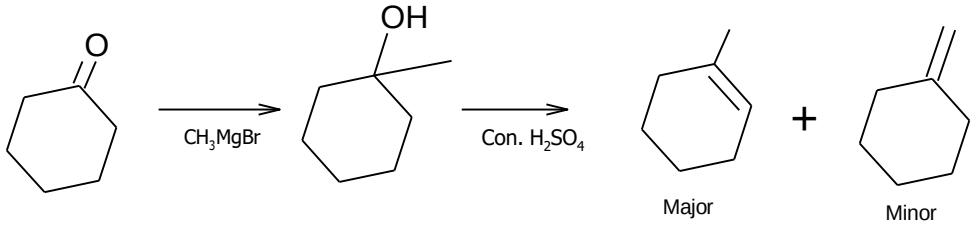


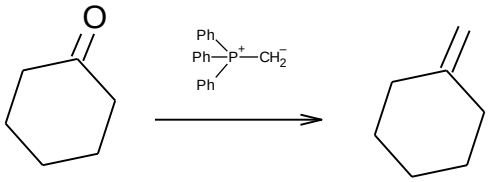


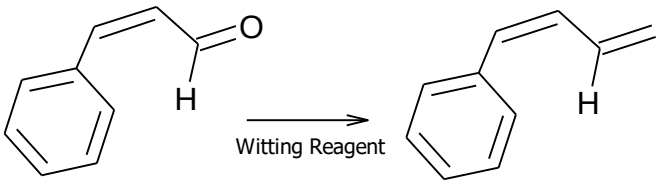
Wittig Reagent: Conversion of carbonyl compounds to olefines by using phosphoranes or phospharus ylides called wittig reaction.

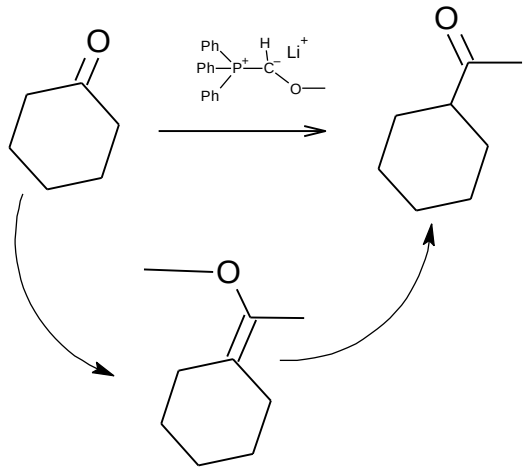


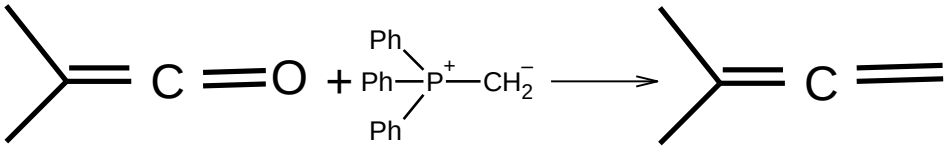

O
Ph
Ph
P
CH2
Li+
HO
Ph - CHO
HO
Ph

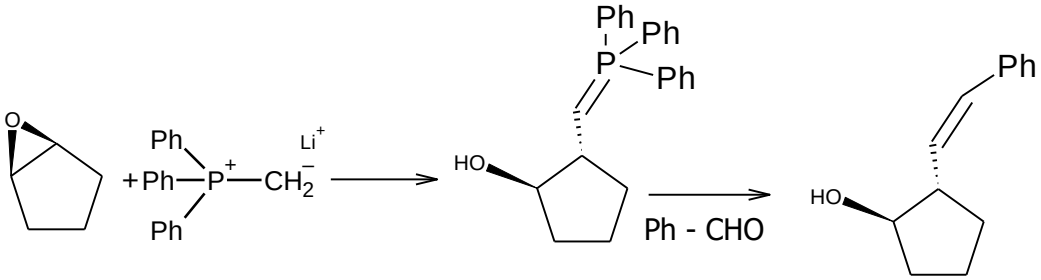

O
CH3MgBr
OH
Con. H2SO4
Major
+
Minor

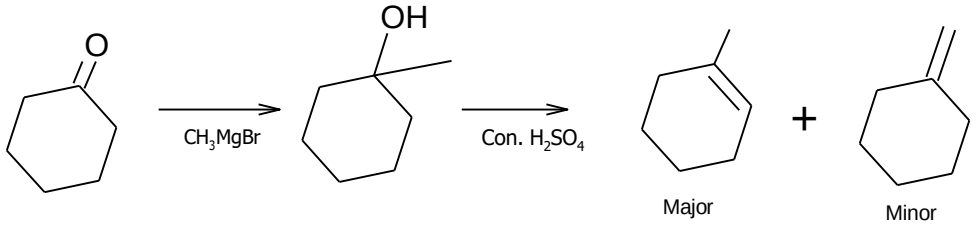

O
Ph
Ph
P
CH2

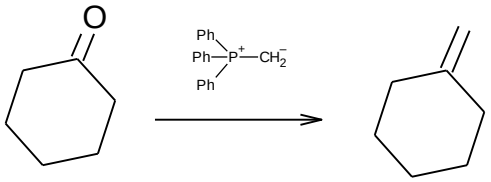

O
H
Witting Reagent
H

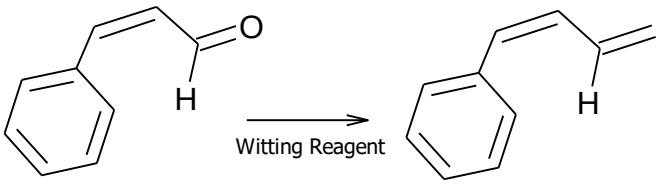

O
Ph
Ph
P
H
C
Li+
O
O
O

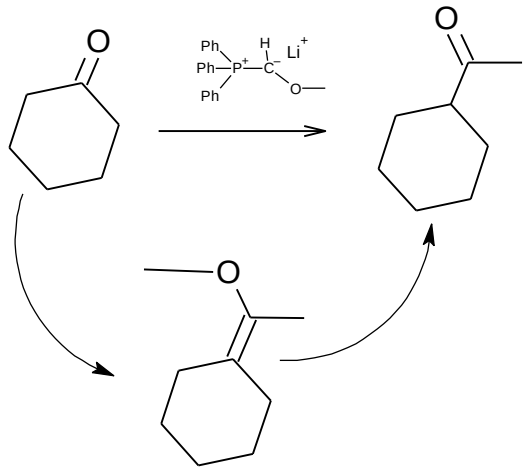

C
O
Ph
Ph
P
CH2
Ph
C

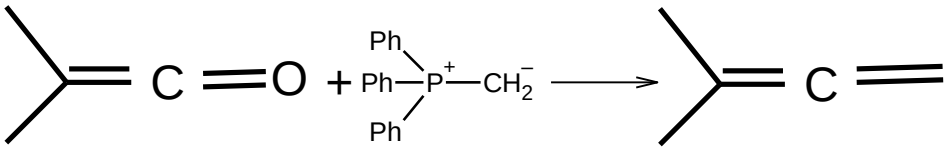

O
Ph
Ph
P
CH2
Li+
HO
Ph - CHO
HO
Ph


O
CH3MgBr
OH
Con. H2SO4
Major
+
Minor


O
Ph
Ph
P
CH2

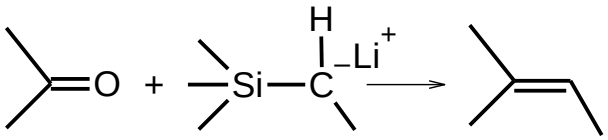

O
H
Witting Reagent
H

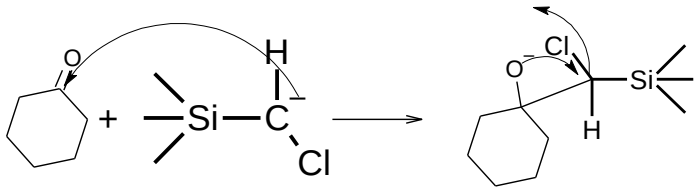

O
Ph
Ph
P
H
C
Li+
O
O
O

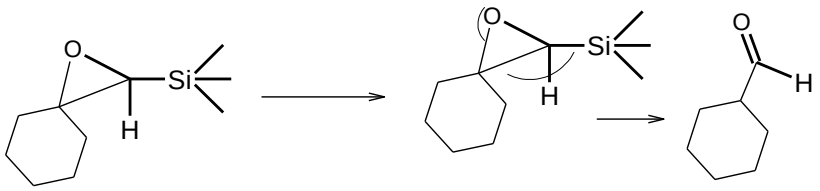

C
O
+
Ph
Ph
P
CH2
Ph
C

Peterson’s olefination

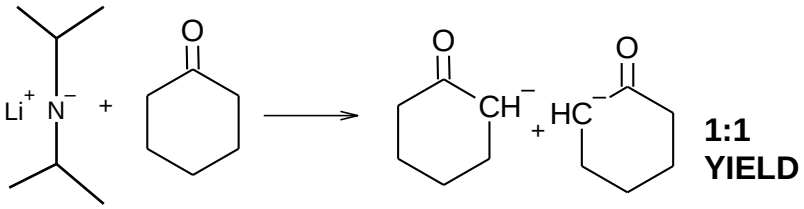
Conversion of carbonyl compound into olefines by using lithio or magneisio derivates of silyl compounds called peterson's olefination.

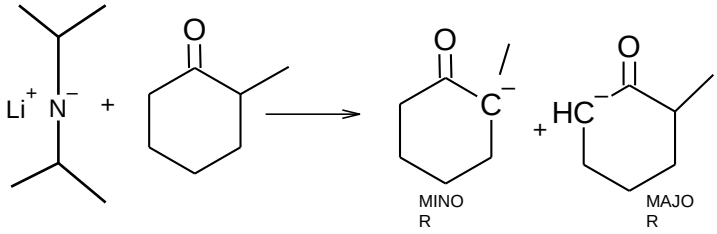


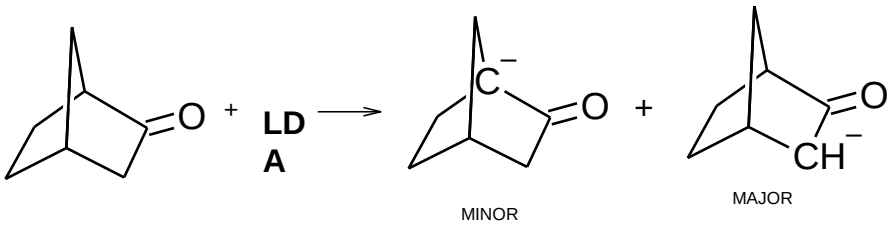


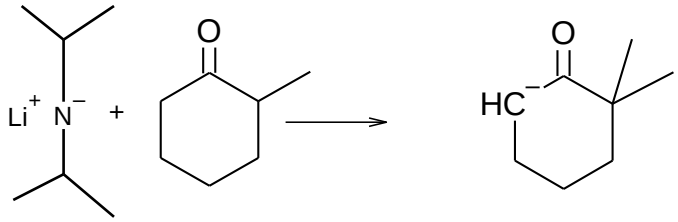


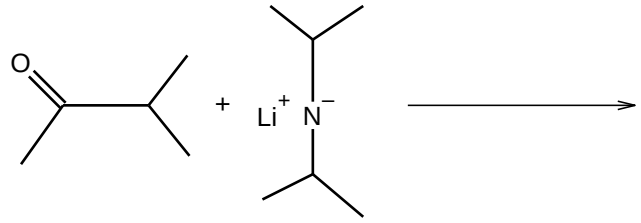
LDA

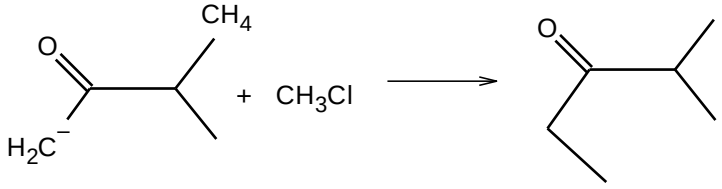

Li+ N−
O
CH−
HC−
1:1
YIELD


Li+ N−
O
C−
HC−
MINO
R
MAJO
R


O
LD
A
C−
O
CH−
MINOR
MAJOR

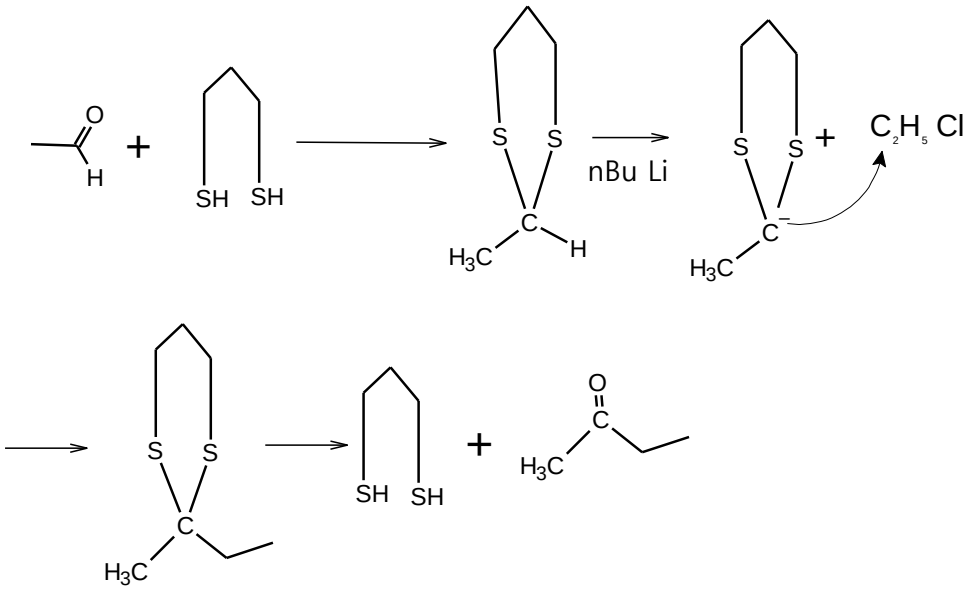

Li+ N−
O
HC−


O
Li+ N−

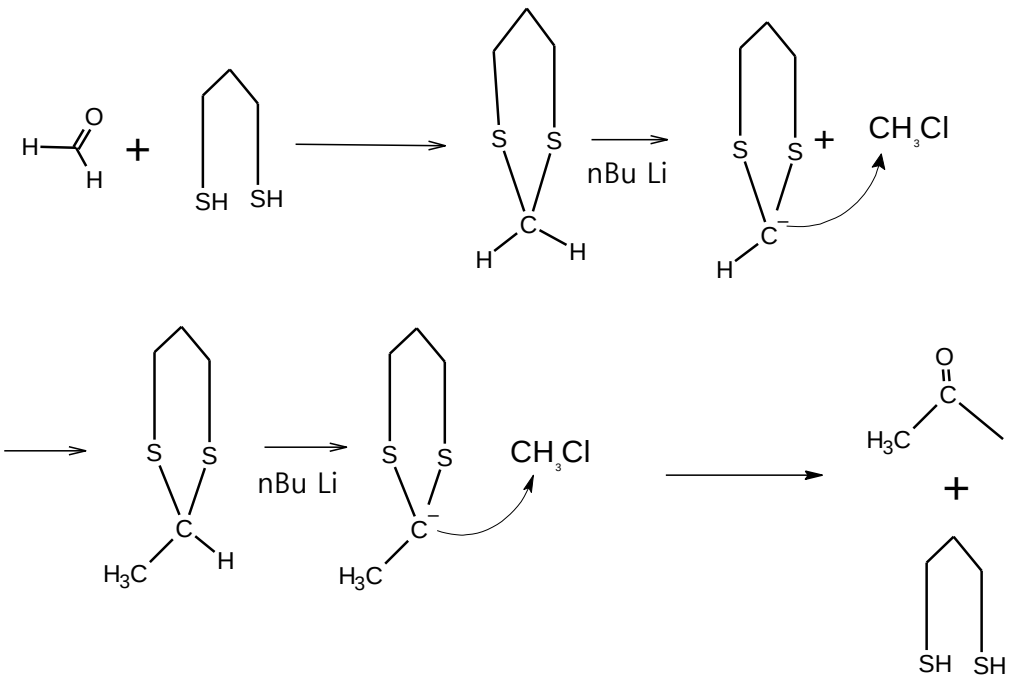

CH4
O
H2C−
CH3Cl
O

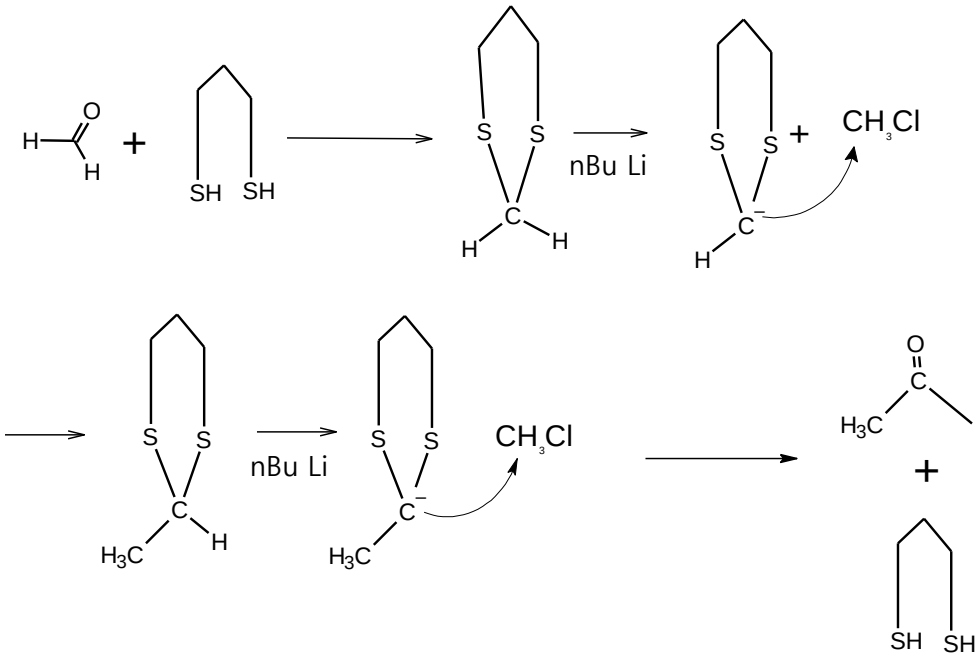
UMPOLOUNG REACTION OR 1,3 DITHIANES

Acetaldehyde to ethyl methyll ketone conversion

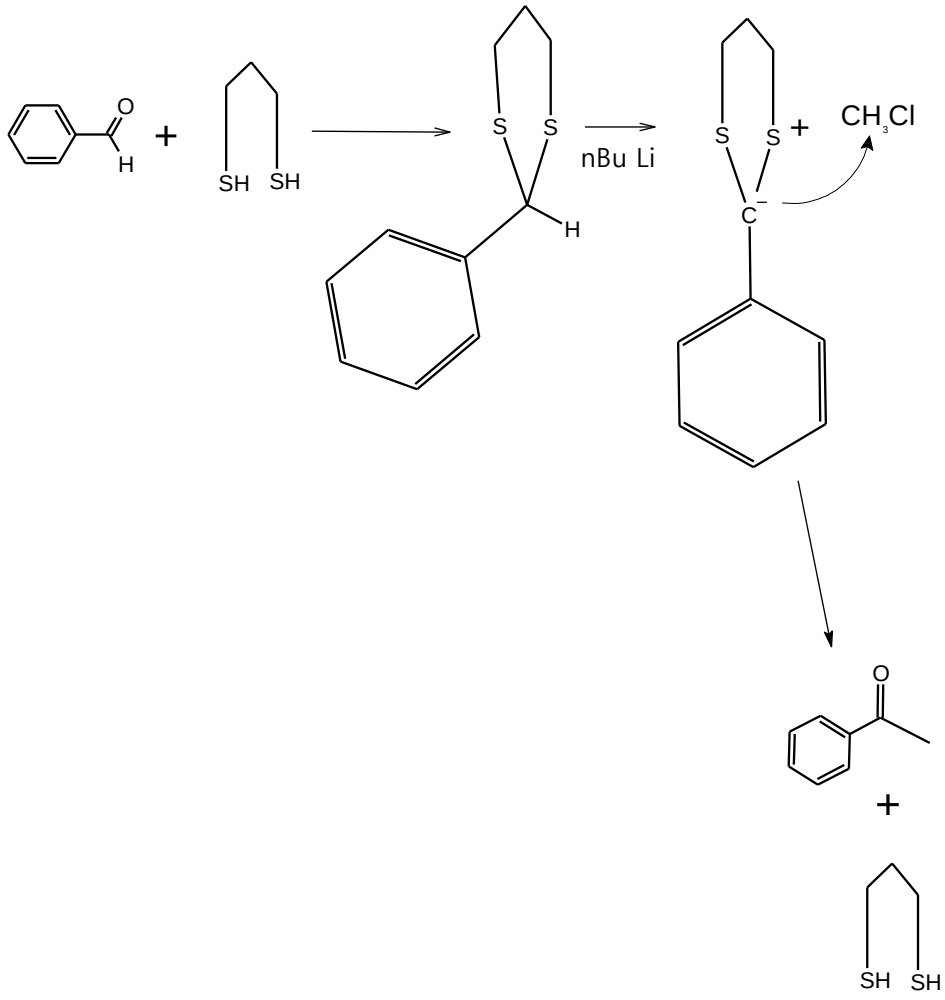


Formalaldehyde to Acetone conversion





Benzaldehyde to acetophenone conversion



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SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

UNIT – 4 GREEN CHEMISTRY – SCY1620

4. GREEN CHEMISTRY

Need - principles - planning of green synthesis, Examples of green reactions - Importance and experimental conditions required, Green reactions in condensation, oxidation, reduction, rearrangement and addition reactions Microwave assisted reactions, solid state synthesis and ionic liquid reaction.

GREEN CHEMISTRY

IT IS AN APPROACH TO DESIGN, MANUFACTURE BY ELIMINATING CHEMICAL HAZARDS.

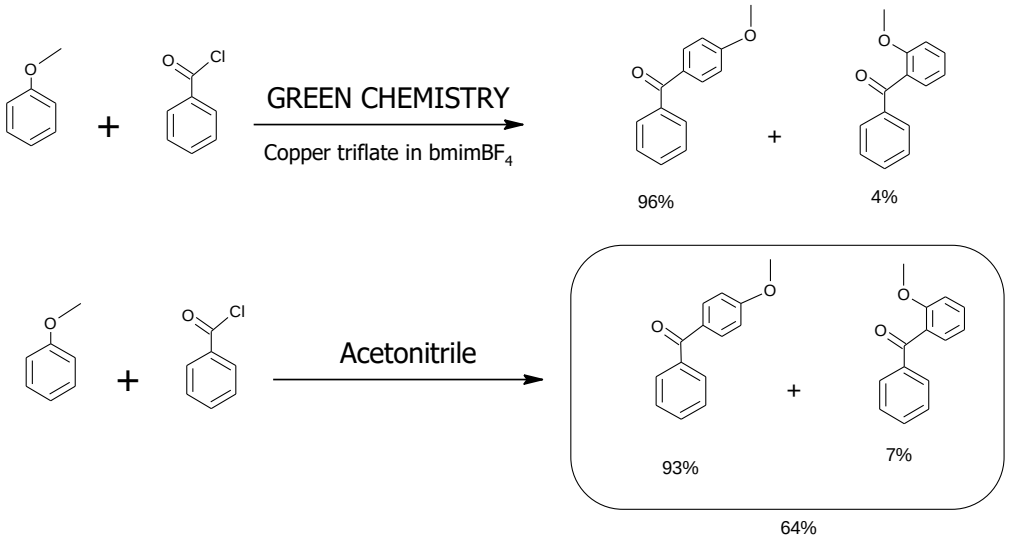
Benfits of Green Chemistry

1. Economical
2. Energy efficient
3. Lowers the cost of production
4. Less waste
5. Fewer accidents
6. Safer products
7. Healthier work place and environment
8. Protect human health and environment
9.Competitive Advantage

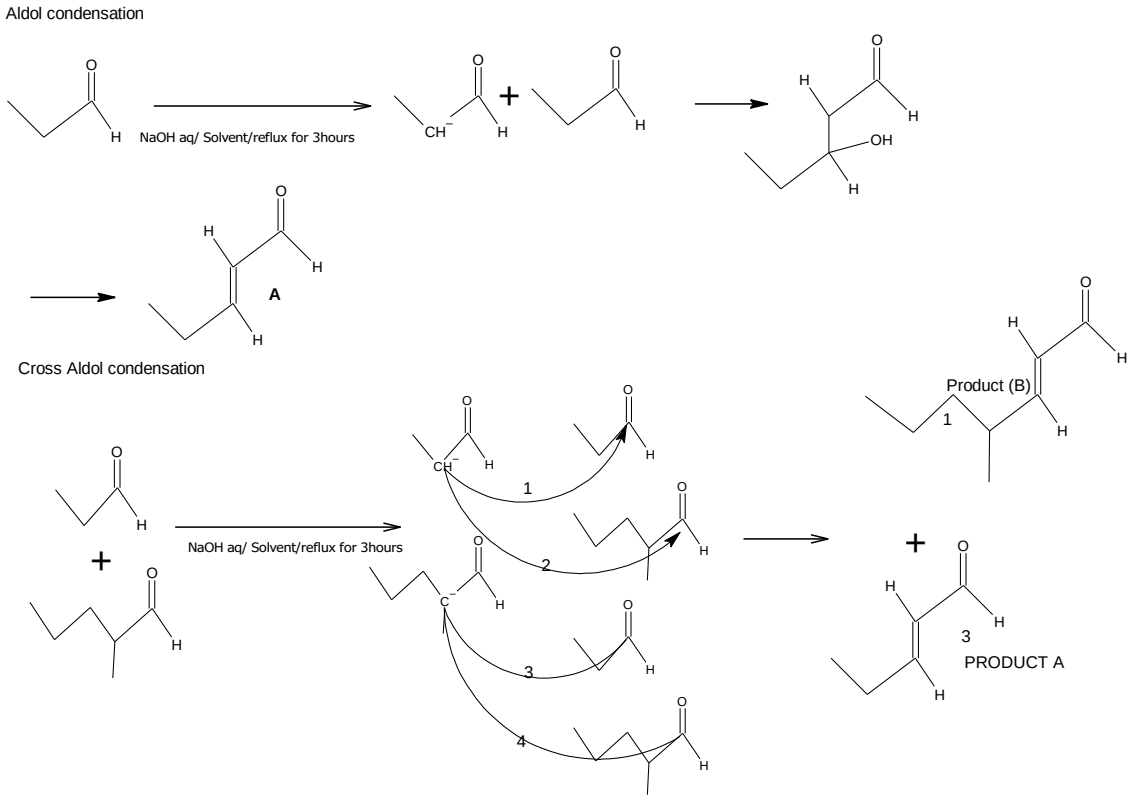
12 Principle

1. PREVENTION
2. ATOM ECONOMY
3. LESS HAZADOUS CHEMICALS
4. DESIGNING THE SAFER CHEMICALS
5. SAFER SOLVENTS AND AUXILARIES
6. DESIGN FOR ENERGY EFFICIENCY
7. USE OF RENEWABLE RESOURCES
8. REDUCE THE DERIVATES
9. CATALYSIS
10.BIODEGRADABILITY
11. REAL TIME ANALYSIS FOR POLLUTION PREVENTION
12. SAFER CHEMISTRY FOR ACCIDENT PREVENTION

ACYLATION IN IONIC LIQUIDS

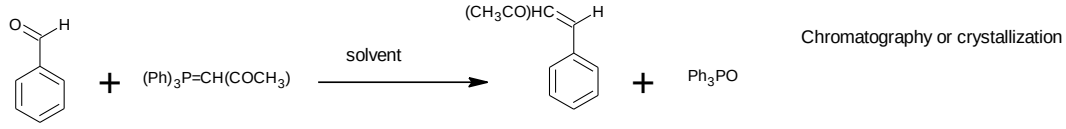


CONDENSATION REACTION IN IONIC LIQUIDS



WITTIG REARRANGEMENT IN IONIC LIQUIDS

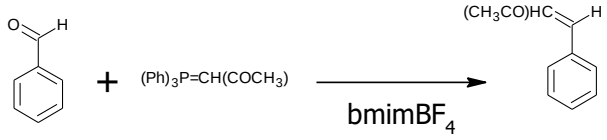
Witting Rearrangement



Chromatography or crystallization

in presence of Ionic liquid

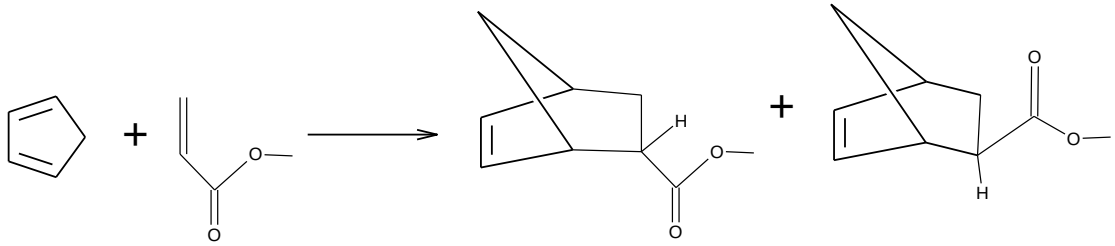
1-butyl-3-methylimidazolium tetrafluoroborate or bmimBF4



EXTRACTION CAN BE DONE WITH TOLUENE
THE SAME IONIC LIQUID CAN BE REUSED.

1 USE = 82%
2ND USE= 83%
6TH USE = 91%

DIESALDER REACTION IONIC LIQUIDS



Endo product

Exo product

emim Cl/(AlCl3) - (48% $AlCl_3$)

basic , 22 hours

Endo/Exo = 4.88

Yield = 32%

emim Cl/(AlCl3) - (51% $AlCl_3$)

Acedic , 22 hours

Endo/Exo = 19

Yield = 53%

emim Cl/(AlCl3) - (48% $AlCl_3$)

basic , 72hours

Endo/Exo = 5.28

Yield = 95%

emim Cl/(AlCl3) - (51% $AlCl_3$)

Acedic , 72 hours

Endo/Exo = 19

Yield = 79%

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SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF CHEMISTRY

UNIT – 5 INTRODUCTION TO PERICYCLIC REACTIONS – SCY1620

4. INTRODUCTION TO PERICYCLIC REACTIONS

Pericyclic reactions are concerted reactions.

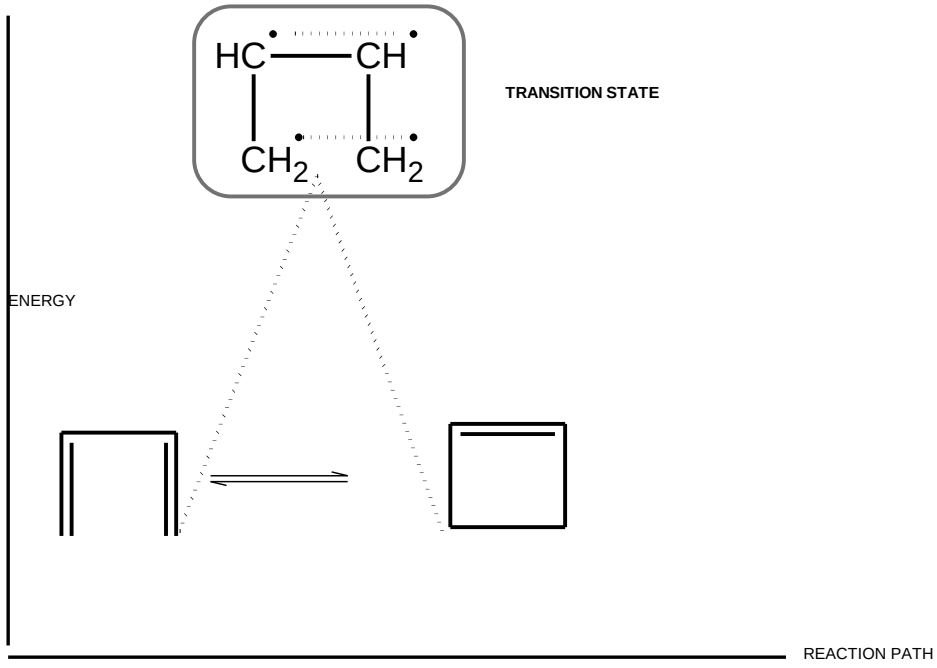
The characteristics of pericyclic reactions

1. It is single step reaction
2.There is no reactive inetermidiate.
3. It forms transition state
4. Simultanious bond formation and bond breaking
5. These are synchronus concerted reactions
6. These are common in olefinic system
7. There reactions are controlled by either heat or light
8. These are kinetically controlled reactions

   SN1 reaction in high polar solvents is very fast

   SN1 Reacion in low polar solvents is very slow

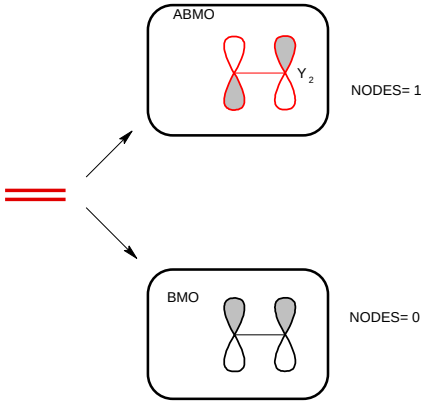
Energy profile diagram of pericyclic reactions



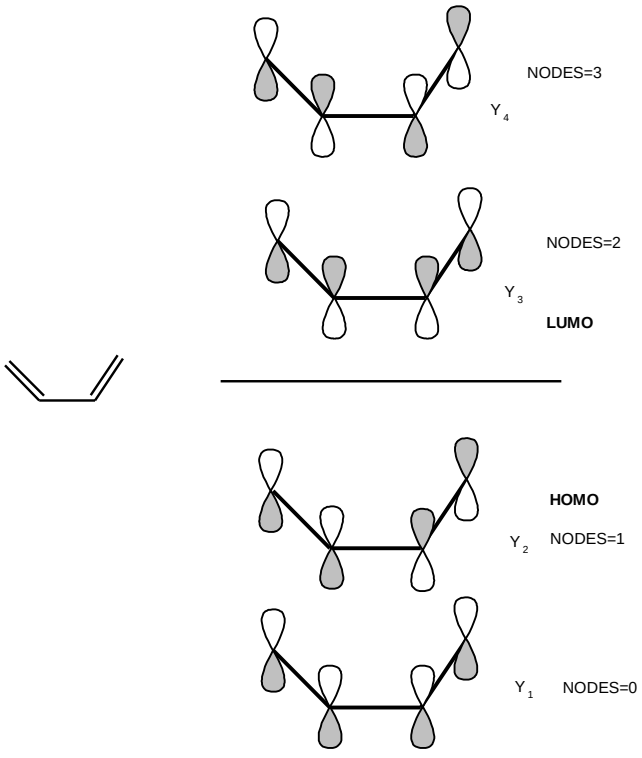
Classification of electrocyclic reactions

1. Electrocyclic reaction
2. Cyclo addition reaction
3. Sigma tropic reactions
4. Chelotropic reaction
5. Group transfer reaction

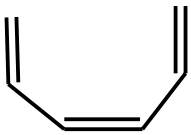
FMO ORBITALS OF ETHYLENE

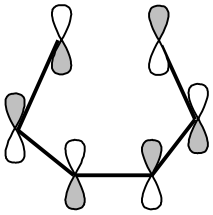


FMO ORBITALS OF 1,3 BUTADIENE



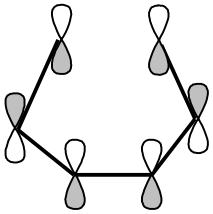
FMO ORBITALS OF 1,3,5 HEXATRIENE



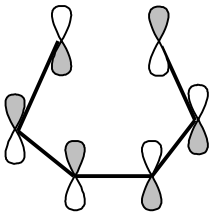


Y_6

NODES=5

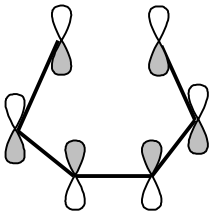


Y_5 NODES=4



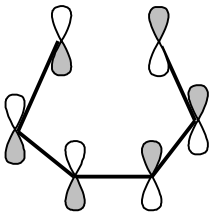
NODES=3

Y_4 **LUMO**

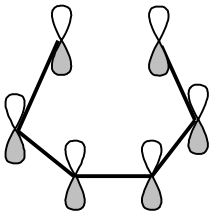


Y_3 **HOMO**

NODES=2



Y_2 NODES = 1



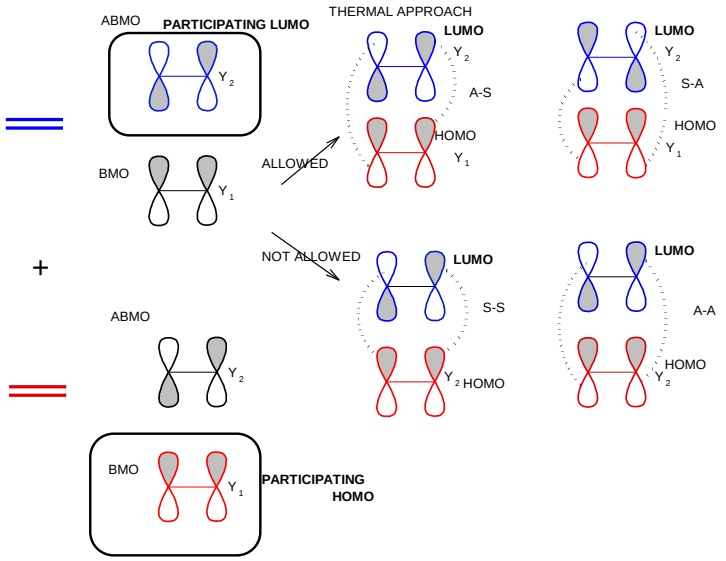
NODES = 0

Y_1

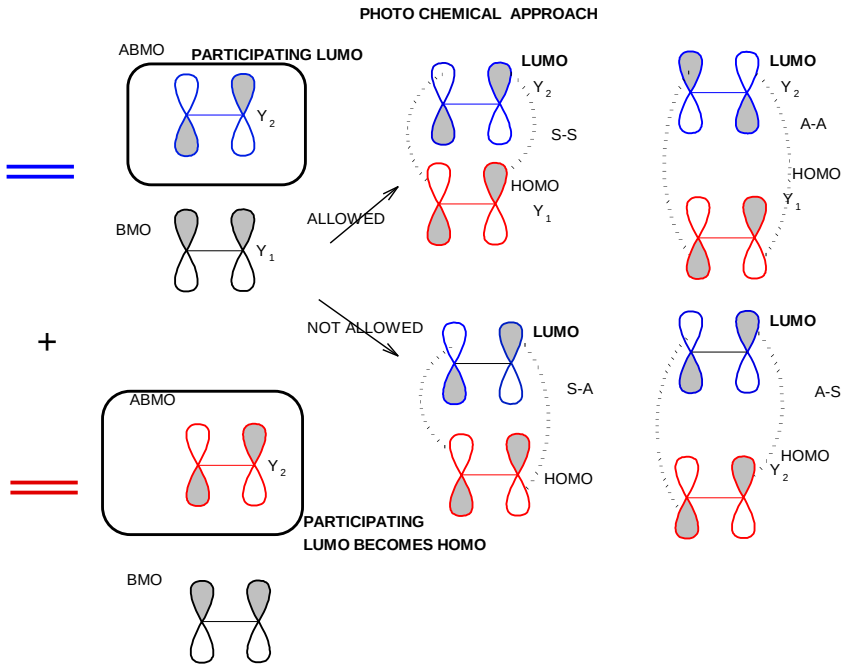
Cyclo Addition Reaction Mechanism Thermal Approach:

Cycloaddition of ethylene + ethylene thermally SUPRA-ANTRA OR ANTRA-SUPRA addition is allowed.

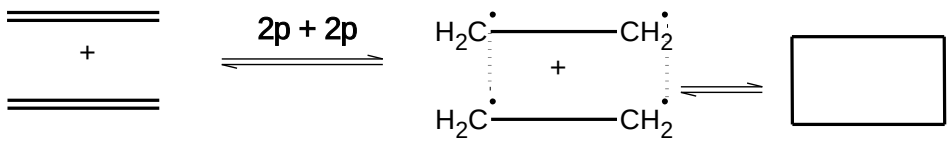
Cycloadditon of ethylene + ethylene photochemically SUPRA-SUPRA OR ANTRA – ANTRA addition is allowed.

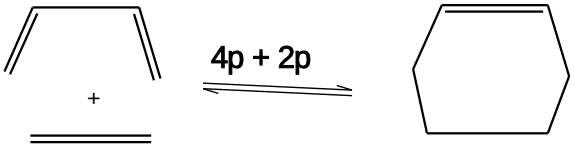


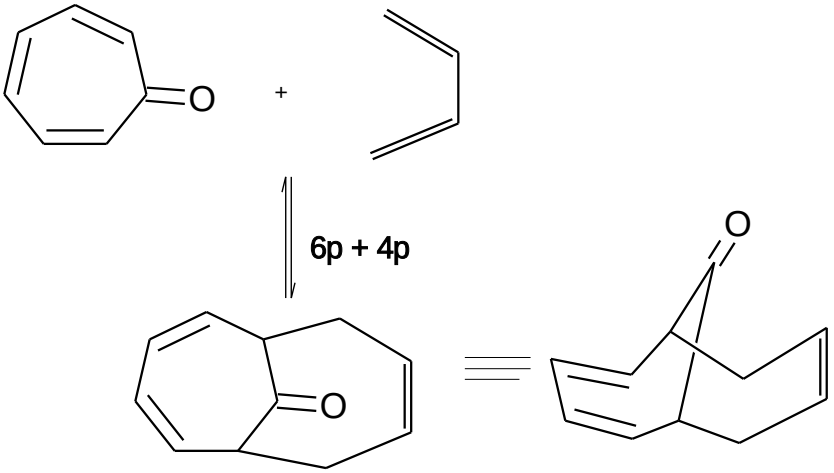
Cyclo Addition Reaction Mechanism Photochemical Approach:

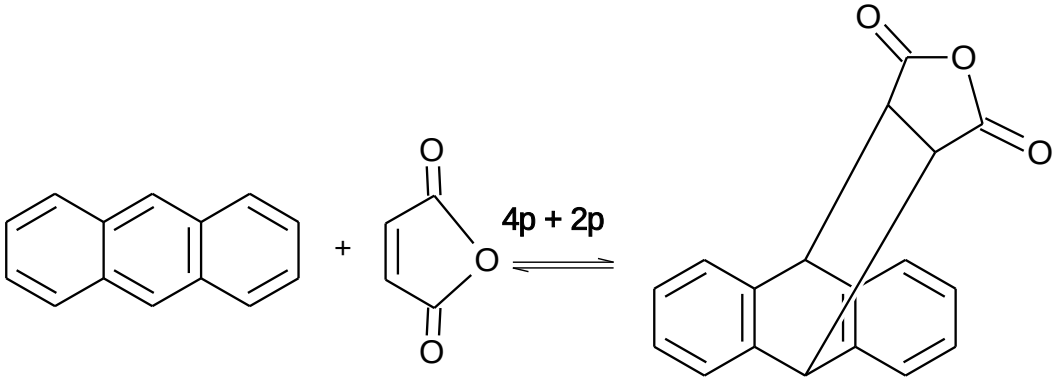


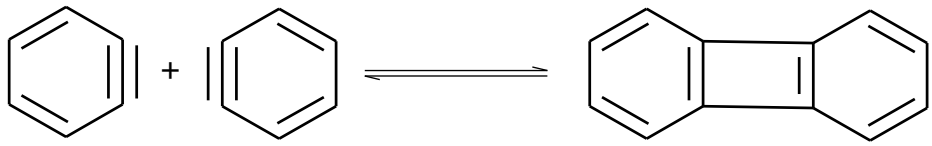
CYCLOADDITION REACTIONS EXAMPLES:



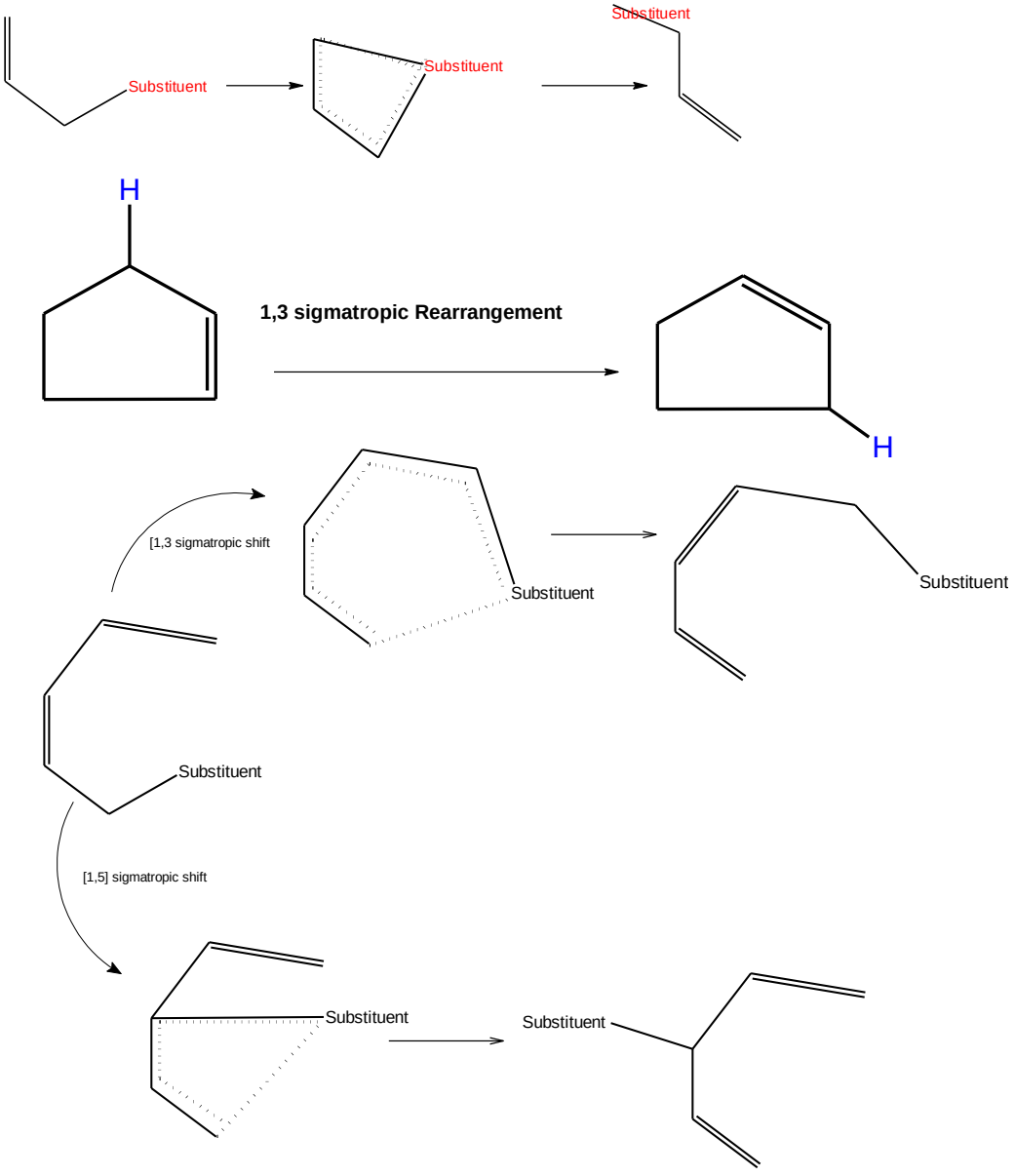




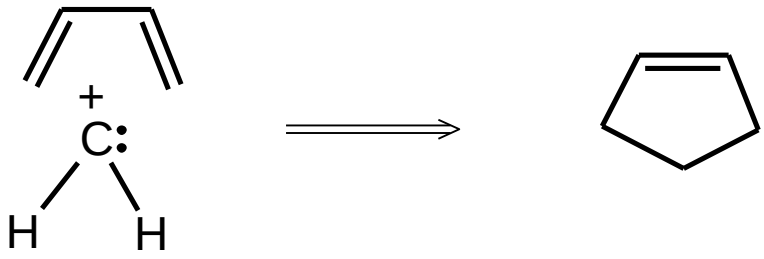


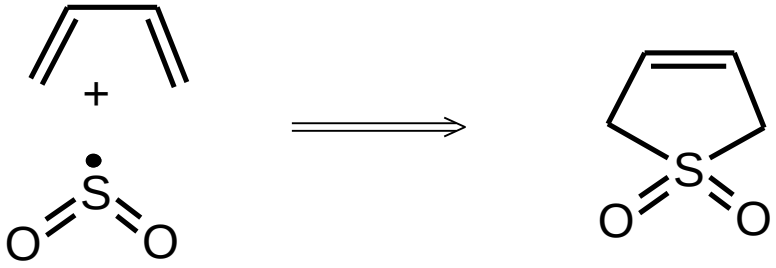


SIGMATROPIC REARRANGEMENTS



CHELOTROPIC REACTIONS

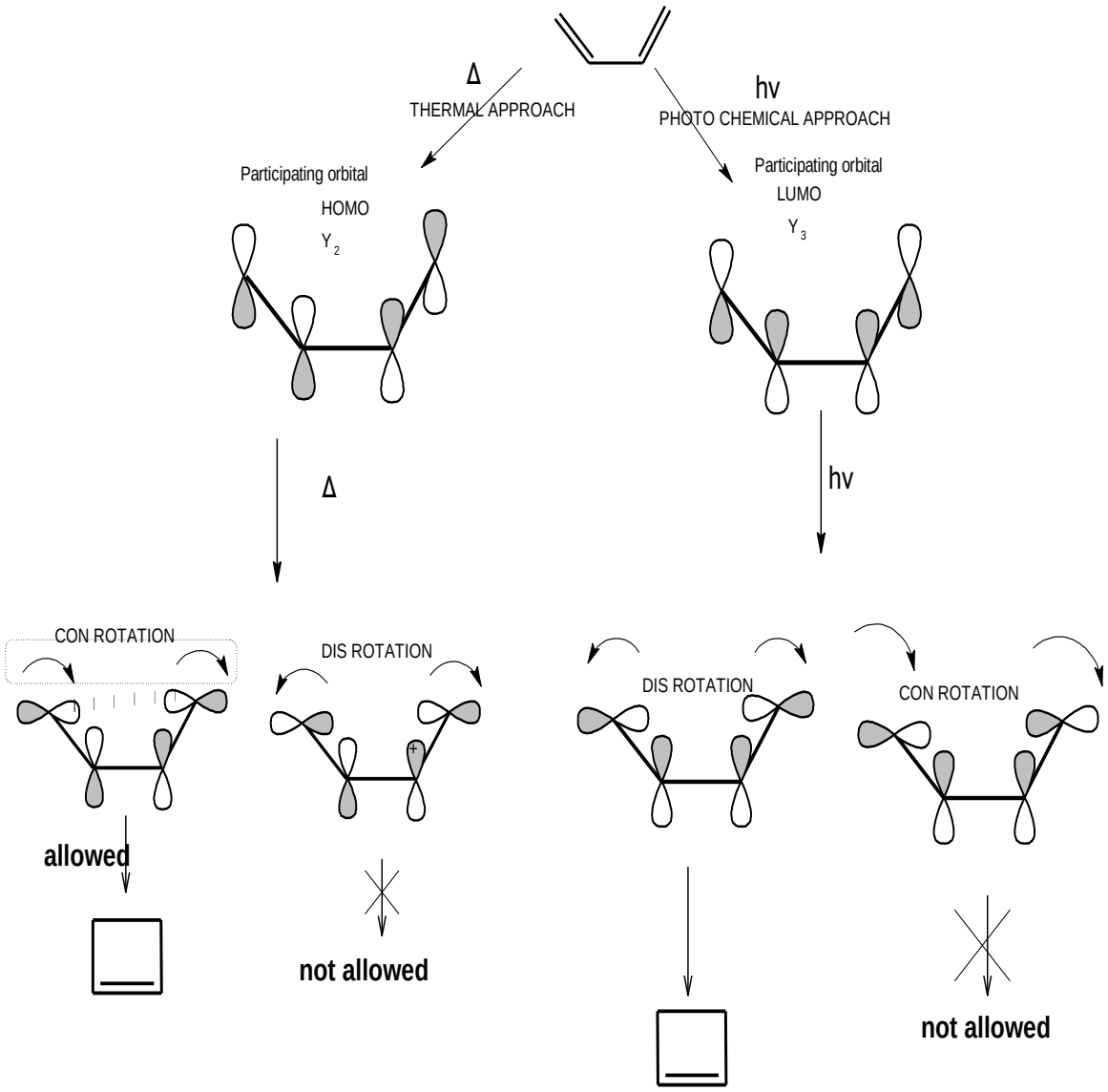




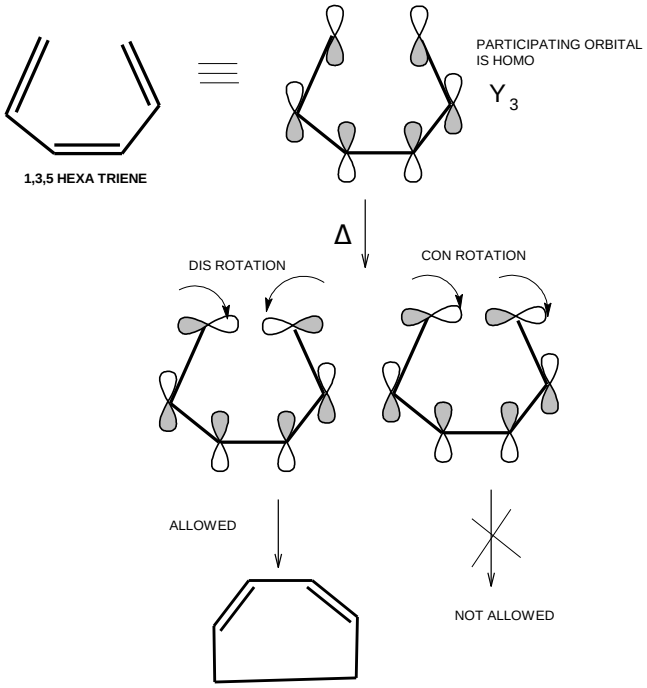
ELECTRO CYCLISATION REACTION MECHANISM OF 1,3 BUTADIENE:

Electro cyclisation of 1,3 butadiene is thermally allowed

Electro cyclisation of 1,3 butadiene is photo chemically allowed.



Electro cyclization of 1,3,5 hexatriene – Thermal approach



Electrocyclization of 1,3,5 hexa triene – Photo chermal approach