Green Chemistry: Principles and Examples

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Sustainability:
Meeting the needs of the present generation without compromising the needs of future generationsis

is the goal

Green Chemistry:

Technologies that are energy efficient,minimise or preferably eliminate the formation of waste,avoid the use of toxic and/or hazardous solvents and reagents and, where possible,utilise renewable raw materials.

is the means

Primary Pollution Prevention not (End-of Pipe)Remediation

The 12 Principles

- Prevention
- Atom Economy & E Factor
- Less Hazardous Chemical Synthesis
- Designing Safer Chemicals
- Safer Solvents and Auxiliaries
- Design for Energy Efficiency
- Use of Renewable Feedbacks
- Reduce Derivatives
- Catalysis
- Design for Degradation,
- Real-time Analysis for Pollution Prevention
- Inherently Safer Chemistry for Accident Prevention

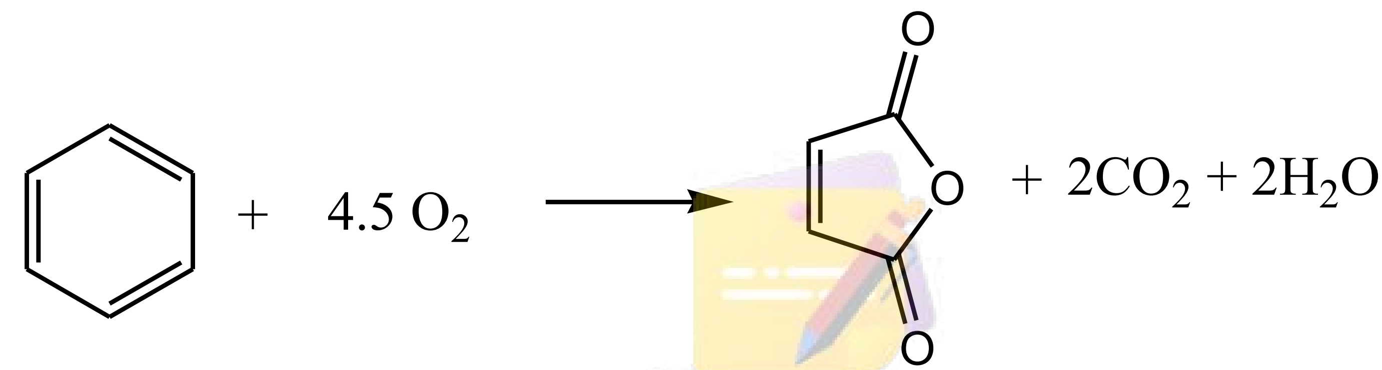
$$A + B + C \text{ ----------------} \rightarrow P + U$$

Reactants **Product + Unwanted Product**

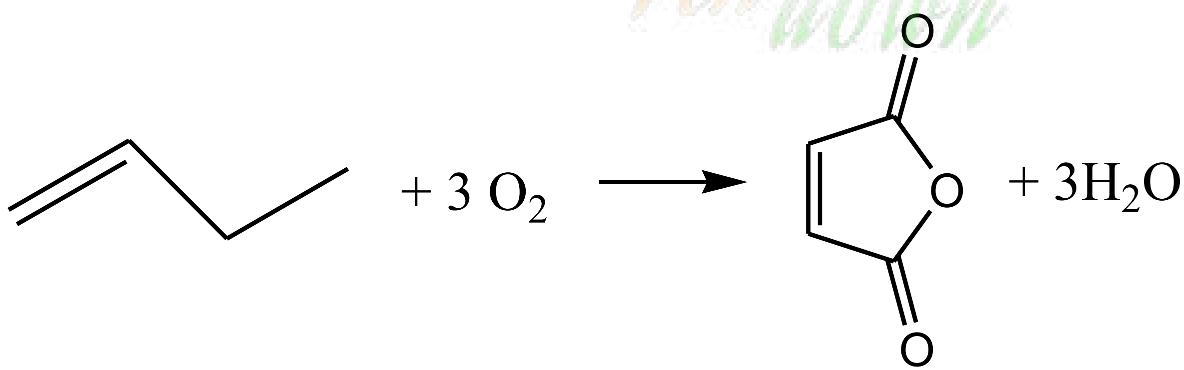
Atom Economy = P ÷ A + B + C

E Factor = U ÷ P

% Atom economy = 100 x rel. mol. mass of desired products / rel. mol. mass of *all* reactants



% atom economy = 44 %

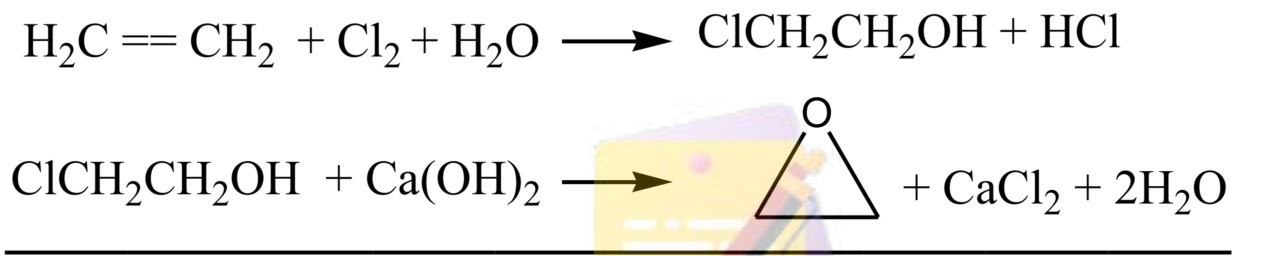


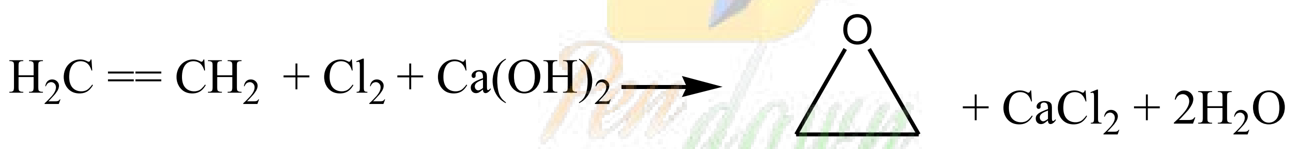
% atom economy = 64.5 %

Routes to Synthesis of Maleic anhydride

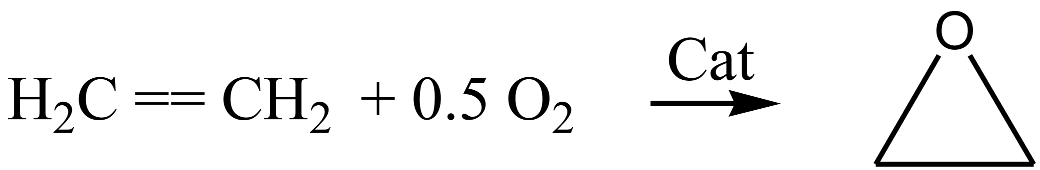
Sheldon 1994: E-Factor

The environmental quotient : Total mass of waste / by mass of product





Atom economy: 25%: E-factor:2.9 (127.6/ 44)



Atom economy: 100%: E-factor:0

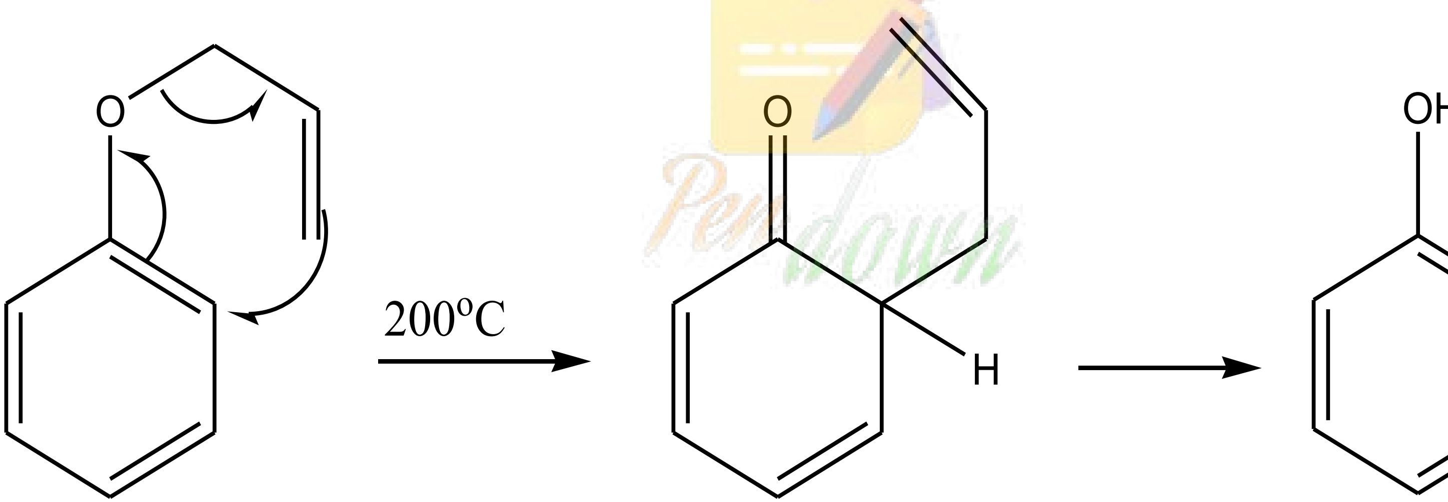
Supercritical CO_2

Supercritical CO_2 as a Reaction Medium

- *T_c 31.0 °C, p_c 73.8 bar, d_c 0.477 kg L^{-1}*
- Low viscosity (*more like a gas than like a liquid*); hence, fast mass transfer
- Cheap and abundantly available
- Easy to remove (N.B. no net production of CO_2)
- Non-toxic,non-inflammable,inert

ATOM ECONOMIC REACTIONS

Rearrangement



Claisen rearrangement of aromatic allyl ethers

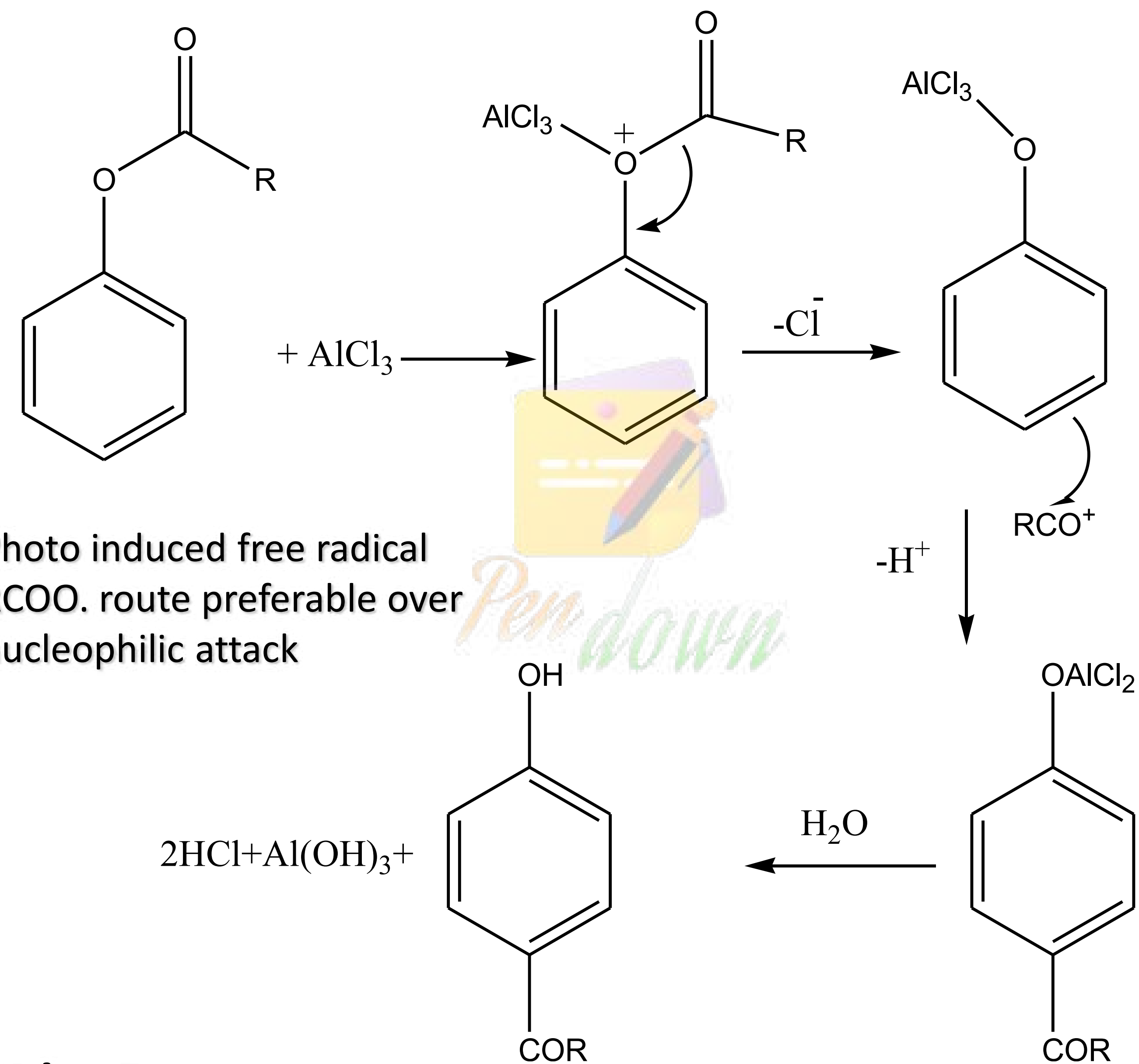
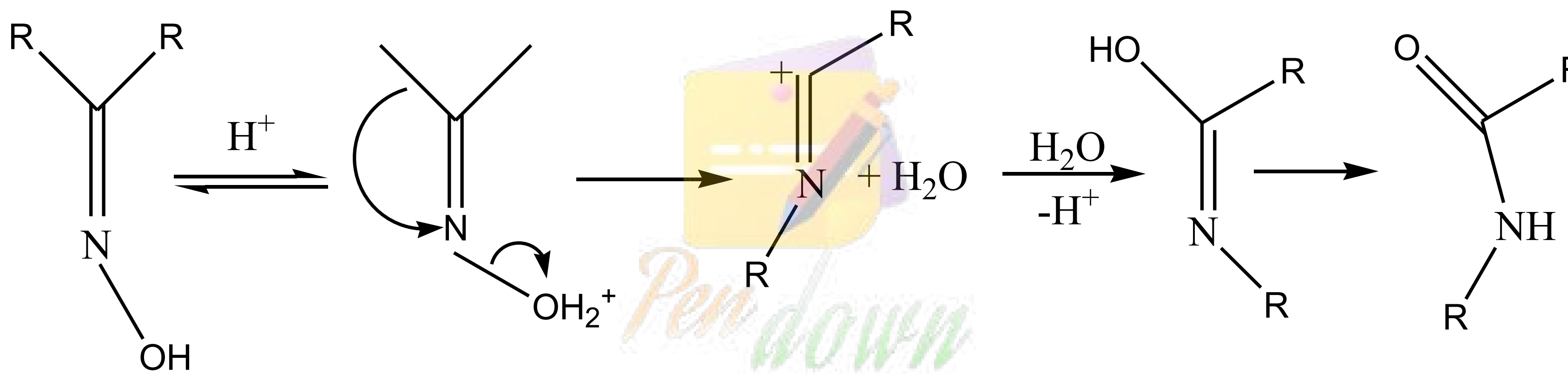


Photo induced free radical RCOO. route preferable over nucleophilic attack

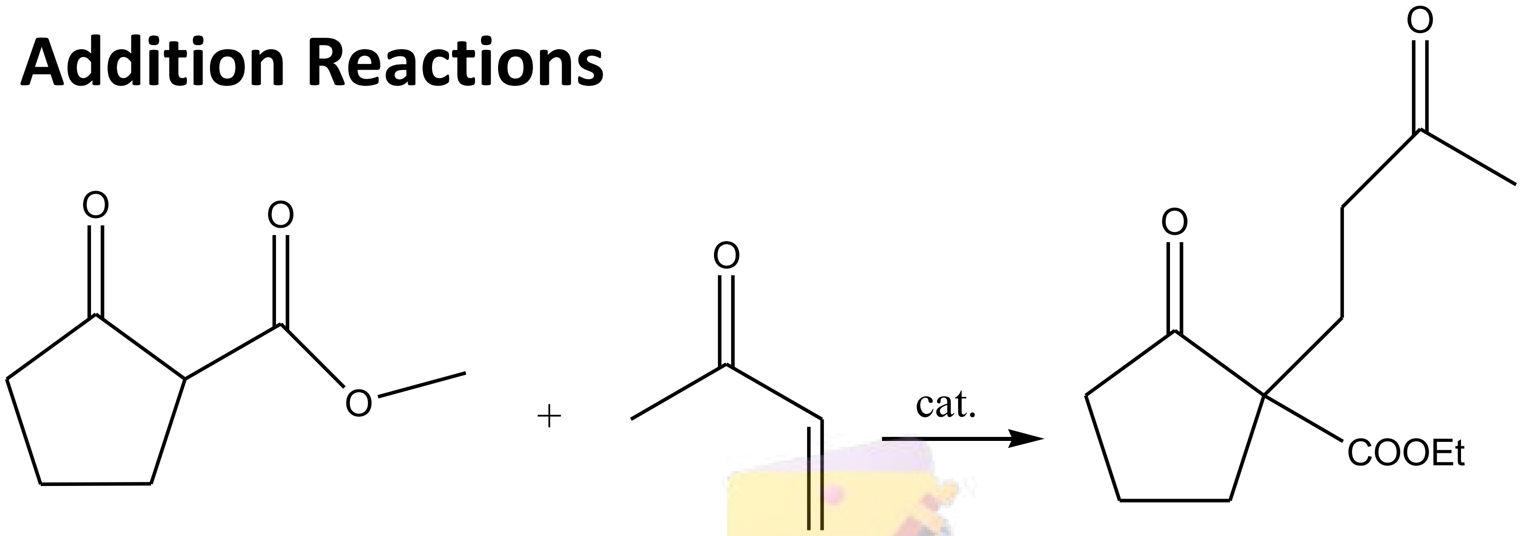
Fries Rearrangement



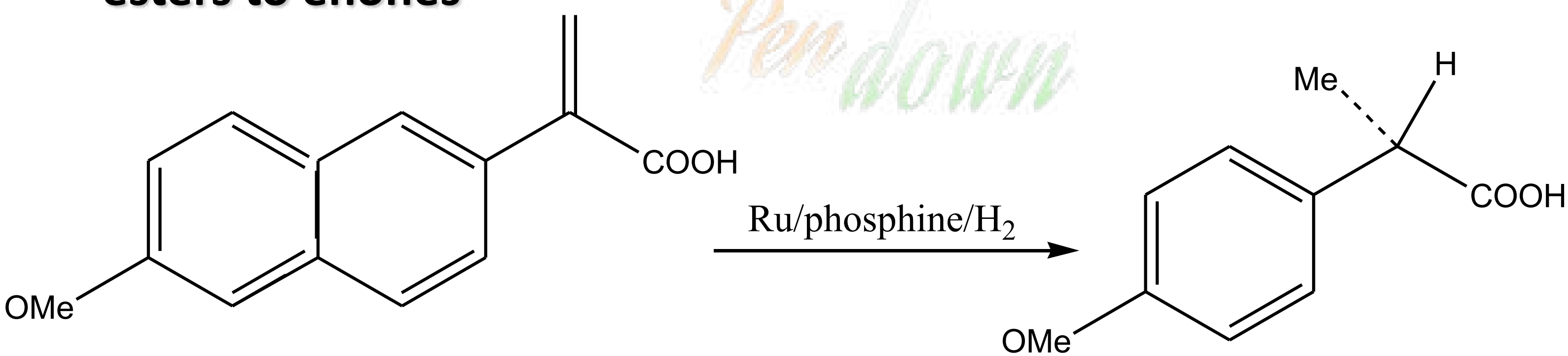
Beckmann Rearrangement :

from cyclohexanone oxime to caprolactam; a key intermediate for nylon 6 *(zeolite is preferable over 20% oleum)*

Addition Reactions



Michael Addition : heterogeneous base catalyzed addition of beta keto esters to enones



S-naproxen

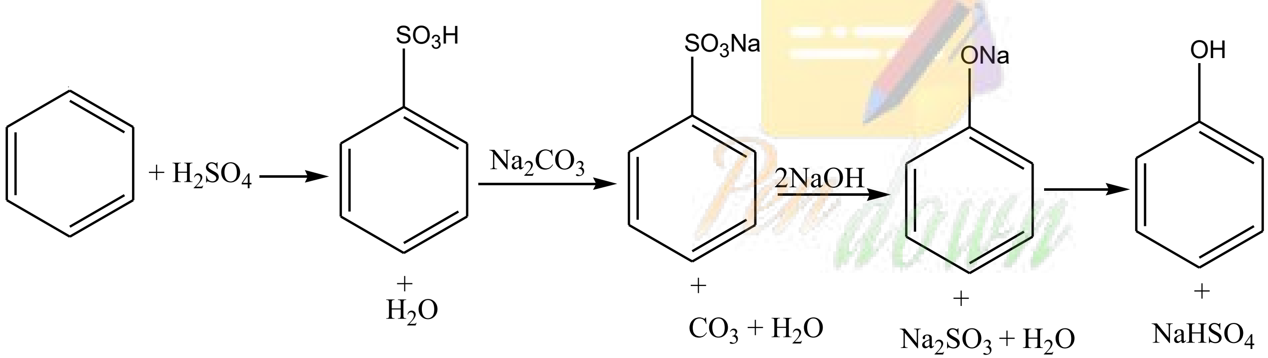
Addition to carbonyl groups: enantioselective catalytic hydrogenation using chiral ligands

ATOM UN-ECONOMIC REACTION

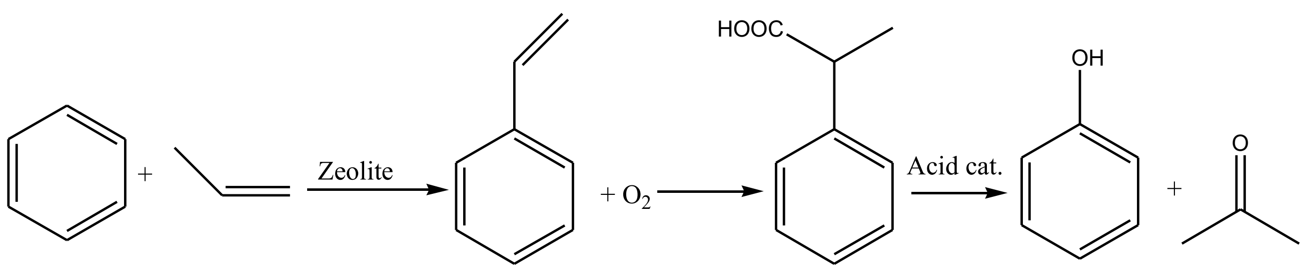
- **Substitution Reactions**

$$CH_3(CH_2)_4\,CH_2OH + SOCl_2 \longrightarrow CH_3(CH_2)_4CH_2Cl + SO_2 + HCl$$

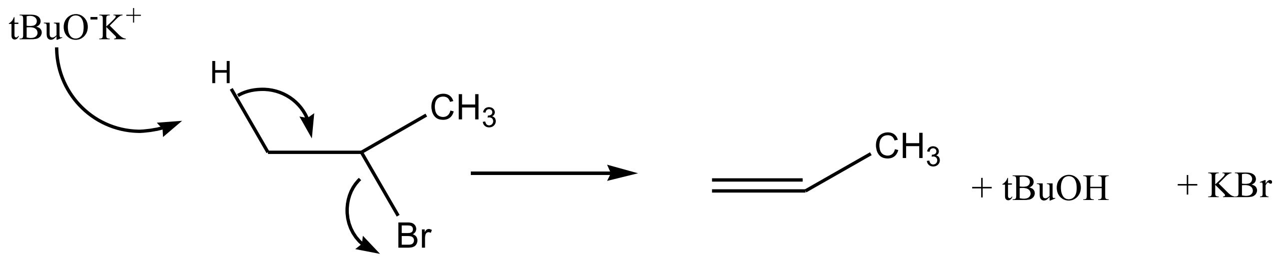
Chlorination of Hexanol
Atom economy = 100 X 120.5 / (102 + 119) = 54.5%



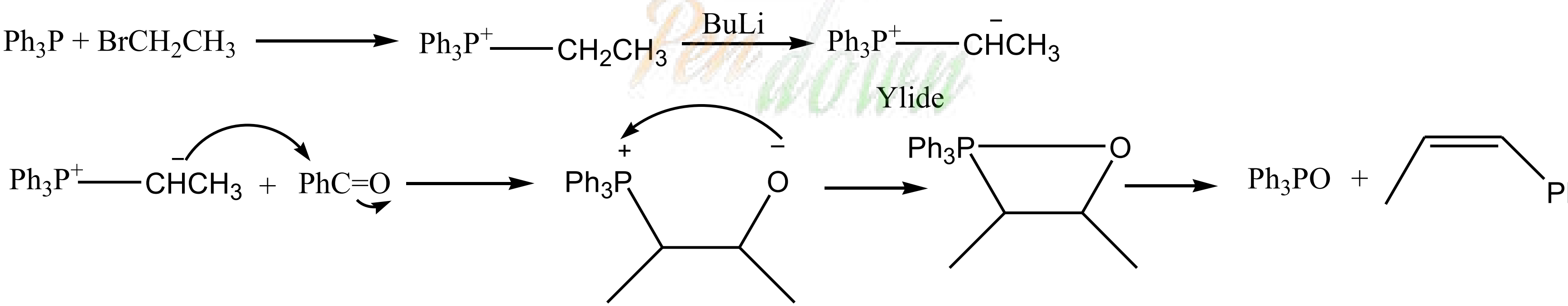
Benzene sulfonation route to Phenol



Cumene route to Phenol



E2 elimination of HBr from 2-bromo propane
Atom economy = 42 /(112+122) = 17.9%



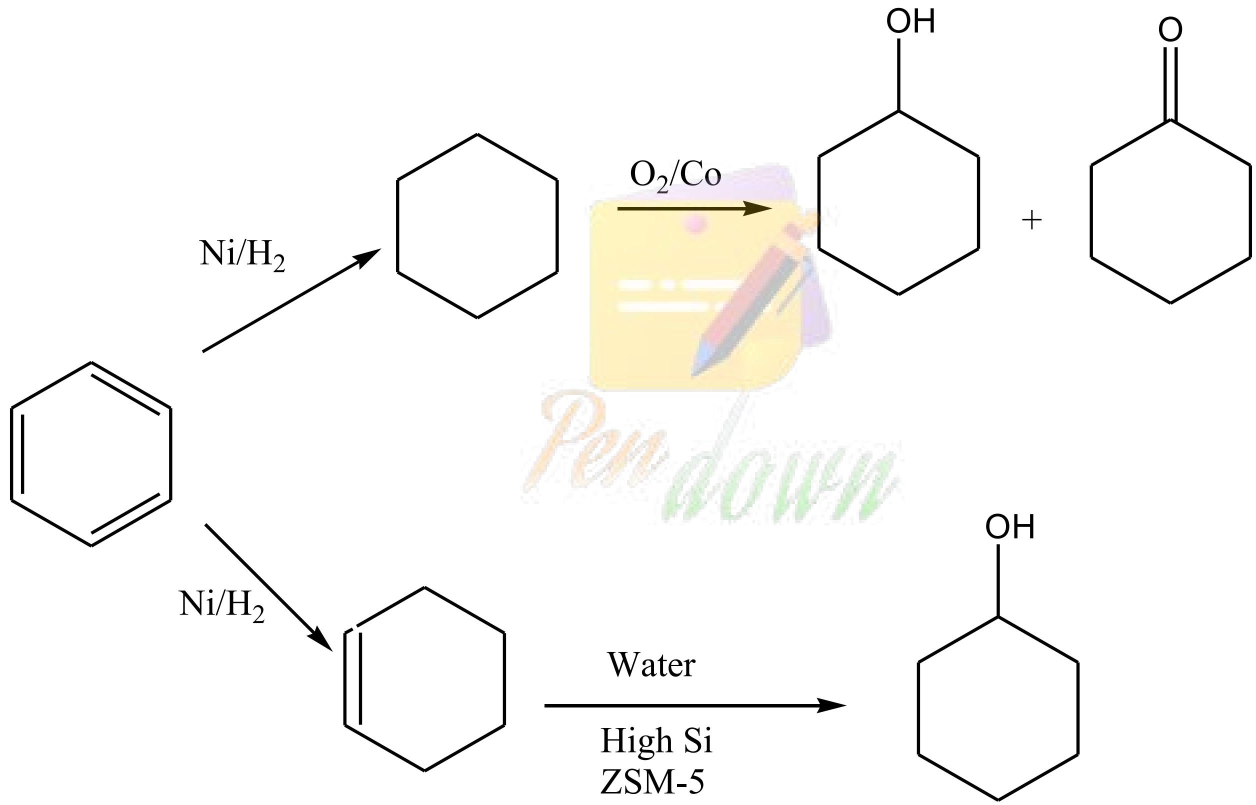
Wittig Reaction: Preparation of Alkenes under mild conditions generates TPPO as waste limiting its commercial use

Catalysis and Green Chemistry

Catalysts, by definition, are hetero- or homogeneous;within and across these two categories there are other classifications:

- Asymmetric Catalysts
- Biocatalysts
- Phase transfer Catalysts
- Photocatalysts
- Nanoparticles as Catalysts

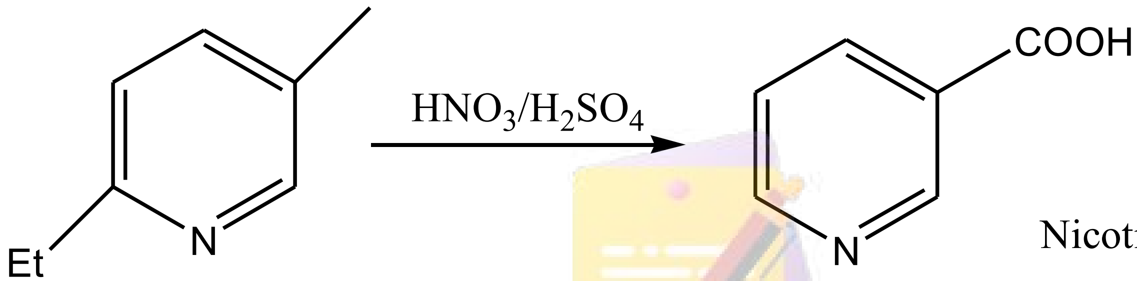
Heterogeneous catalysts



Production of Cyclohexanol

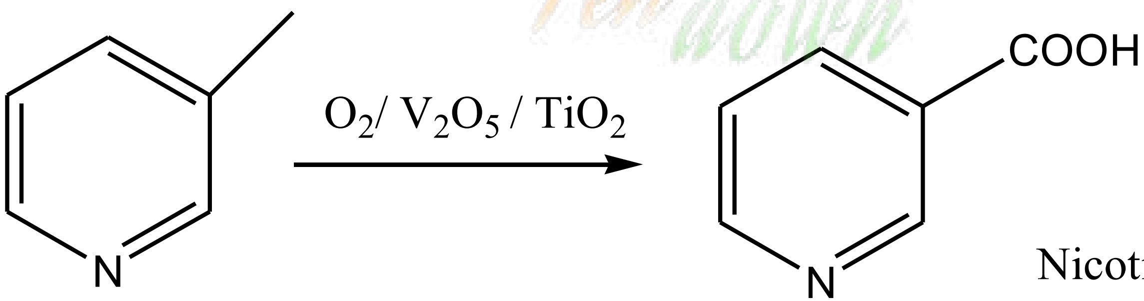
Production of Nicotinic Acid

(i)



Nicotinic Acid

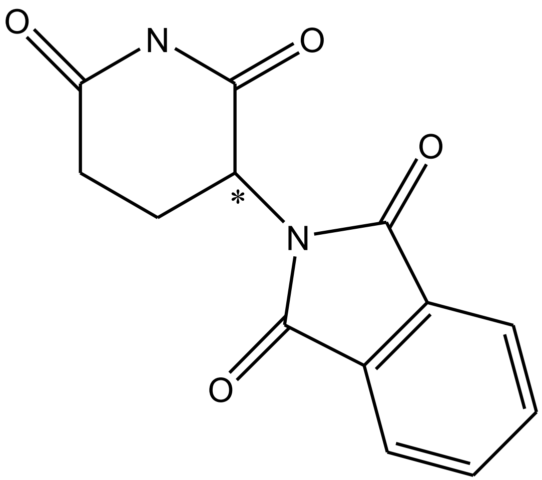
(ii)



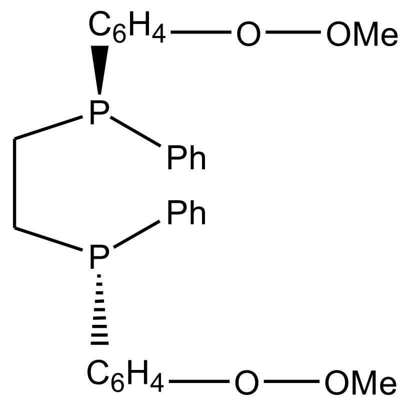
Nicotinic Acid

(ii) Catalytic route is green route

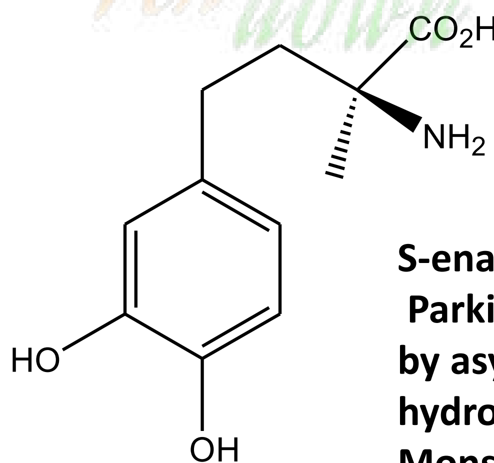
Asymmetric Catalysts



Thalidomide
(* Chiral Centre)



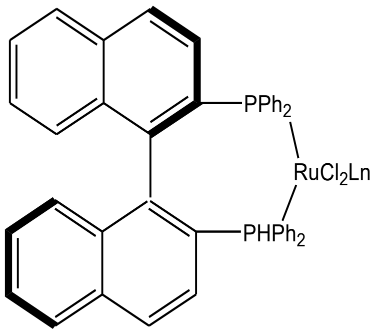
DIPAMP **Chiral phosphine**



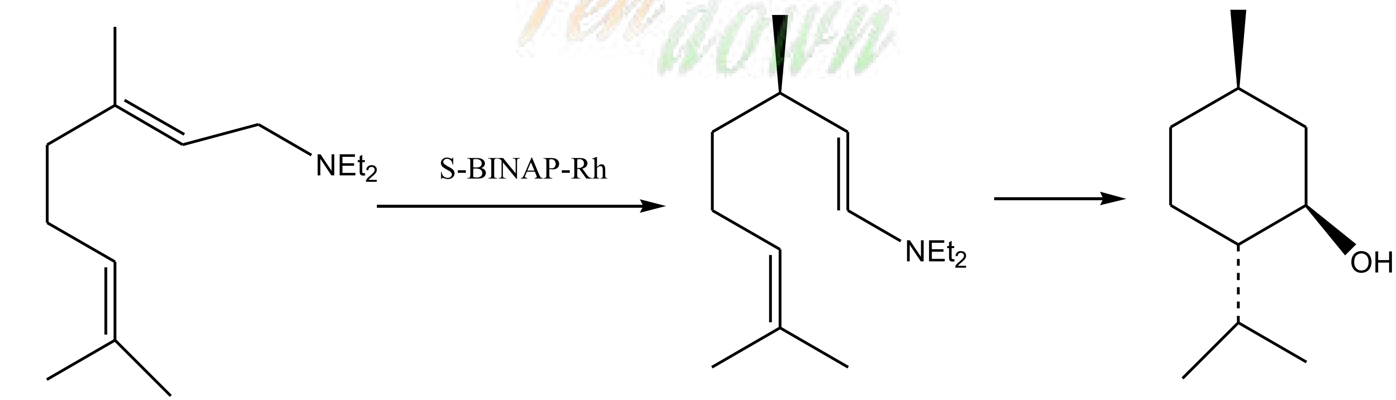
S-enantiomer drug for Parkinson's disease made by asymmetric hydrogenation by Monsanto

L-Dopa

Commercial Synthesis of l- menthol



BINAP-Ru/Rh

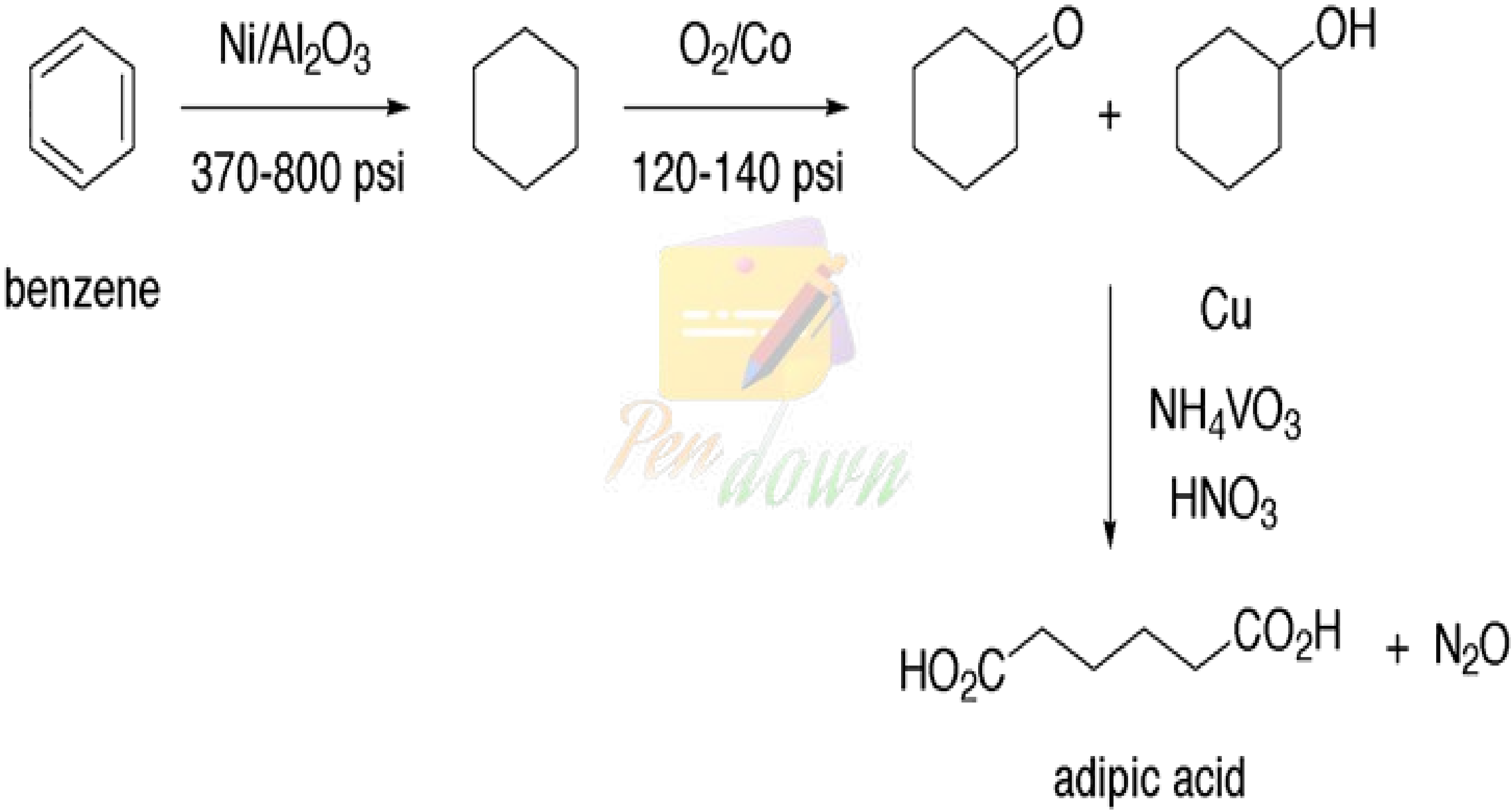


diethyl geranylamine

(R)-Citronellal enamine

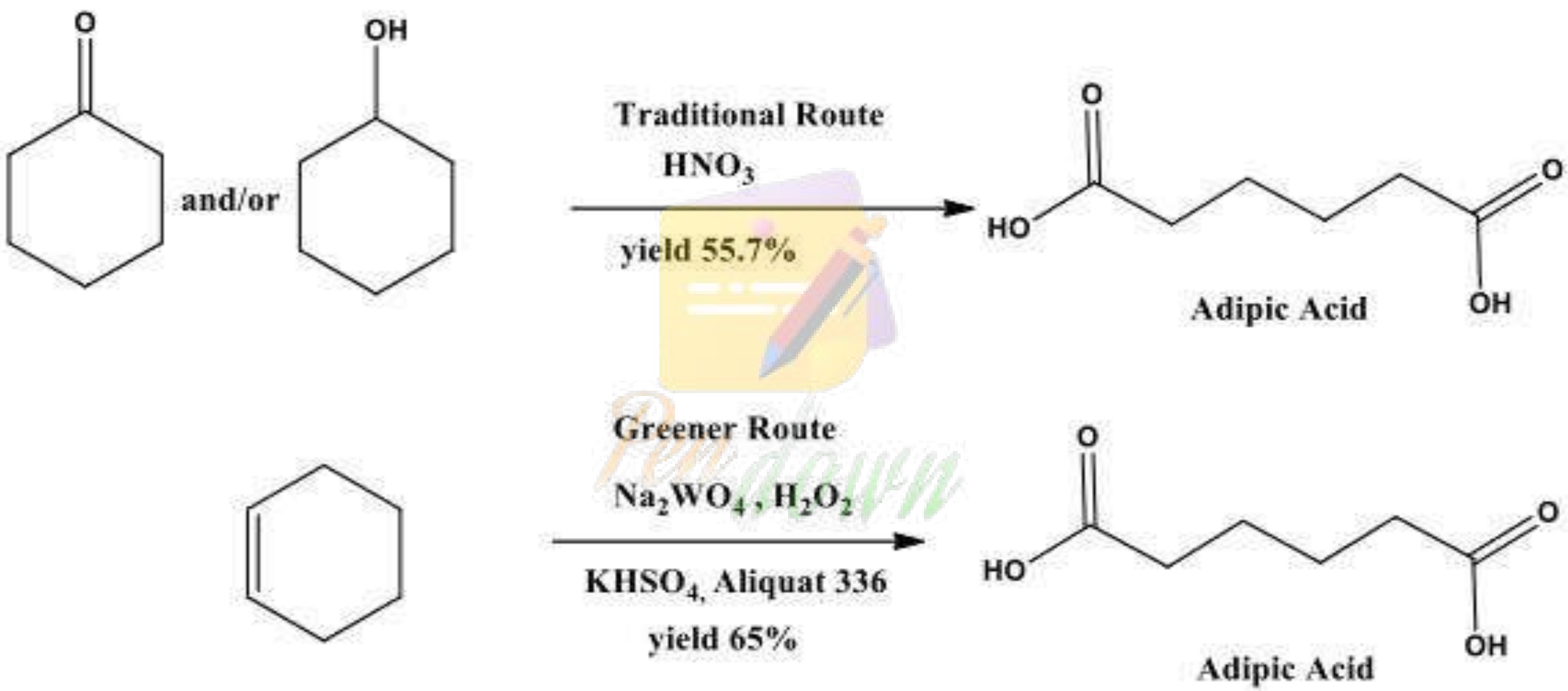
(−) Menthol

Synthesis of Adipic Acid: Traditional Route



2.2 million tons of adipic acid is consumed globally, mostly in the production of Nylon-6,6.
In the traditional synthesis process large amount of N_2O has been produced which is a green house gas and potential pollutant.

Synthesis of Adipic Acid



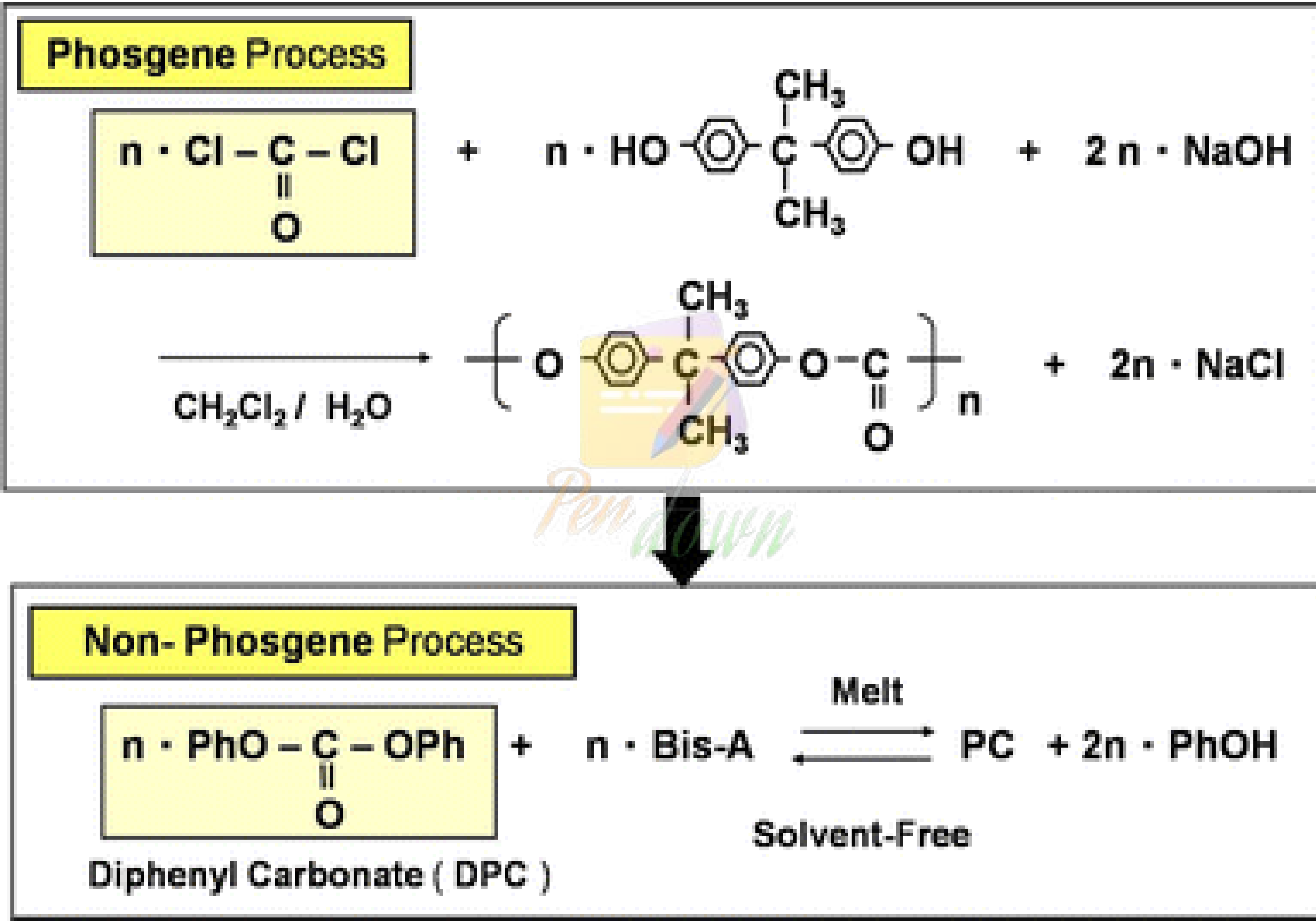
Green Route is known as Noyori Synthesis

Production of Polymer Polycarbonate (PC)

Uses: electrical and electronic equipments, auto parts and accessories, medical devices, optical media, safety helmets, sport goods, aircraft and missile components.

Traditional Baeyer Method used a reaction between Bisphenol -A and phosgene-a lethally poisonous gas

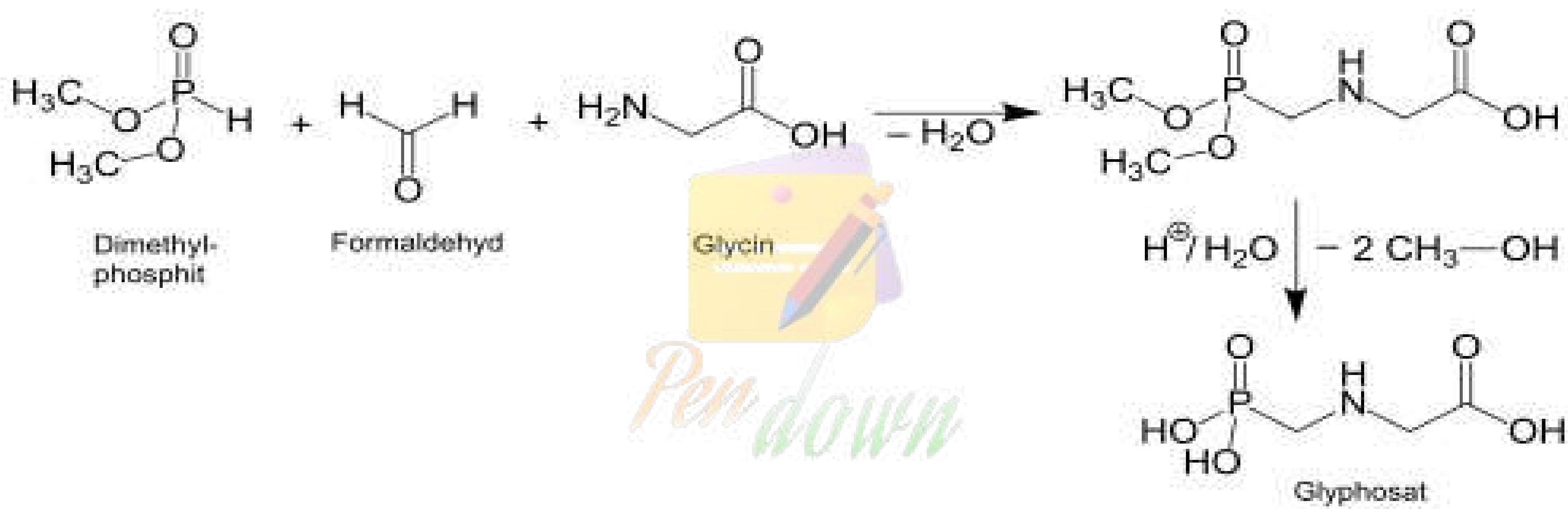
In green Asahi Process diphenyl carbonate and Bisphenol -A are taken in molten state without solvent : Komiya 2003


Phosgene Process
n · Cl – C – Cl
O
+
n · HO
CH3
C
CH3
OH
+
2 n · NaOH
CH2Cl2 / H2O
O
O – C
O
n
+
2n · NaCl
Non- Phosgene Process
n · PhO – C – OPh
O
Diphenyl Carbonate (DPC)
+
n · Bis-A
Melt
Solvent-Free
PC
+ 2n · PhOH

Asahi Process : for PC Production

- Phosgene – free process
- Incorporation of CO_2- byproduct carbon dioxide used as starting material
- No need for PC purification
- No diethylene glycol (DEG) formation
- Waste –free process

Monsanto's Herbicide or Weedicide- "RoundUp" or Glyphosate 1974



It is an organophosphorus compound specifically a phosphonate.Can also be classified as an amino acid

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