# Chapter 4

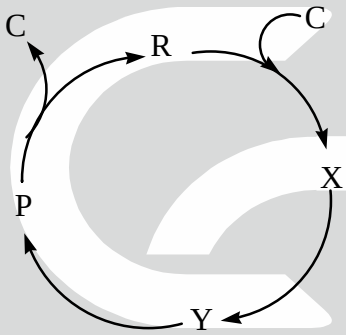
## Homogeneous Catalysis

**HOMOGENEOUS CATALYSIS :**

The catalysis in which, the reactant and catalyst are in the same phase. It is usually solid or liquid. But the most difficult problem is the separation of catalyst after the reaction.

**Terminology used in Catalysis :**

**(1)** **Turn Over :** Catalysis occurs in cycles where the active form of the catalyst gets regenerated and turn over describes one loop (cycle) through the catalytic cycle.




**(2)** **Turn Over Number (TON) :** The absolute number of passes through the catalytic cycle before the catalyst becomes deactivated is called TON.

It is defined as amount of reactant in moles devided by the catalyst involves in mole multiplied by % in of the product.

$$TON = \frac{\text{Amount of Reactant}}{\text{Amount of catalyst}} \times \text{yield of product (taken in decimal)}$$

Higher is the TON value longer the life of the catalyst. TON is unitless.

**(3)** **Turn Over Frequency (TOF) or Turn over rate :**

It is the number of passes through the catalytic cycle per unit time (often per hour).

Higher is TOF more effective is the catalyst.

$$TOF = \frac{TON}{Time} (s^{-1})$$

The first effective homogeneous catalyst to be discovered is **WILKINSON CATALYST.** It is used in hydrogeneration of alkene and alkyne.

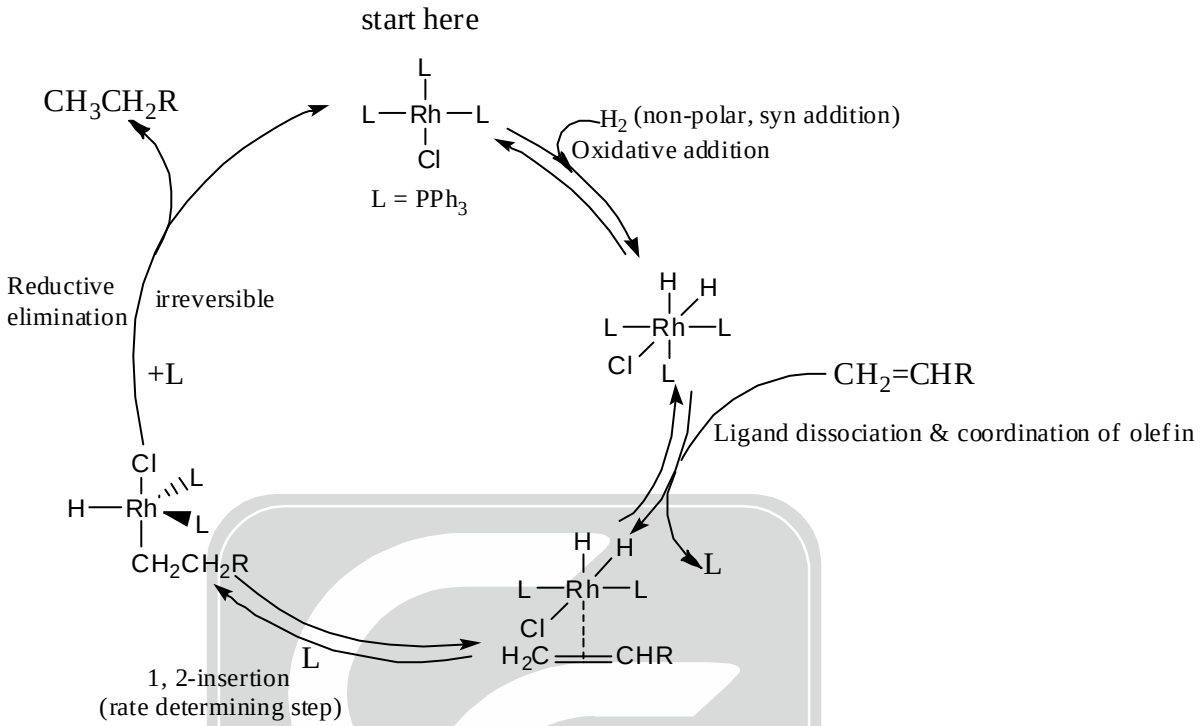
$$RCH = CH_2 \xrightarrow{H_2/Ni} RCH_2–CH_3$$

**IUPAC NAME :** $(PPh_3)_3RhCl$ Chloro-tris (triphenylphosphine) Rhodium (I)

In this catalysis the solvated catalyst undergo oxidative addition of Hydrogen then an alkene co-ordinate to the metal and react with a coordinated Hydrogen ligand to form a alkyl group and lastly reductive elimination takes place to regenerate the catalyst.

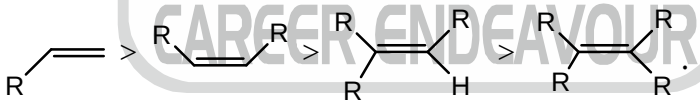
$$RCH=CH_2 + H_2 \xrightarrow{W.C.} RCH_2–CH_3$$

It involves three reversible steps : oxidative addition of $H_2$, substitution by the olefin of $PPh_3$ that is labilized in trans position vs. the hydride ligand (trans effect). The last step, reductive elimination of the alkyl and hydride ligands to yield the alkane, is totally irreversible.




Ethylene gives a very slow reaction with wilkinson catalyst because a stable Rhodium ethylene complex will form which does not undergo oxidative addition. Ethylene takes the site created by $PPh_3$ dissociation in the I$^{st}$ step. This type of catalytic cycle is called as Tolmann Catalytic Cycle.

**Note :** Hydrogenation via W.C. is sterically sensitive, as bulkyness increases rate of hydrogenation decreases as



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## OLEFINE HYDROFORMYLATION (OXO PROCESS)

It is discovered by Otto Roelene 1938.

Hydroformylation is the addition of Hydrogen and formyl group across a double bond.

$$R\,CH = CH_2 + H_2 + CO \xrightarrow[\text{octacarbonyl dicobalt}]{Co_2(CO)_8} \underset{\text{n-product}}{R\,CH_2 - CH_2 - CHO} + \underset{\text{Iso-product}}{R - \underset{\displaystyle CHO}{\underset{|}{CH}} - CH_3}$$

Net effect is

(1) increase one carbon atom

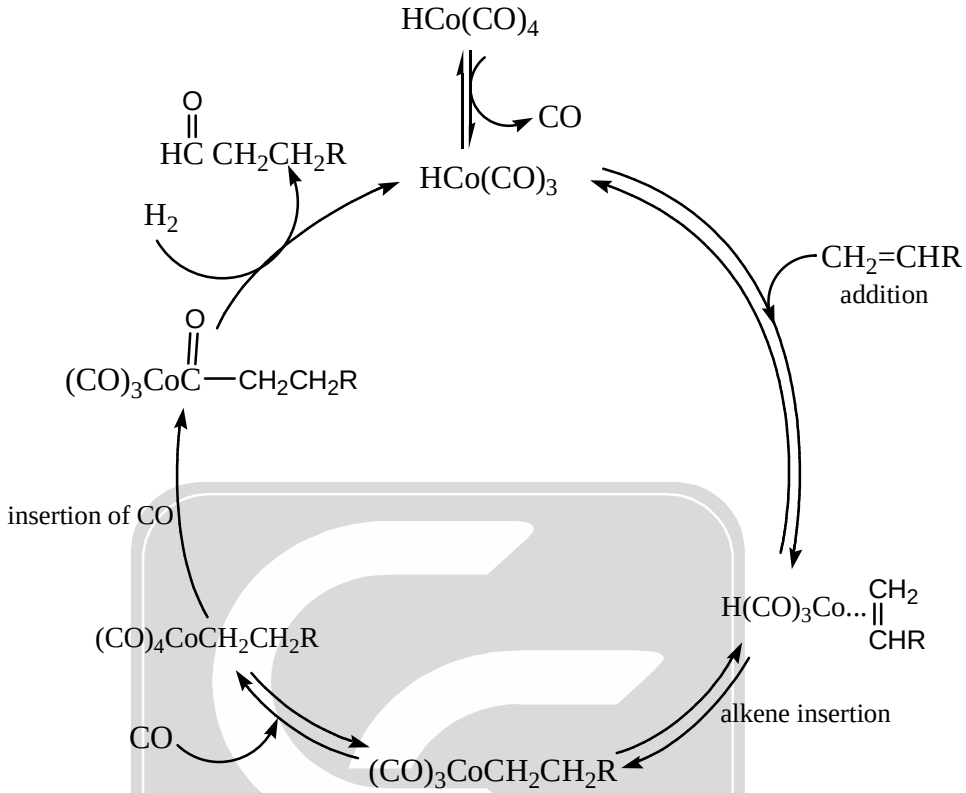
(2) introduction of oxygen into the product.

(3) n- product is more desirable because it is easily biodegradable when convert into detergents.

$$\text{eg. : } CH_3\,CH_2\,CH_2\,CHO \xrightarrow{H_2} \underset{\substack{\text{n- Butanol}\\ \text{Plasticiser}}}{CH_3—CH_2—CH_2—CH_2—OH}$$

**Catalyst :** $\underset{(18\,e^-)}{Co_2(CO)_8} \xrightarrow{H_2} \underset{(18\,e^-)}{HCo(CO)_4} \xrightarrow{-CO} \underset{(16\,e^-)}{HCo(CO)_3}$

n- Butanol is used to make plasticiser which make plastics soft and flexible.




**WACKER PROCESS**: This is the catalytic addition of oxygen to alkene.

$$CH_2 = CH_2 + \tfrac{1}{2}\,O_2 \xrightarrow[H_2O]{[PdCl_4]^{2-},\,[CuCl_4]^{2-}} CH_3 - CHO$$

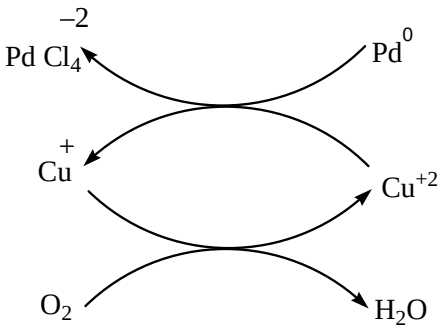
**Catalyst :** Pd (+2); $[Pd\,Cl_4]^{-2}$ or $[PdCl_2]$

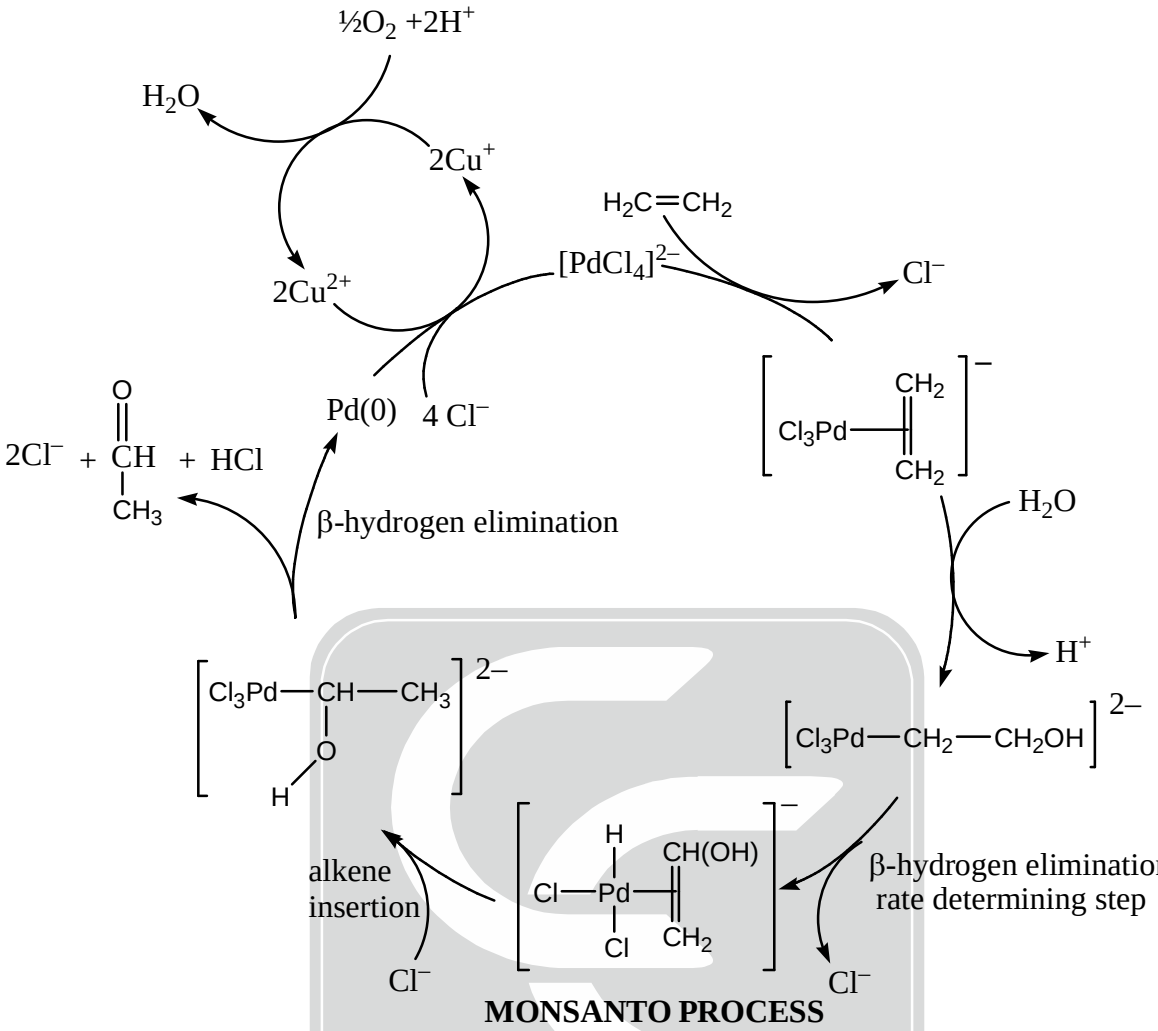
**Co-catalyst :** $Cu(+2)$; $CuCl_2$ or $[CuCl_4]^{2-}$

$$CH_2 = CH_2 + H_2O + PdCl_4^{-2} \longrightarrow CH_3CHO + Pd(\text{deactivated}) + 2HCl + 2Cl^-$$

$$Pd + 2\,CuCl_2 + 2Cl^- \longrightarrow PdCl_4^{-2}\,(\text{activated}) + 2CuCl(\text{deactivated})$$

$$2\,CuCl + \tfrac{1}{2}\,O_2 + 2HCl \longrightarrow 2\,CuCl_2\,(\text{activate}) + H_2O$$



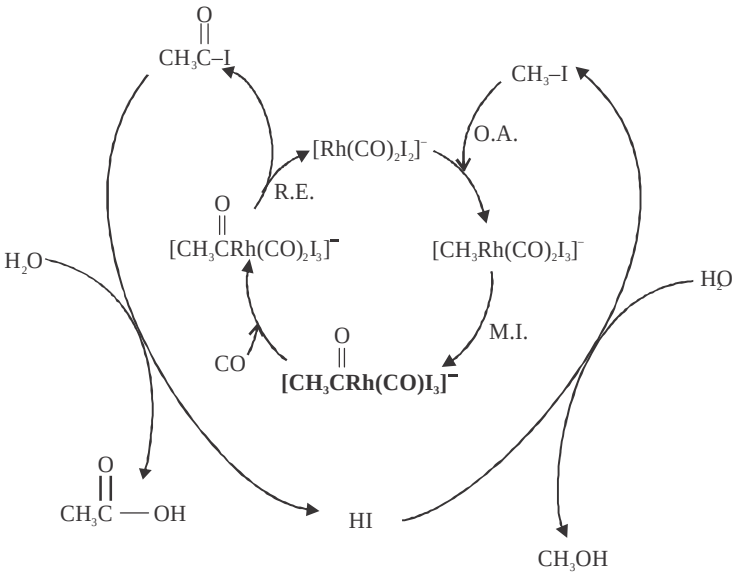



**MONSANTO PROCESS**

(1) The Monsanto process is an important method for the manufacture of acetic acid by catalytic carbonylation of methanol.

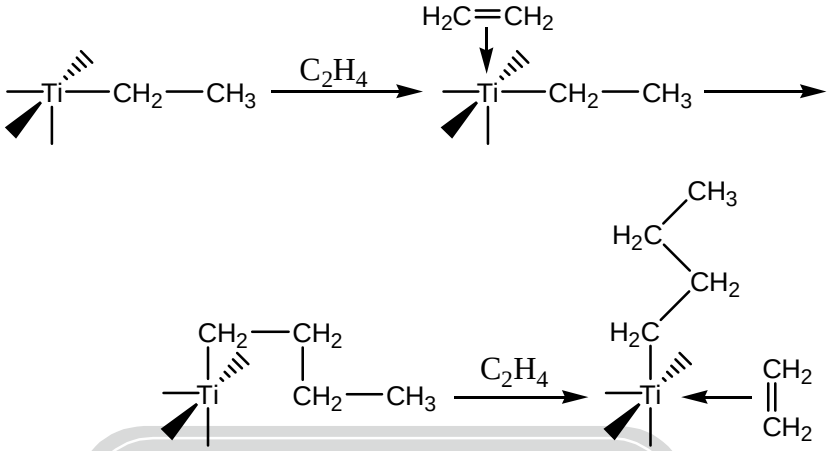
(2) This process operates at a pressure of 30–60 atm and a temperature of 150–200 °C and gives a selectivity greater than 99%.

$$CH_3OH + CO \xrightarrow{[Rh(CO)_2I_2]^-} CH_3COOH$$



## ZIEGLER-NATTA CATALYSIS

The Ziegler-Natta catalyst is heterogeneous and it is made by treating titanium tetrachloride with triethylaluminium to form a fibrous material that is partially alkylated ($Et_2AlCl$ is used as a cocatalyst). The titanium does not have a filled coordination sphere and acts like a Lewis acid, accepting ethylene or propylene as another ligand. The reaction is thought to proceed like Wilkinson's catalyst.

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## SOLVED PROBLEMS

1. In a homogeneous catalytic reaction 1 mole of substrate and 1 micromole (1μ mole) of catalyst produces 1 milimole of product in 10 seconds. What is TOF?

**Soln..** R = 1 M  Catalyst = $10^{-6}$ M  Time = 10 second

Product = $10^{-3}$ M = 0.001M

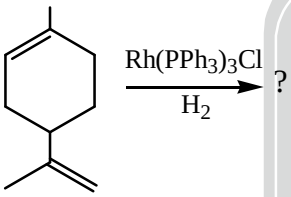
$$TON = \frac{1}{10^{-6}} \times 10^{-3}$$

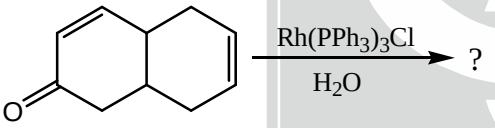
$$TON = 10^3$$

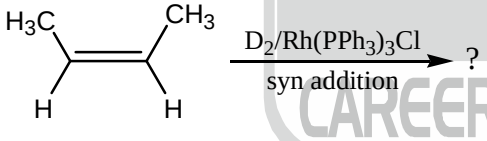
$$TOF = \frac{TON}{Time} = \frac{10^3}{10} = 10^2 \ sec^{-1}$$

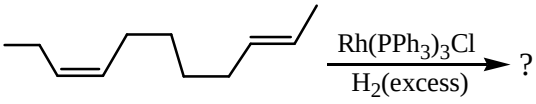
$$\boxed{TOF = 10^2 \text{ second}^{-1}}$$

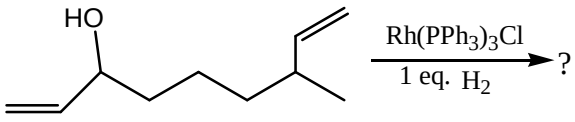
2. Find the product of following reactions

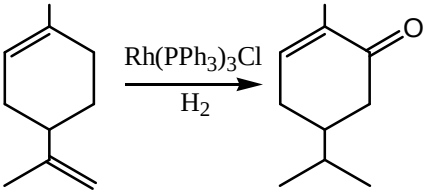
(i) 

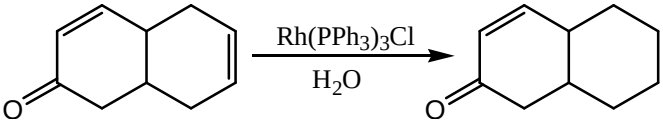

(ii) 

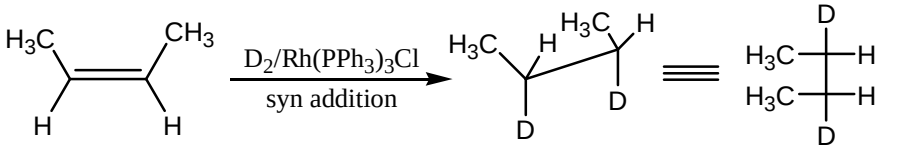

(iii) 


(iv) 

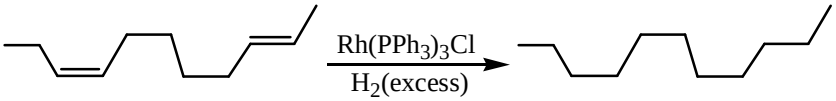

(v) 

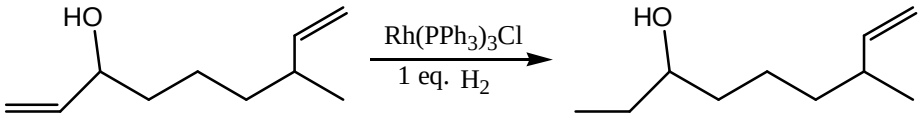

**Soln.** (i) 


(ii) 

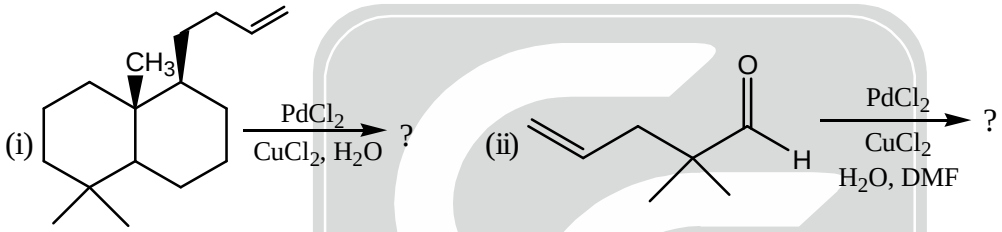
(iii) 


Meso product

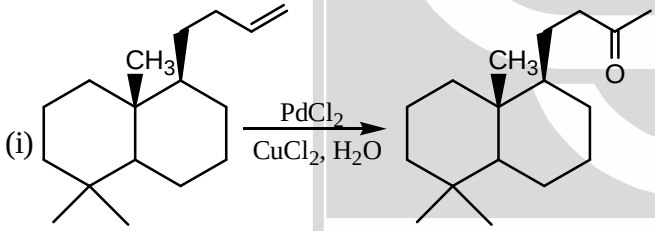
(iv) 

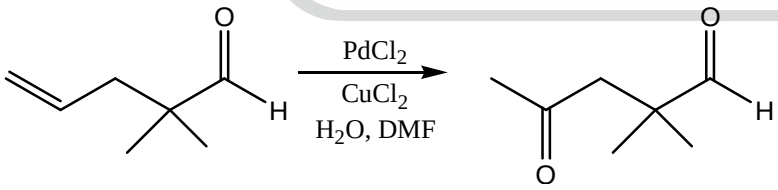

(v) 


3. Find out the product in the Wacker process?




**Soln.**

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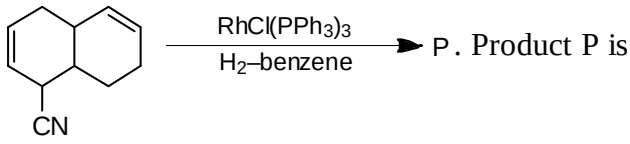
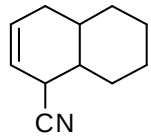
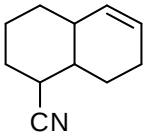
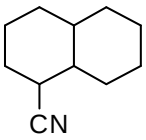
## UNSOLVED PROBLEMS

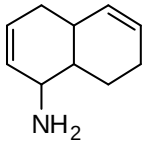
1. 

. Product P is

(a) 


(b) 


(c) 


(d) 


**Ans.** (b)

2. The co-catalyst used in the Wacker process is

(a) $Cu_2I_2$ (b) CuI (c) CuO (d) $Cu_2Cl_2$

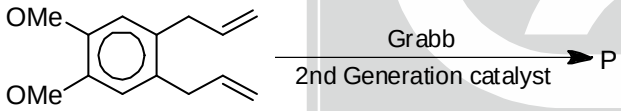
**Ans.** (b)

3. $CH_3 - CH = CH_2 \xrightarrow[H_2O\ /\ DMF]{[PdCl_4]^{-}\ /\ CuI} P$. Product P is

(a) $CH_3CH_2CHO$ (b) $CH_3COCH_3$

(c) $CH_3CH_2CH_2CHO$ (d) $CH_3COCH_2CH_3$

**Ans.** (b)

4. 


Product P contain number of double bond is

(a) 3 (b) 4 (c) 5 (d) 6

**Ans.** (b)

5. The Pre-catalyst used in the hydroformylation of alkene is

(a) $CO_2(CO)_6$ (b) $[HCO(CO)_4]$ (c) $[HCO(CO)_3]$ (d) $[HCO(CO)_5]$

**Ans.** (b)

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