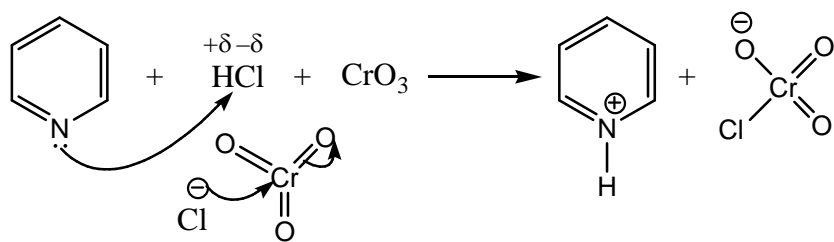
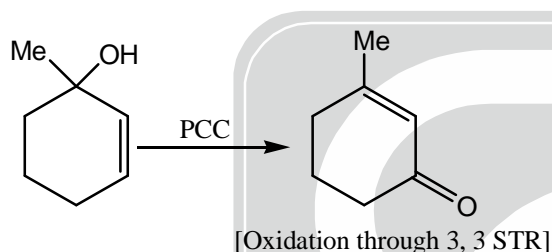
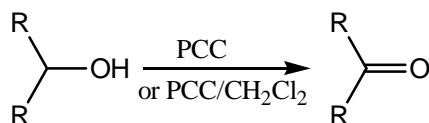
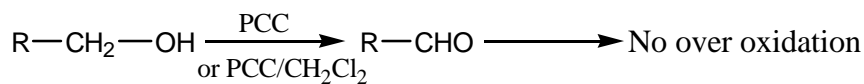


### 3.7. Pyridinium Chloro Chromate (PCC):

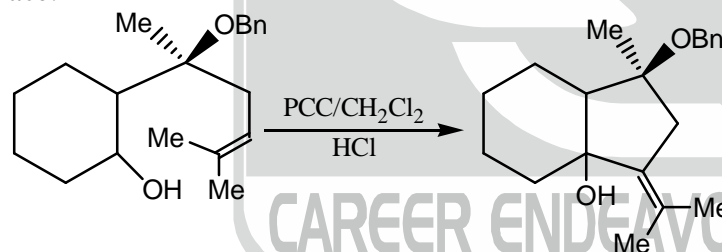


PCC is a very important oxidising reagent which will give controlled oxidation in the case of primary alcohol. It does not give over oxidation during the oxidation of primary alcohol.

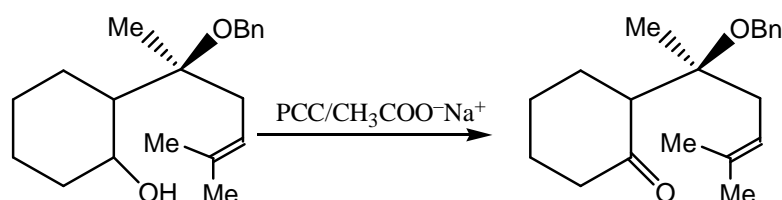
It does not oxidise *t*-alcohol. But in the case of 3°-allylic alcohol having at least one  $\gamma$ -hydrogen through [3, 3] sigma tropic rearrangement. PCC will give oxidation with the migration of double bond.



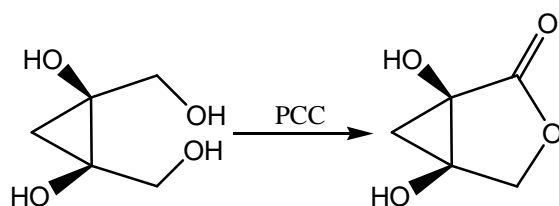
☞ Acid catalysed oxidation of alcohol with double bond present in the compound, by PCC cyclization takes place.

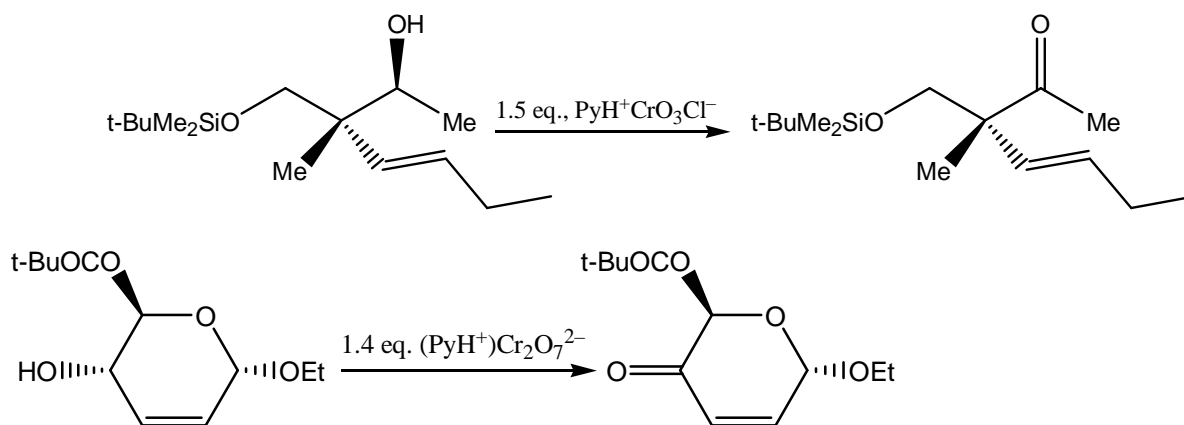
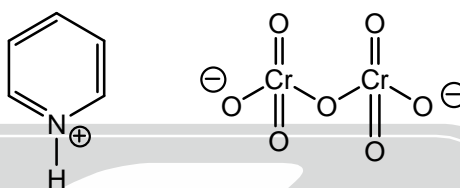


☞ If PCC reagent is used with buffer solution such as  $\text{NH}_4\text{Cl}/\text{H}_2\text{O}$  (Buffer),  $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ ,  $\text{NaHSO}_3/\text{H}_2\text{O}$ ,  $(\text{CH}_3\text{COO}^- \text{Na}^+)$  (Buffer) then no acid catalysed cyclization or no any acid catalysed reaction will occur.



In 1, 4 diols or 1.5 diols PCC reagent is used then it will give controlled oxidation and form cyclic ester or lactone ring.

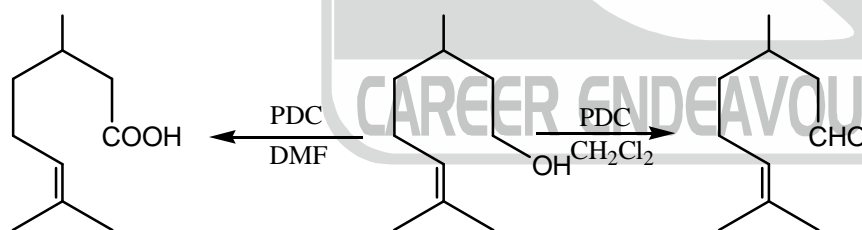


**Example:****3.8. Pyridinium Dichromate (PDC):**

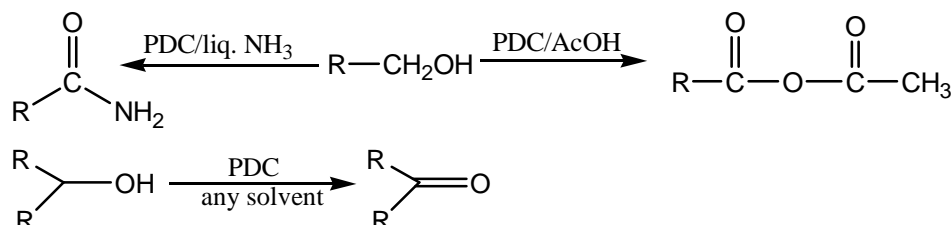
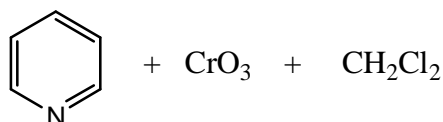
PDC is soluble in H<sub>2</sub>O, DMF and DMSO but sparingly soluble in CH<sub>2</sub>Cl<sub>2</sub> or CHCl<sub>3</sub>. The reagent is less acidic than PCC. Hence, oxidation in CH<sub>2</sub>Cl<sub>2</sub> can be carried out under nearly neutral conditions. This permits the conversion of primary alcohol containing acid sensitive group into the corresponding aldehyde or ketones.



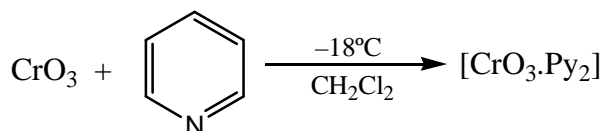
In DMF solution however PDC oxidizes non-conjugated primary alcohol to corresponding carboxylic acid and in CH<sub>2</sub>Cl<sub>2</sub> to give aldehyde.



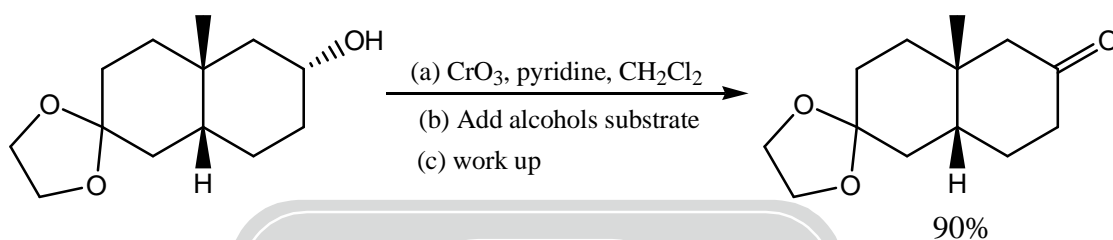
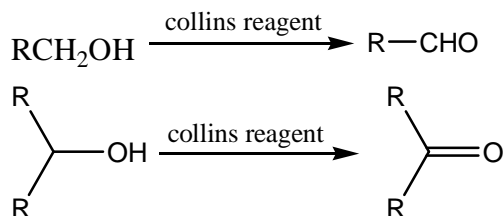
In carboxylic acid solvent, PDC oxidizes primary alcohol to anhydrides and in the presence of liq. NH<sub>3</sub> convert into amide.

**3.9. Collins-Ratcliffe Reagent:**

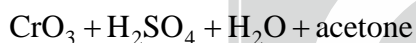
Collins reagent is a mild reagent for the oxidation of alcohols that contain acid sensitive groups. Collins reagent prepared by adding  $\text{CrO}_3$  to a mixture of pyridine- $\text{CH}_2\text{Cl}_2$ .



Collins reagent primary alcohol oxidised to aldehyde and secondary alcohol to ketone respectively.

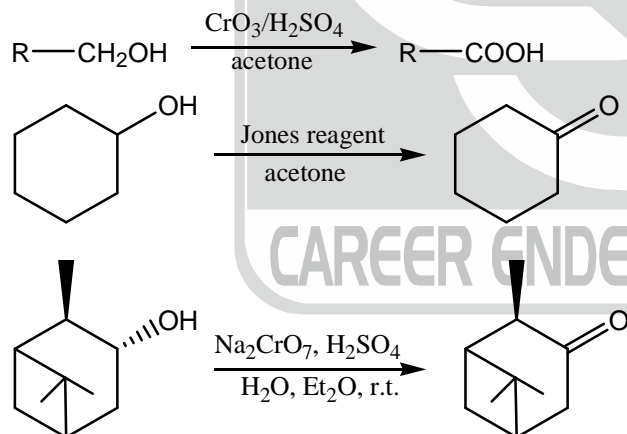


### 3.10. Jones reagent:

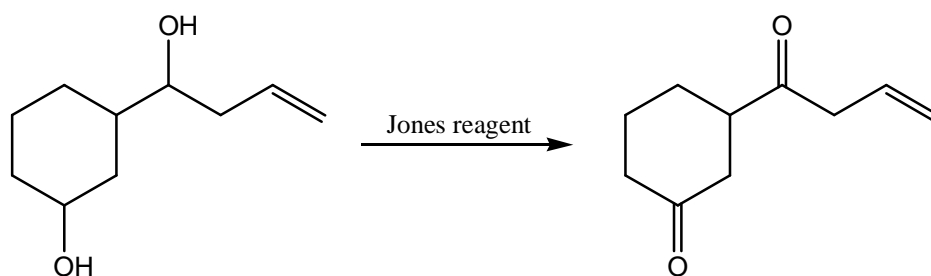


Or,  $\text{Na}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \text{acetone}$

Oxidation of primary alcohols with Jones Reagent may result in the conversion of the aldehyde initially formed to the corresponding carboxylic acids.

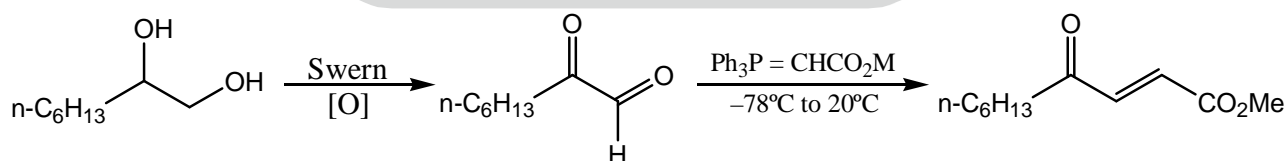
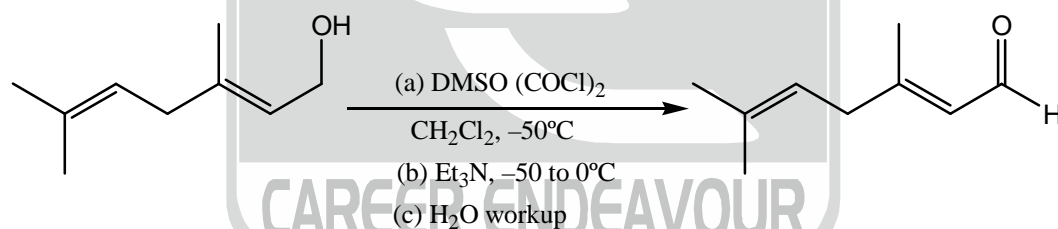
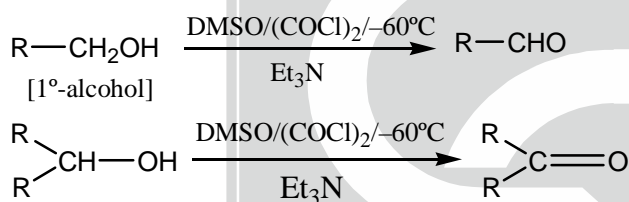
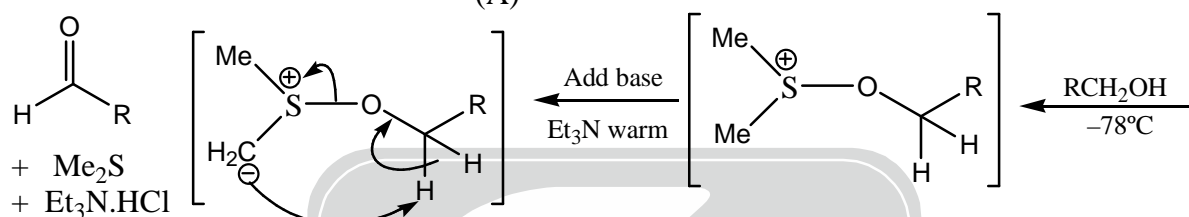
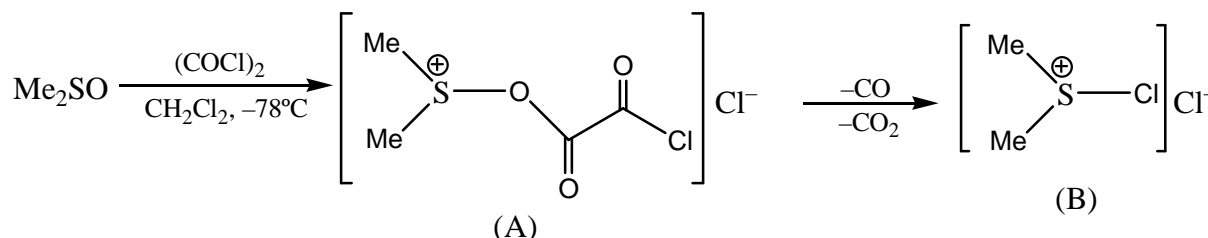



Jones reagent used for the oxidation of primary and secondary alcohols and does not effect any group present in the compound.

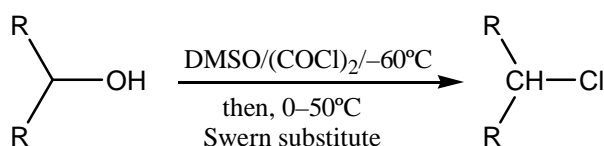
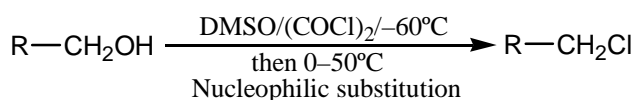


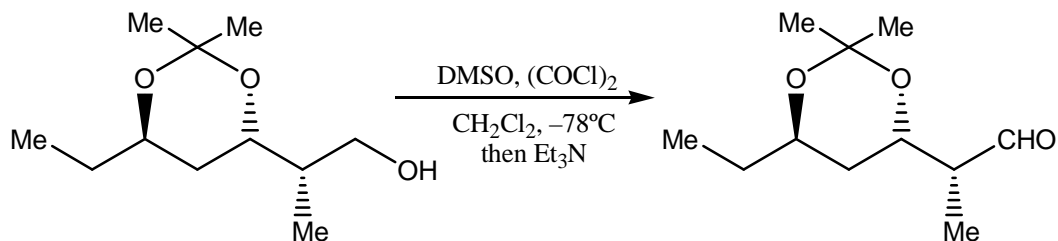
**3.11. Swern Oxidation:**

Activation of dimethylsulfoxide (DMSO) by oxalyl chloride produce intermediate (A) that decompose rapidly at  $-78^\circ\text{C}$  to furnish chlorodimethylsulfonium chloride (B) along with CO and  $\text{CO}_2$ . Reaction of (B) with  $\text{RCH}_2\text{OH}$  (or  $\text{R}_2\text{CHOH}$ ) leads to intermediate (C), which upon addition of  $\text{Et}_3\text{N}$  and warming afford the corresponding carbonyl compound  $\text{Me}_2\text{S}$ ,  $\text{Et}_3\text{NH}^+\text{Cl}^-$

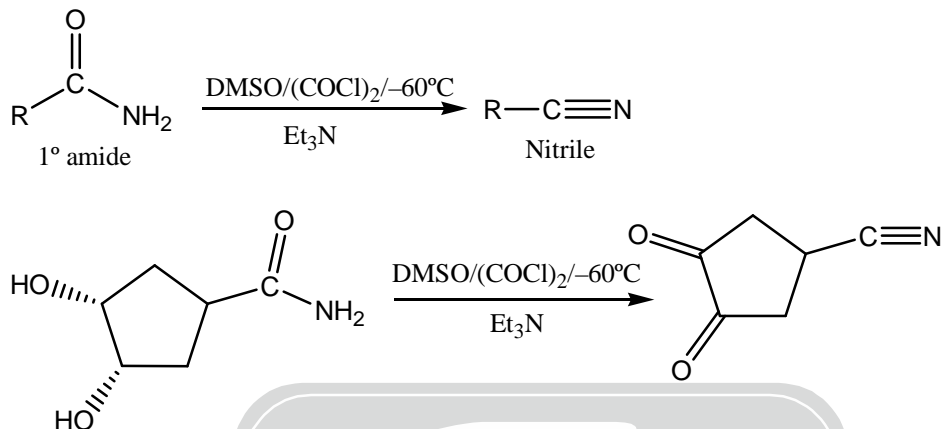


 If base is not present then  $\text{Nu}^-$  substitution will occur at the end of reaction and swern substitution will occur.

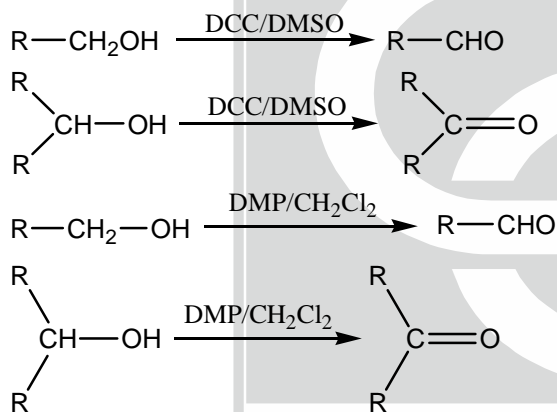




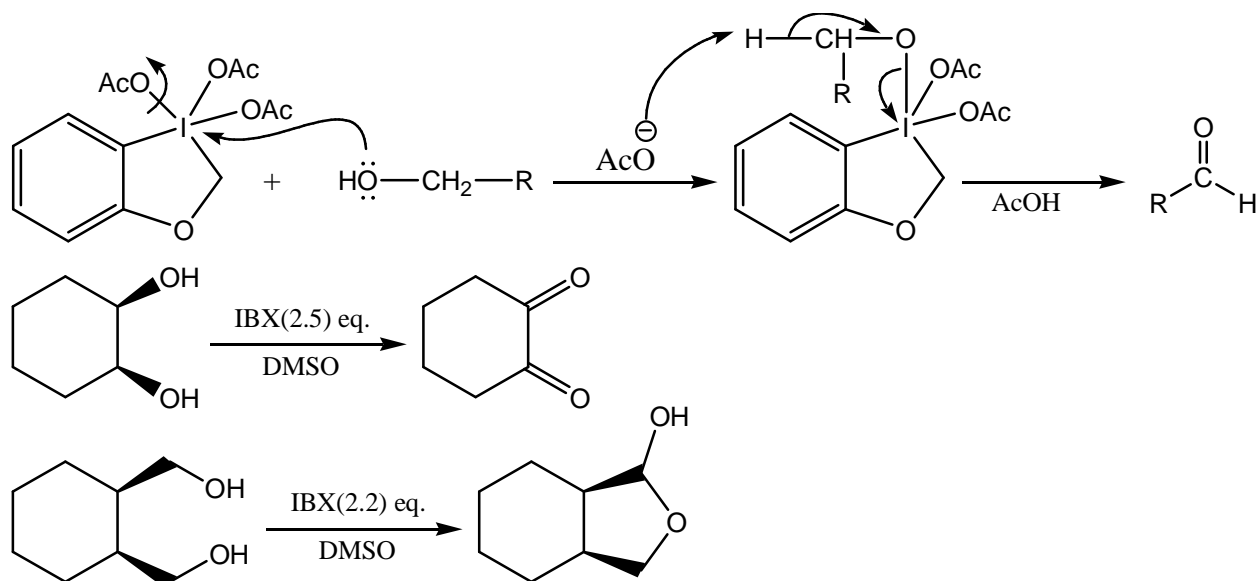
☞ Swern reagent can also be used for the oxidation of primary amide substrate into nitrile or cyanide.

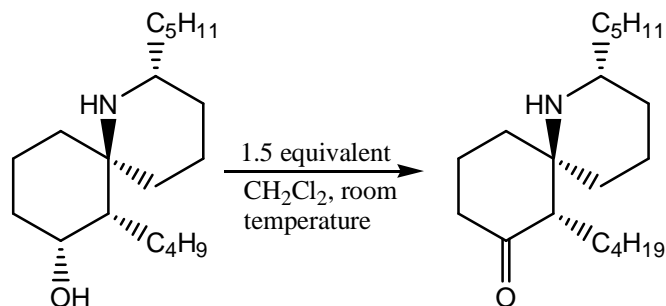
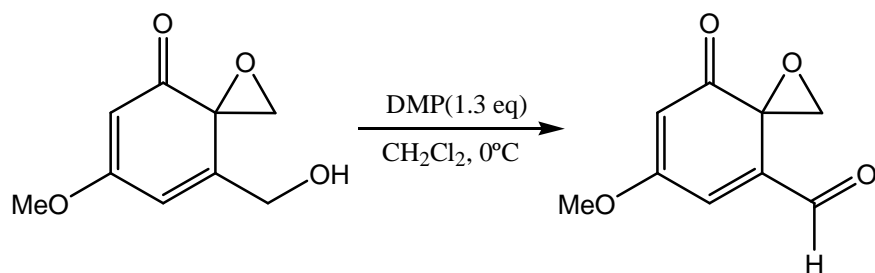


### 3.12. Moffatt oxidation: [DCC/DMSO]

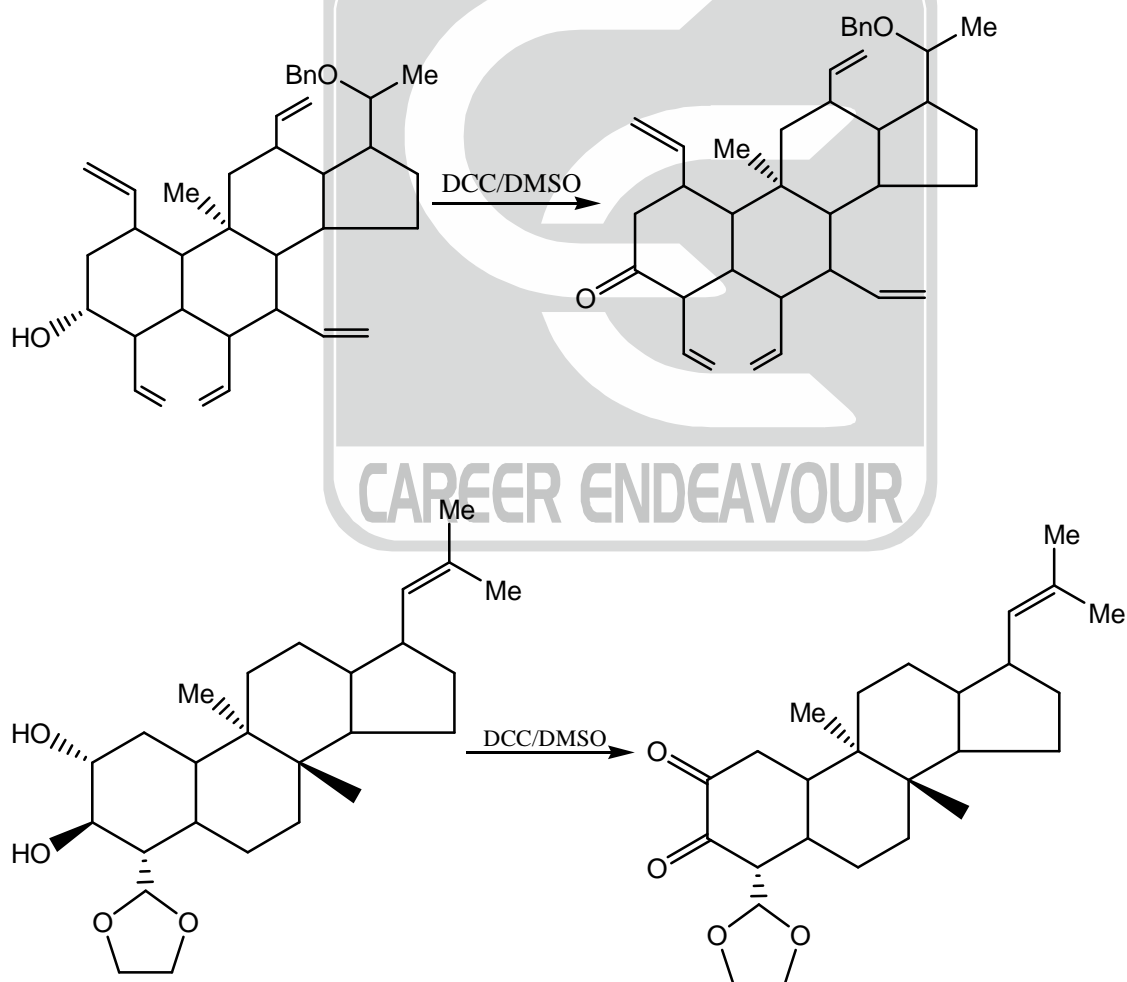


**Mechanism:**



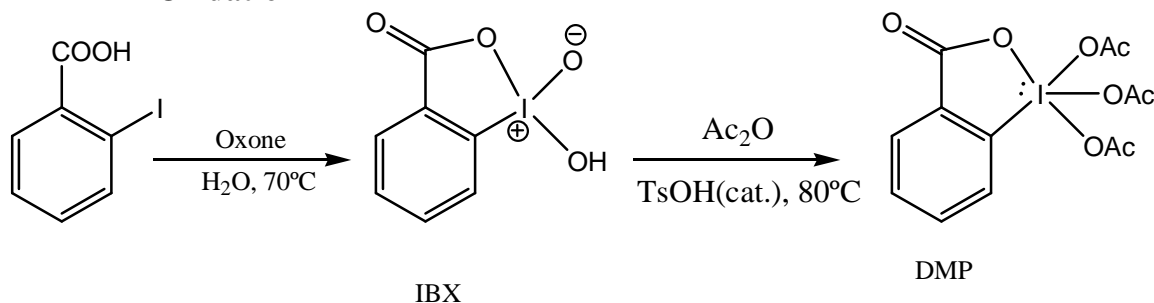


When dicyclohexyl carbodiimide reagent is mixed with DMSO oxidizing reagent then it is specially used for the oxidation of steroidal alcohol.

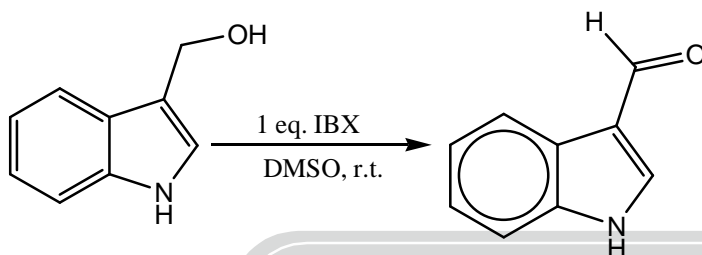


### 3.13. Dess-Martin Periodinane:

#### DMP-Oxidation



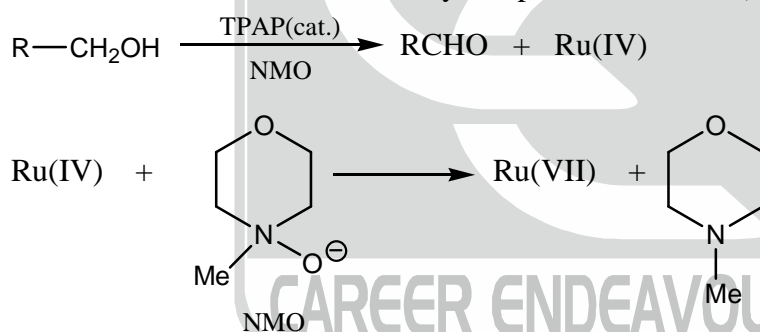
It is a hypervalent iodine based oxidising reagent which is highly specific for the oxidation of primary and secondary alcohol and does not effect any sensitive functional group.



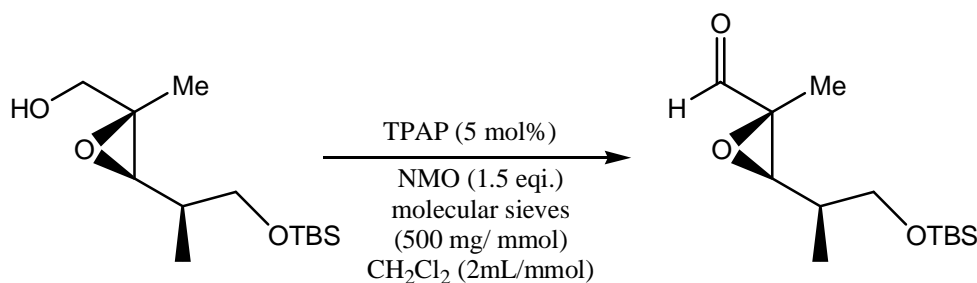
### 3.14. Tetrapropylammonium Perruthenate (TPAP):

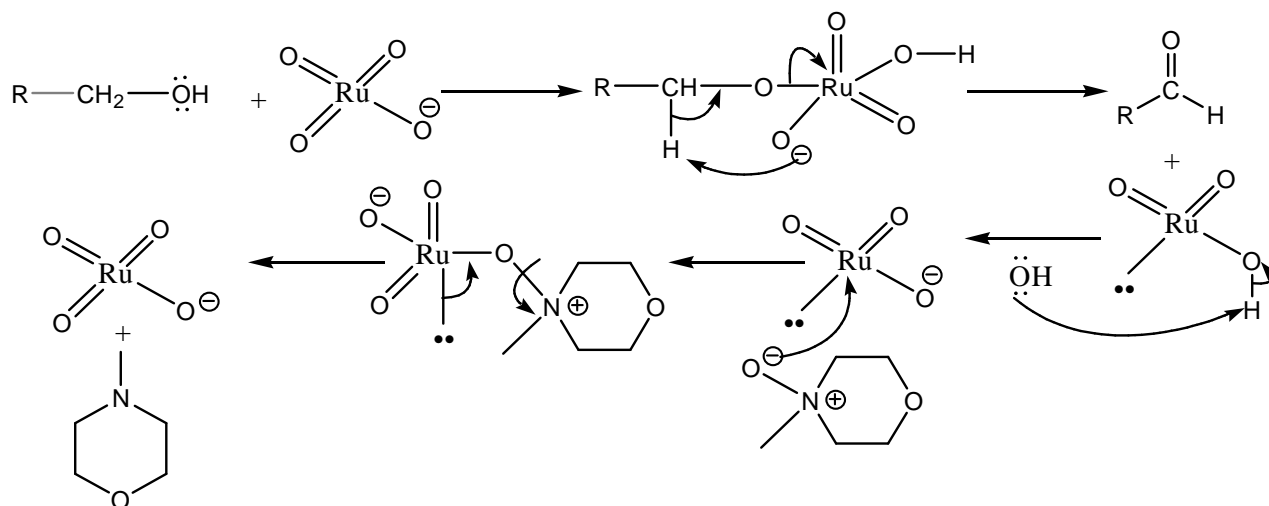
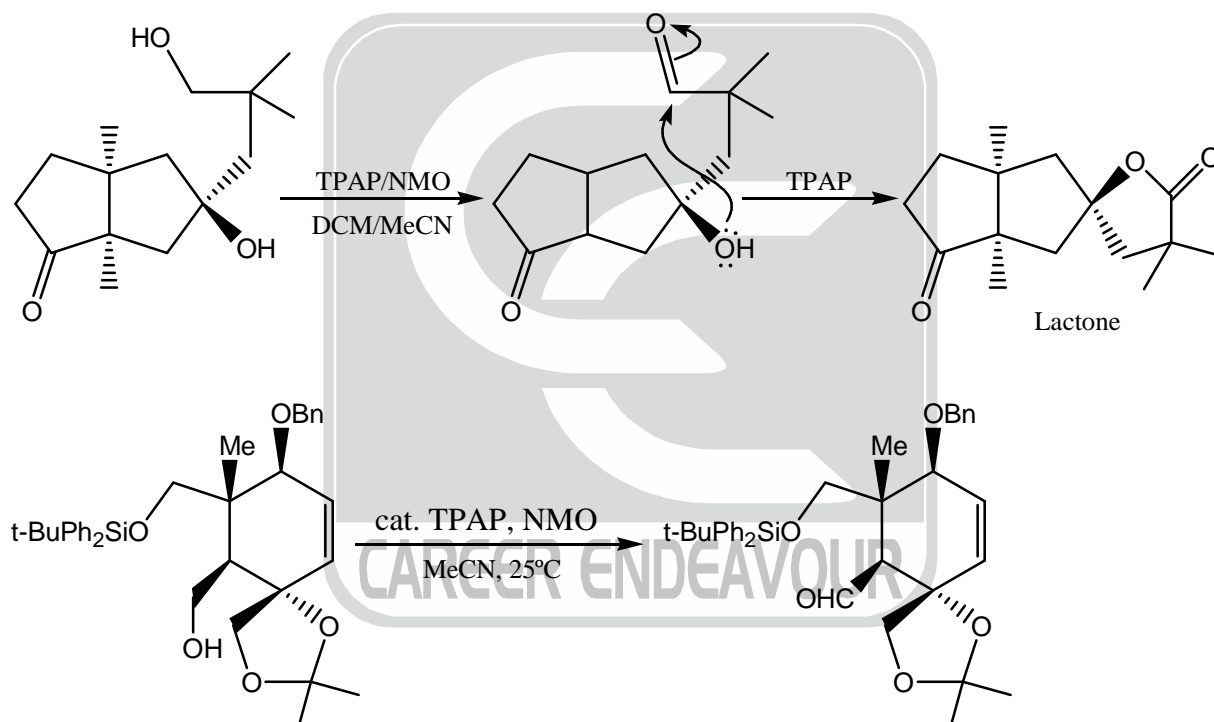
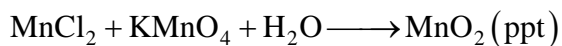


TPAP is an air stable oxidant for primary and secondary alcohols. It is used in catalytic amount in the presence of a Co-oxidant such as N-methylmorpholine-N-oxide (NMO).

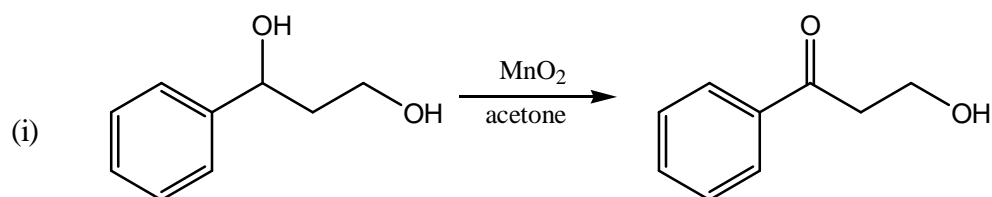


TPAP tolerates a wide variety of functional groups including double bonds, enolates, halides epoxides, esters, and lactones. Protecting groups such as MEM, trityl, silyl and benzyl ethers, THP and acetals are not effected.

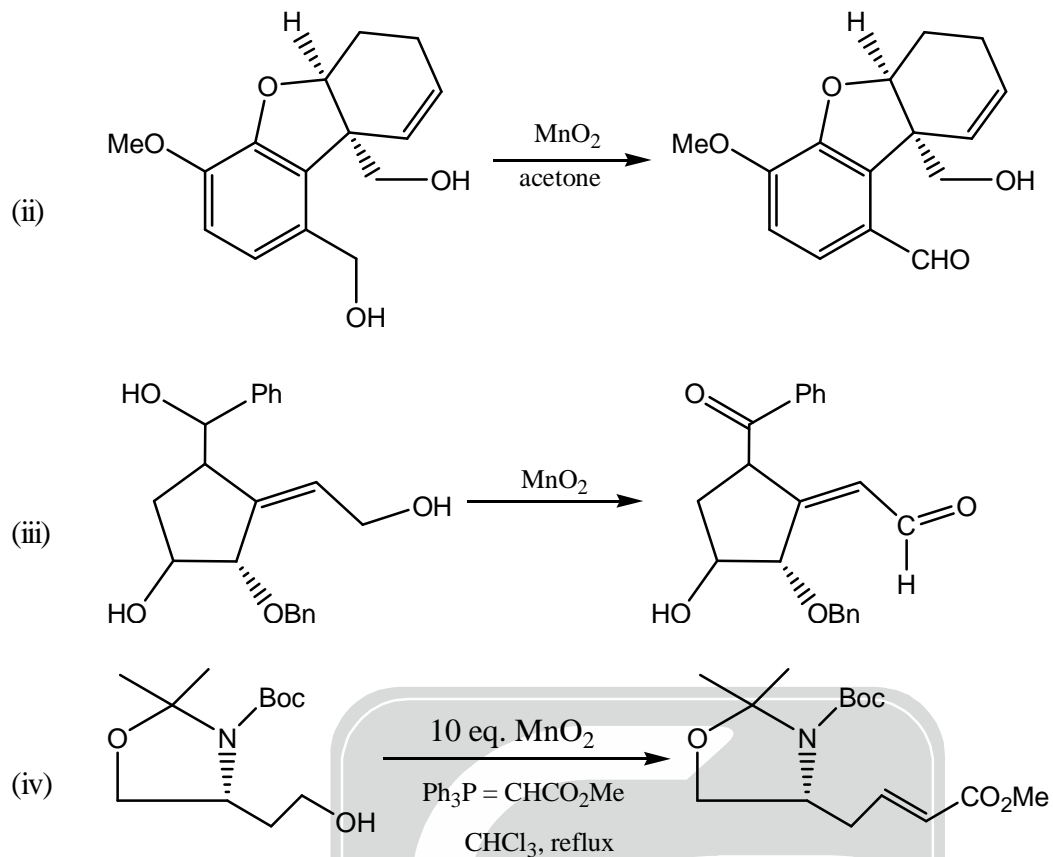


**Mechanism:****Examples:****3.15. Activated Manganese Dioxide(MnO<sub>2</sub>):**

MnO<sub>2</sub> is highly chemoselective oxidant-Allylic, Benzylic, and propargylic alcohols are oxidised faster than saturated alcohols. The oxidation takes place under mild condition in H<sub>2</sub>O, acetone and CHCl<sub>3</sub>.

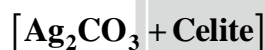






$\text{KMnO}_4$  (absorbed on a solid support) and useful alternative to  $\text{MnO}_2$  in the oxidation of allylic or benzylic alcohol.

### 3.16. Silver carbonate on Celite 'Fetizon's reagent':

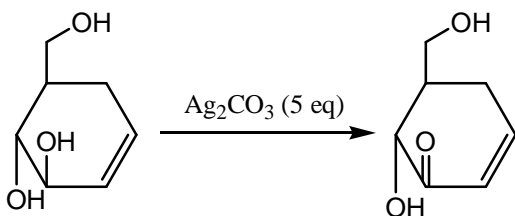
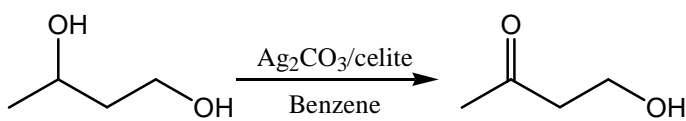


Fetizon's reagent will give chemoselective oxidation of secondary alcohols in the presence of primary alcohols.

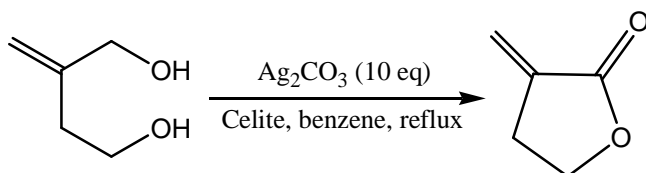


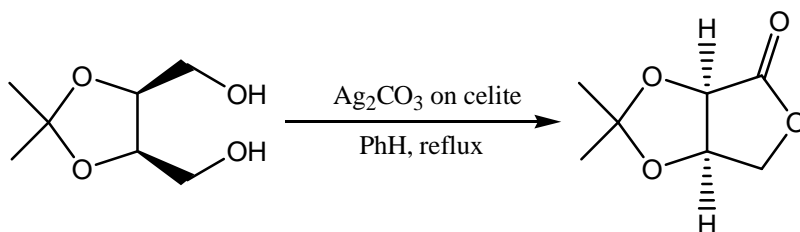
Ease of alcohol oxidation:

Allylic  $\approx$  Benzylic  $-\text{OH} \gg 2^\circ-\text{OH} > 1^\circ-\text{OH}$  (less hindered)  $> 1^\circ-\text{OH}$

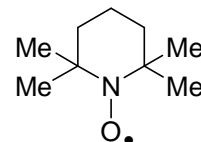


Oxidation of 1, 4 or 1, 5 alcohols to gives 5 or 6 membered lactones respectively.

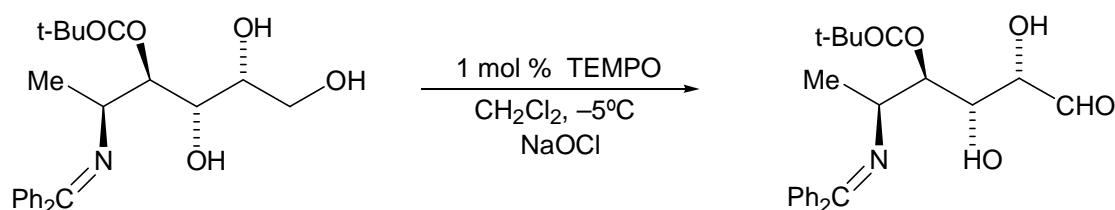
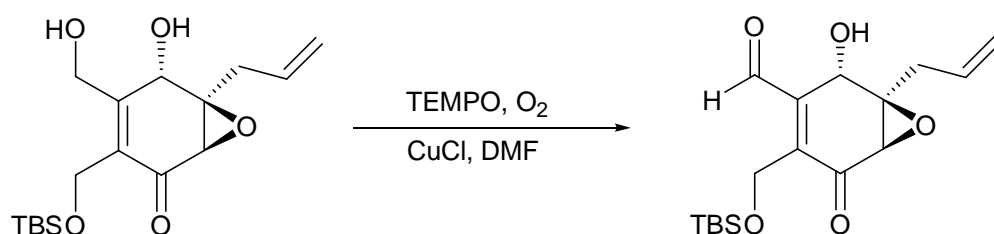
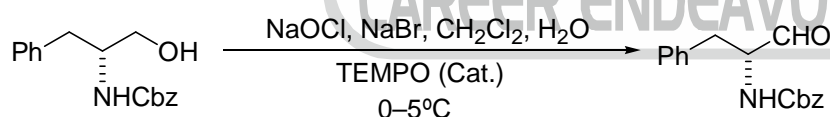
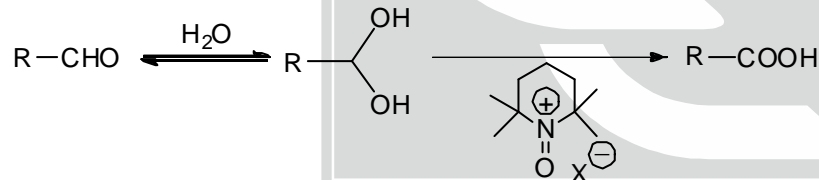
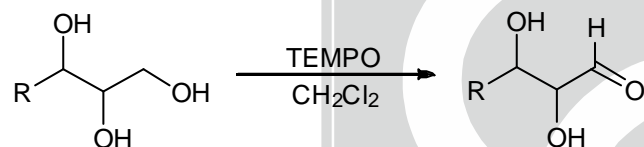
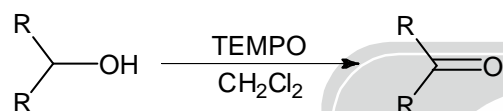
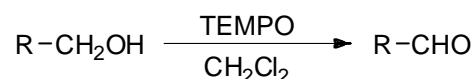




### 3.17. 2, 2, 6, 6 Tetramethyl 1-Piperidinyloxy (TEMPO)

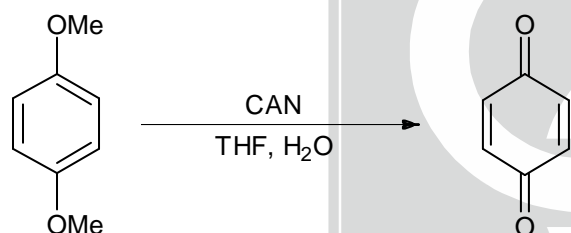
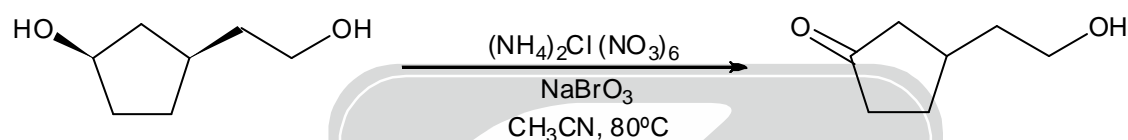
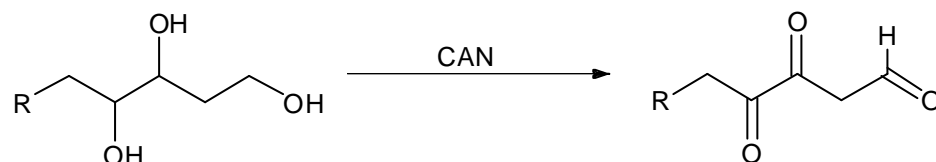
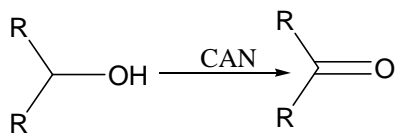
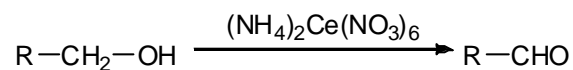


TEMPO is a commercially available nitroxyl radical-containing reagent that catalyses the oxidation of primary and secondary alcohol. TEMPO primary alcohols are oxidised faster than secondary.



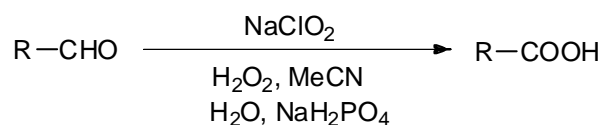
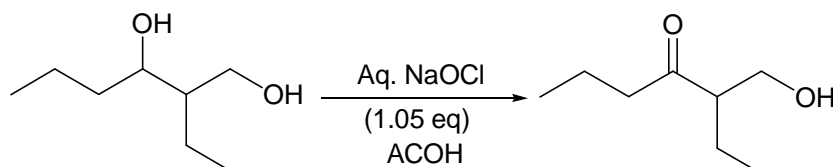
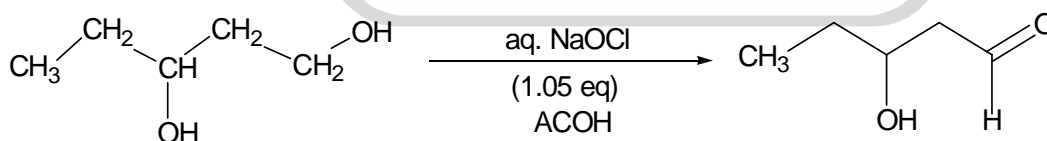
### 3.18. Ceric Ammonium Nitrate (CAN):

Chemoselective oxidation of a secondary OH group in the presence of a primary OH group has been achieved with  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ ,  $\text{NaBrO}_3$ . CAN does not affect any double bond present in the group.



### 3.19. Sodium Hypochlorite (NaOCl):

Chemoselective oxidation of a secondary OH group in the presence of a primary OH group is possible with  $\text{NaOCl}$  in aqueous acetic acid.



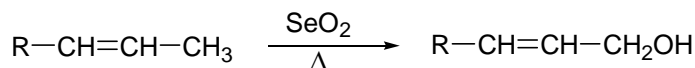
### 3.20. Selenium Dioxide:

$\text{SeO}_2$ ,  $\text{SeO}_2 / \text{ACOH}$ ,  $\text{SeO}_2 / \text{H}_2\text{O}$ ,  $\text{SeO}_2 / \text{ACOH-H}_2\text{O}$

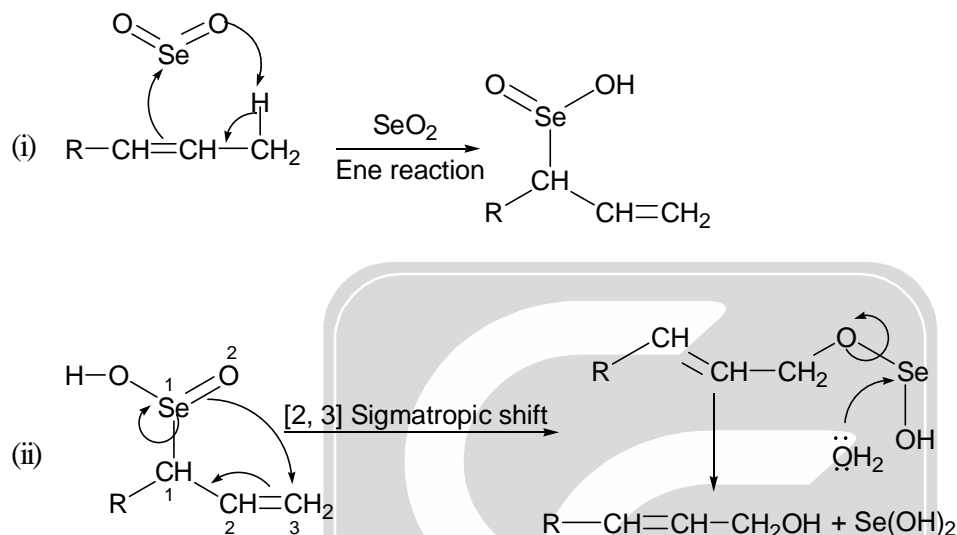
$\text{SeO}_2$  is specially used for the oxidation of allylic carbon, having at least one allylic hydrogen into allylic alcohol. Mechanism based on following pericyclic reaction.

(i) Ene reaction

(ii) [2, 3] Sigmatropic shift

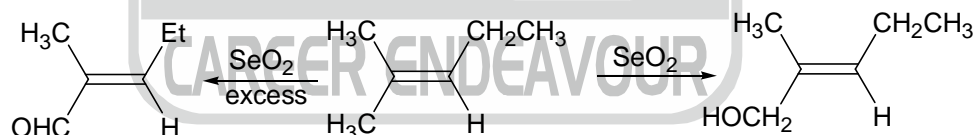


**Mechanism:**

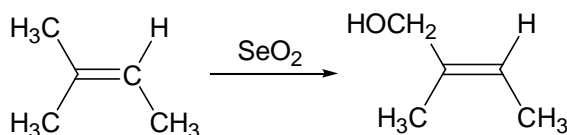


Selenium dioxide exhibits a useful stereochemistry in reaction with trisubstituted gem-dimethyl alkenes. The products are always predominantly the E-allylic alcohols.

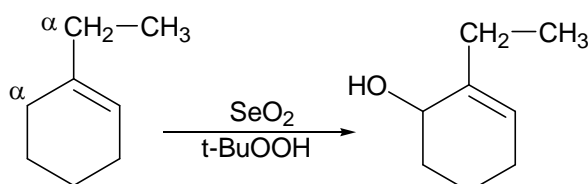
In this reaction the methyl group *trans* to main chain will react rather than the *cis*, thus only one (E) isomer is formed.



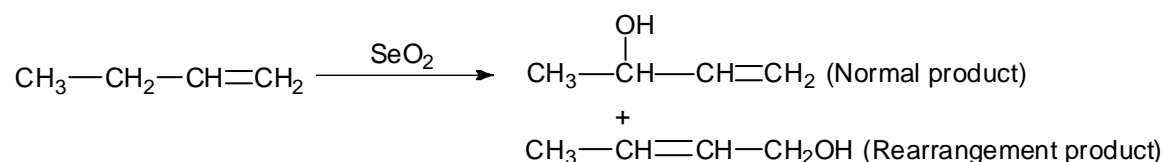
Tri-substituted alkenes are oxidised selectively at the more substituted end of C-C double bond including that the ene reaction is electrophilic in character. Tri-substituted alkenes are preferentially oxidised at one of the allylic group at the di-substituted carbon.



When double bond is in the ring, oxidation whenever possible occurs with in the ring and again  $\alpha$  to more substituted end of the double bond. (Indicate that ene reaction electrophilic in nature).

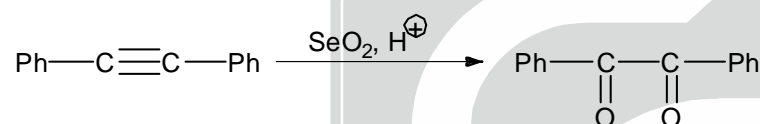
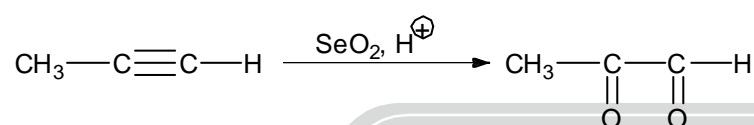
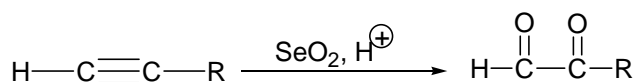
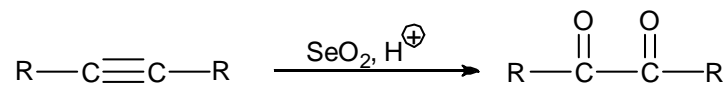


In the case of terminal alkenes, allylic rearrangement takes place

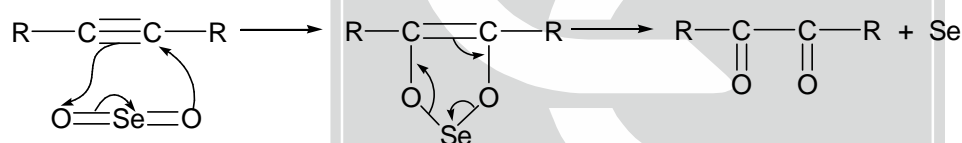


### Oxidation of alkynes:

SeO<sub>2</sub> with small amount of conc. H<sub>2</sub>SO<sub>4</sub>

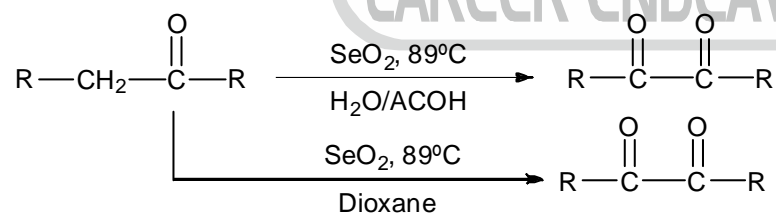


### Mechanism:



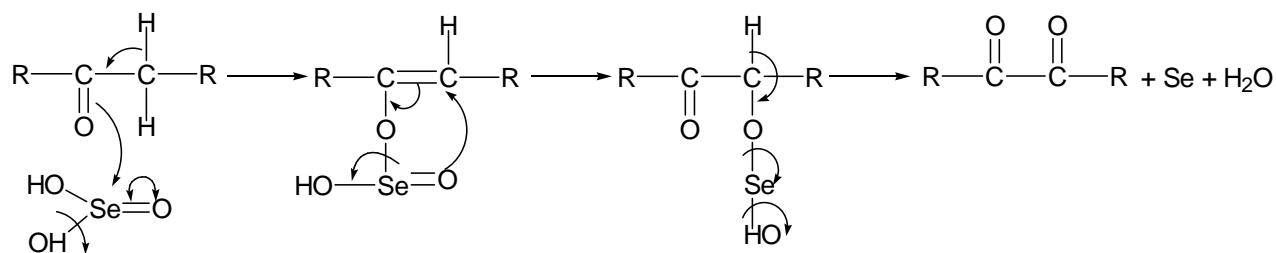
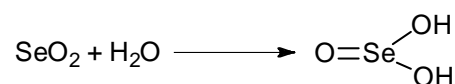
### Oxidation of Carbonyl Compound:

SeO<sub>2</sub> oxidises α-carbon of carbonyl group. This oxidation can only be possible if carbon has at least two hydrogen.

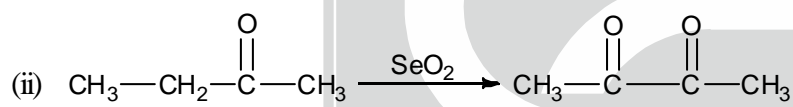
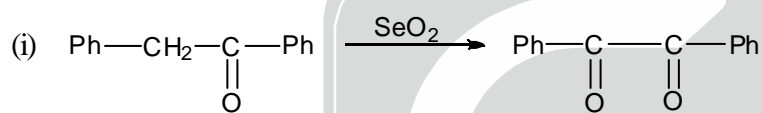
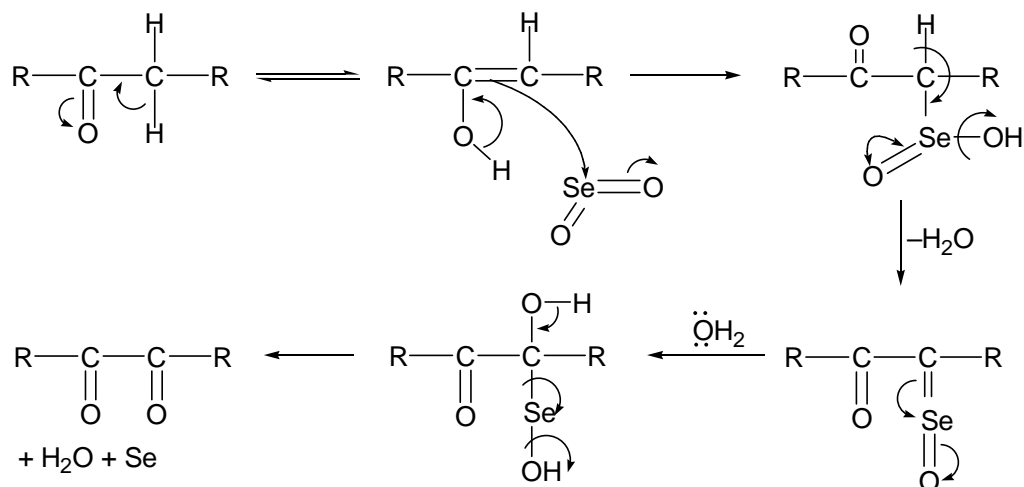


### Mechanism:

If water present



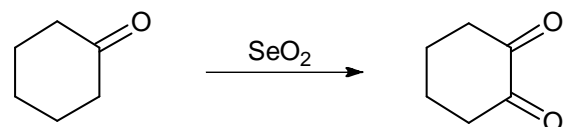
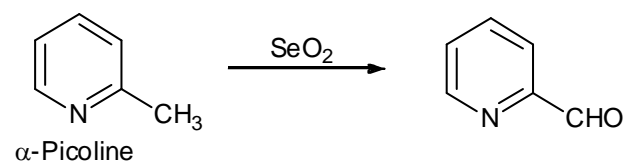
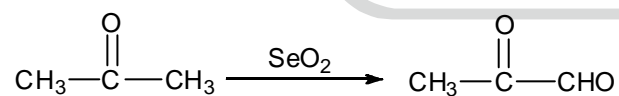
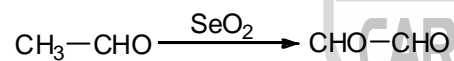
In absence of water:

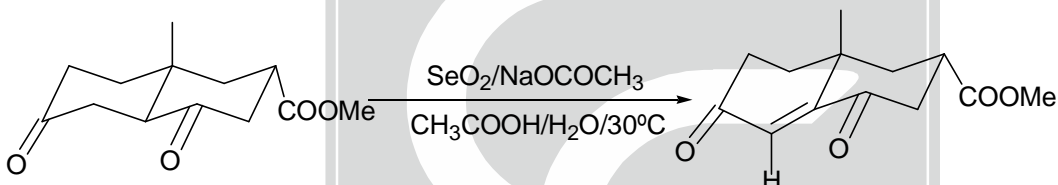
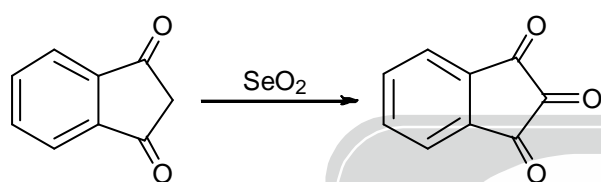
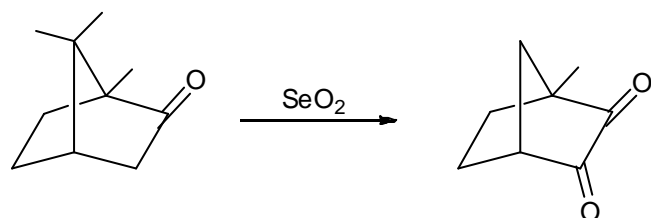
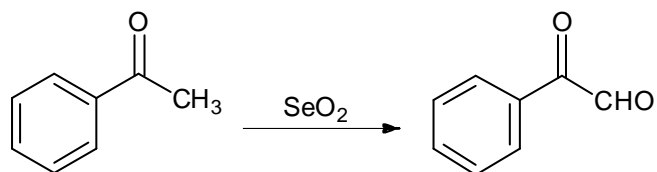
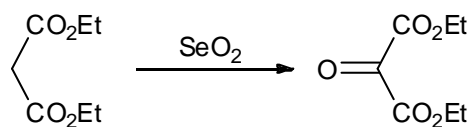


**Note:** Reactivity order

$[\text{CH}_2 > \text{CH}_3 > \text{CH}]$

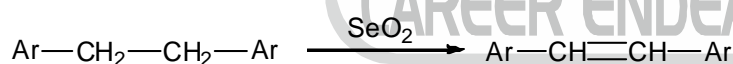
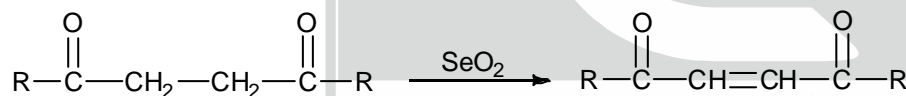
Reactivity of  $\text{CH}_2$  group is more than  $\text{CH}_3$  group. Because enolization of methylene group occurs more readily than methyl group.



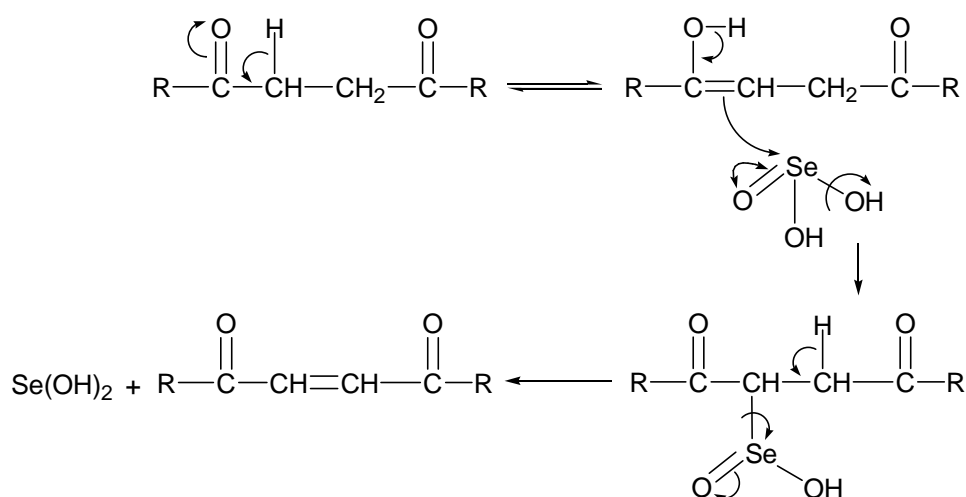


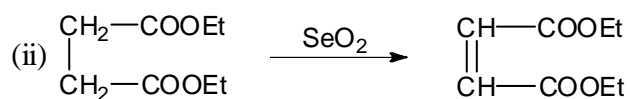
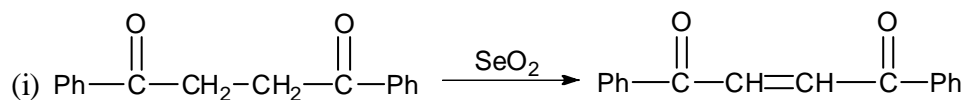
### Dehydrogenation:

SeO<sub>2</sub> used to dehydrogenate 1, 4-dicarbonyl compound and 1, 2 diarylethane.

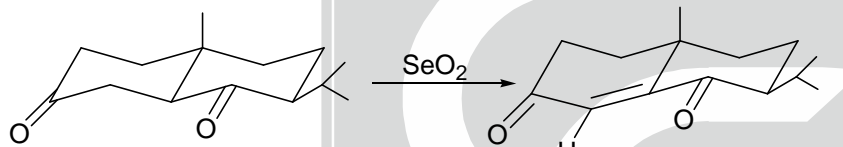
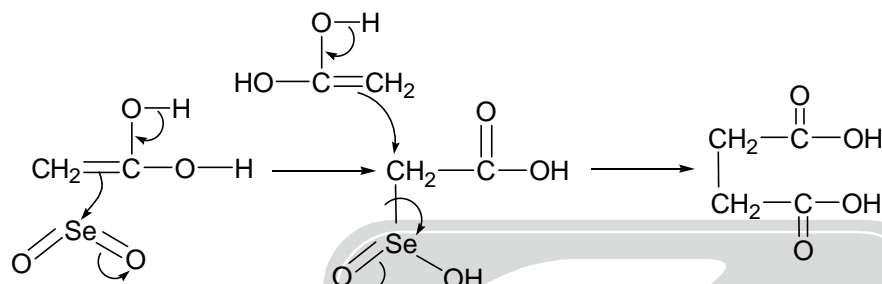
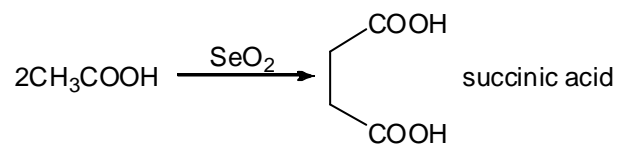


### Mechanism:

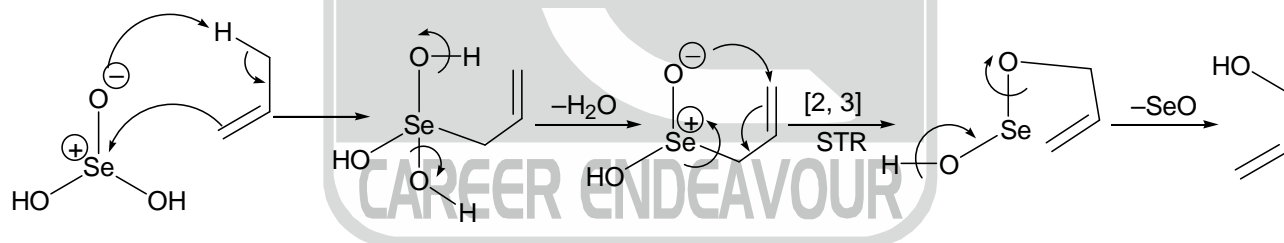




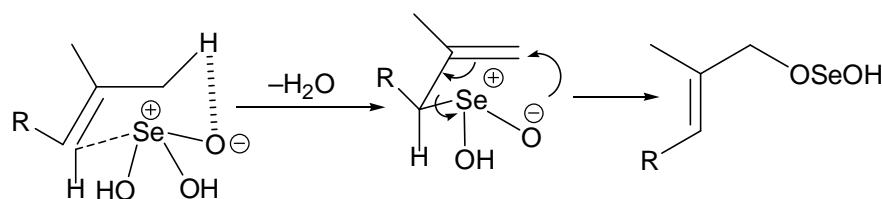
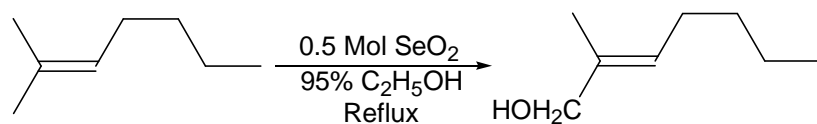
Acetic acid undergoes dehydration to give succinic acid



**Hydrated form of  $\text{SeO}_2$ :**

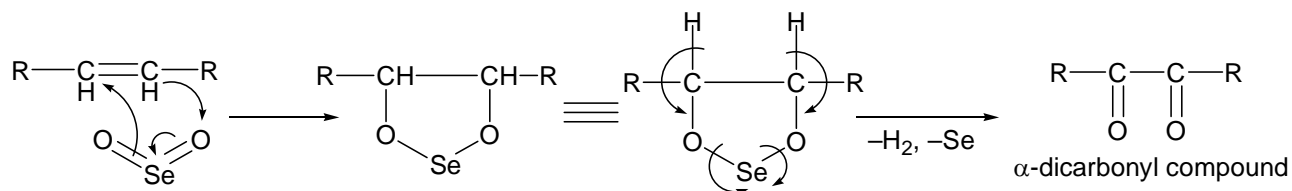


**\* E-Selectivity:**

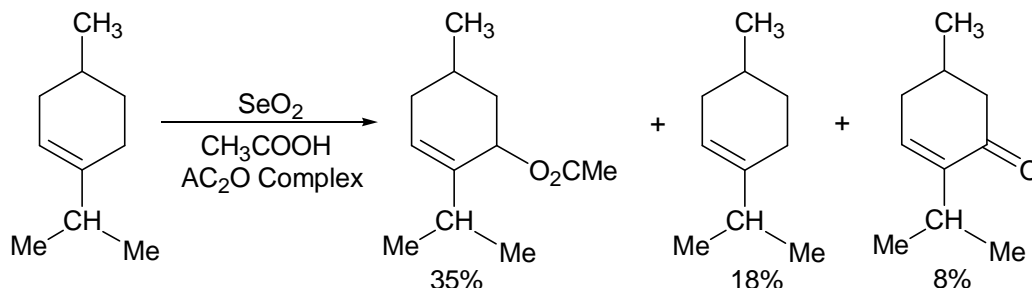


“R must be equatorial” in the above transition state. When there is no allylic hydrogen in the substrate then oxidation of only C = C occurs as shown below

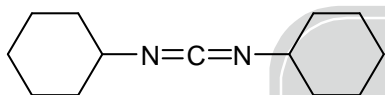




\* The alcohols that are initial product can be further oxidized to carbonyl group by  $\text{SeO}_2$ , and the conjugated carbonyl compound is usually isolated. If the alcohol is the desired product, the oxidation can be run in acetic acid solvent in which acetic ester are formed.

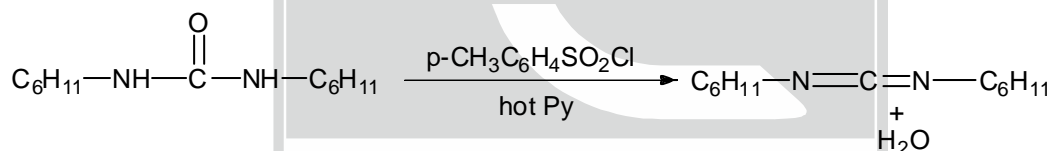


### 3.21. N, N-Dicyclohexylcarbodiimide (DCC):

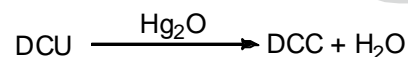


**Introduction:** DCC is a powerful dehydrating agent are stored under anhydrous conditions. It is commercially available as a waxy low melting solid, which melt at  $34\text{--}35^\circ\text{C}$ .

**Preparation:** (i) By oxidation of DCU with p-toluenesulfonyl chloride in hot pyridine.

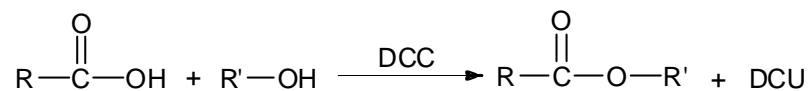


(ii) By heating DCU with mercuric oxide ( $\text{Hg}_2\text{O}$ )

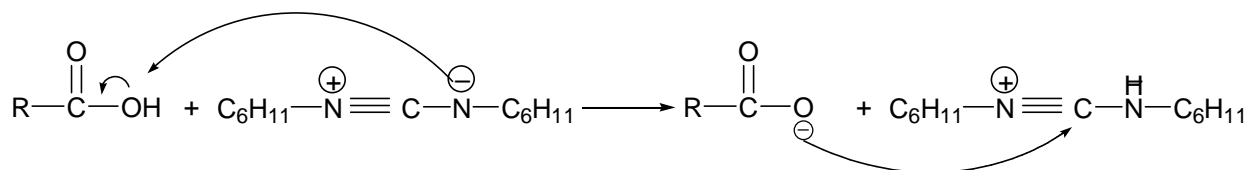


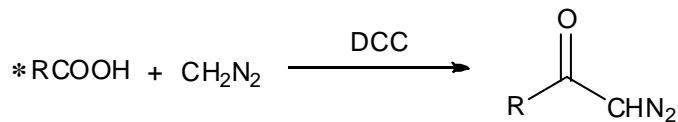
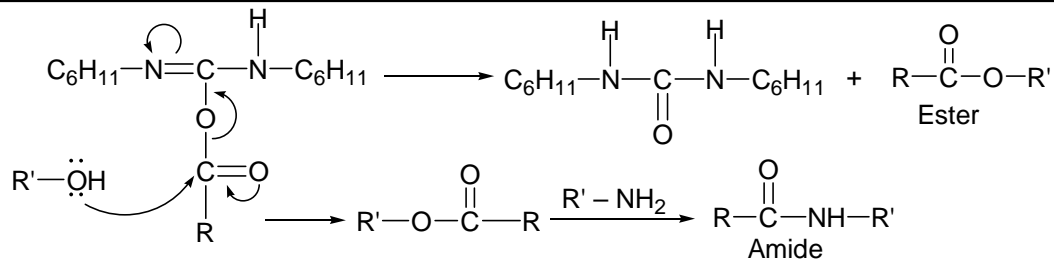
**Applications:**

(A) Synthesis of esters and amides:



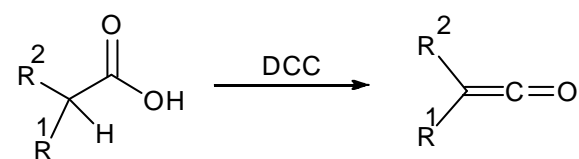
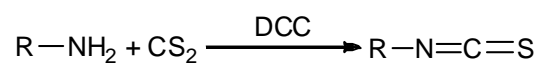
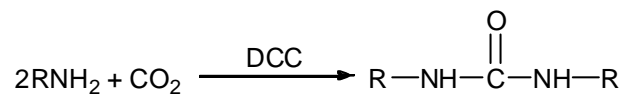
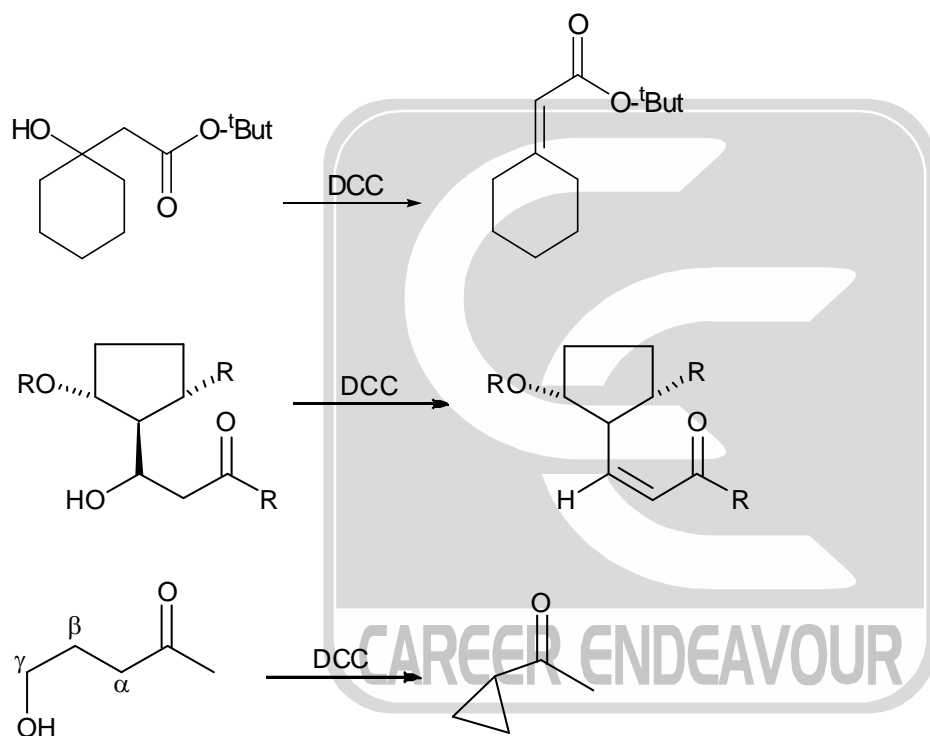
**Mechanism:**

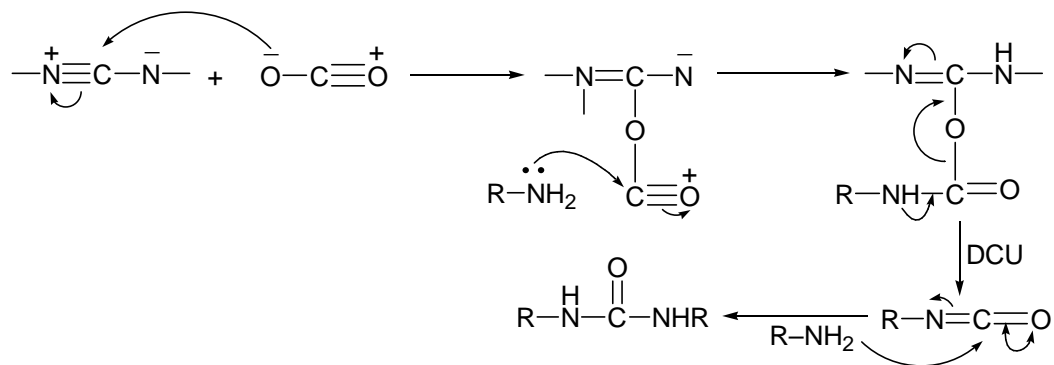
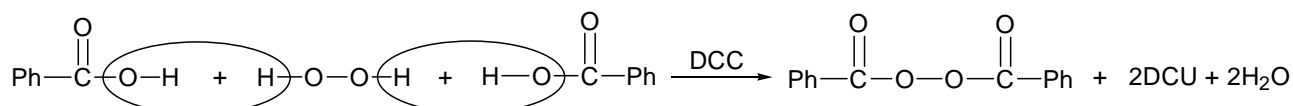
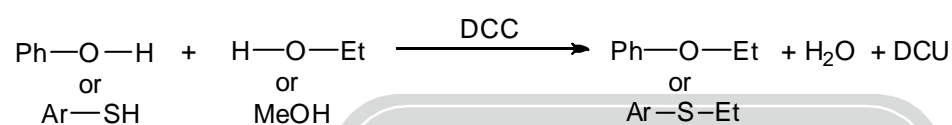
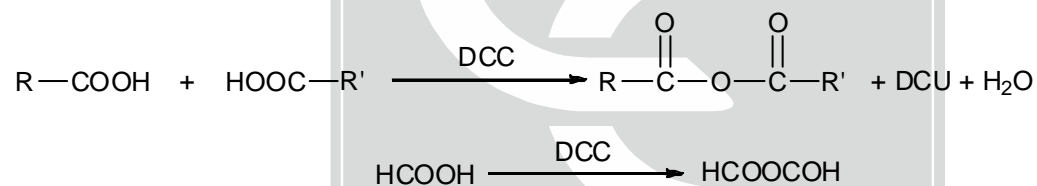
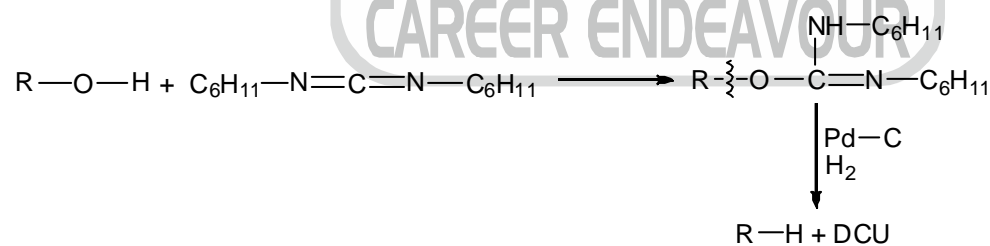




### (B) Miscellaneous Functions :

$\beta$ -hydroxyester/ $\beta$ -hydroxy ketons on reaction with DCC undergoes dehydration as shown in the following examples.



**(C) Synthesis of organic diacyl peroxide****(D) Ether Formation****(E) Formation of Anhydrides****(F) Dehydroxylation of alcohols:****(G) Formation of Lactone and Lactams:**