SeO_2 ; Oxidising agent

Selenium dioxide is still regarded as most reliable and predictable for oxidation of alkenes. It is produced by burning selenium in oxygen in presence of traces of nitrogen peroxide which acts as catalyst

$$Se + O_2 \longrightarrow SeO_2$$ purified by sublimation

It is also prepared by oxidation of selenium with nitric acid followed by dehydration of selenious acid

$$Se + \underset{\text{conc}}{HNO_3} \xrightarrow{\text{exothermic reaction}} \underset{\text{powder}}{} \xrightarrow{-NO_2} O=Se(OH)_2 \xrightarrow[-H_2O]{\text{Dehydrated}\ \Delta} SeO_2$$

Purified by sublimation

It may also prepared by passing the vapours of sulphuryl fluoride over selenium and silica in a glass vessel

$$2\,SO_2F_2 + SiO_2 + Se \longrightarrow SeO_2 + 2SO_2 + SiF_4$$

The reaction of this oxide with water produces selenious acid H_2SeO_3. The most important acid of selenium is selenic acid H_2SeO_4 which is as strong as sulphuric acid and more easily reduced

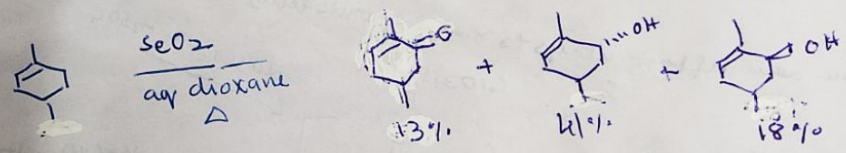
$$SeO_2 + H_2O\ (\text{Hot}) \xrightarrow{\Delta} O=S(OH)_2$$ weak acid, corrosive

Selenious Acid

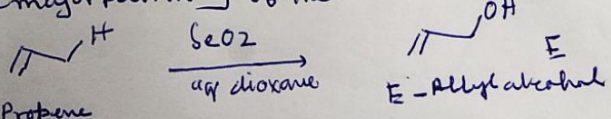
$$SeO_2 + H_2O_2 \xrightarrow[\text{Hydrogen peroxide}]{} HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Se}}-OH$$ Selenic acid

oxo acid

In 1970, Trachtenberg examined the variety of variety of substituted cyclohexene system under the conditions of refluxing them in wet dioxane bath



Selenium dioxide generally produces unrearranged (E)-allylic alcohol. An ene reaction – 2,3-sigmatropic rearrangement sequence being the probable major pathway of the mechanism

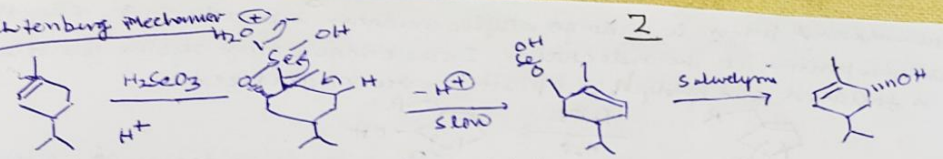


Propene

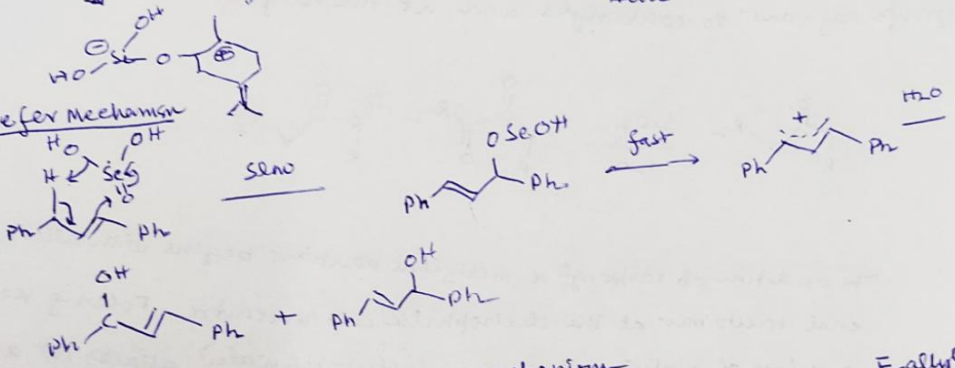
E-Allyl alcohol

Early proposals concerning the mechanism was proposed by Trachtenberg which proceeded through oxaselenocyclobutane intermediate

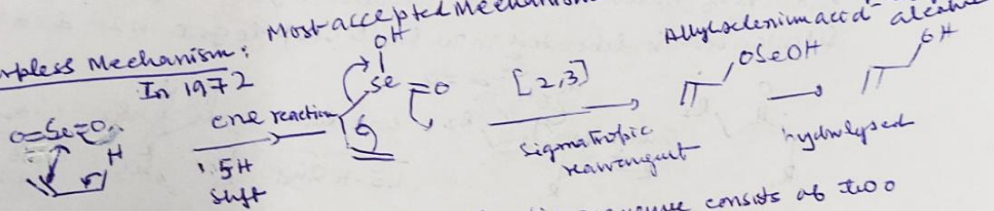
Tr achtenberg Mechanism



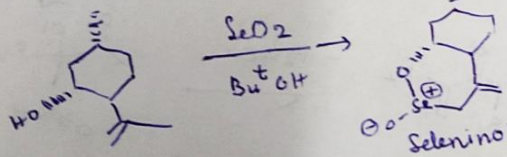
Schaefer Mechanism



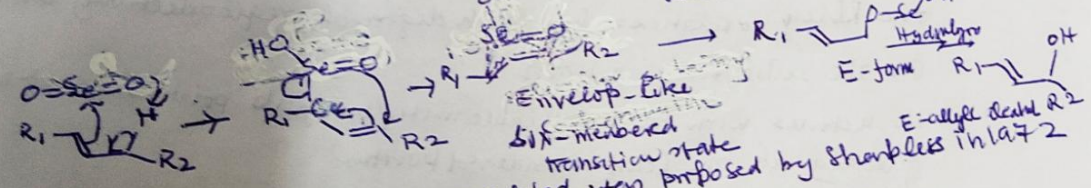
Sharpless Mechanism: In 1972 — Most accepted Mechanism



The fully regio- and stereospecific sequence consists of two consecutive pericyclic reactions (an ene reaction and 2,3-sigmatropic rearrangement)

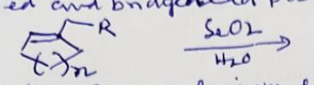


Evidence of intial ene reaction was provided by isolation of selenoketone, presumed to be Trapped form of allyl selenium acid intermediate

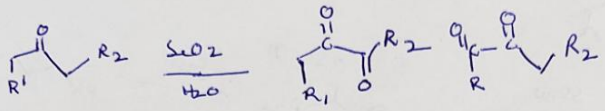


A new mechanism, now generally accepted was proposed by Sharpless in 1972 Here the reaction proceeds through two pericyclic reactions, an ene reaction followed by 2,3-sigmatropic shift for transformation into E-allyl selenium acid. The hydrolysis of allyl selenium acid leads to formation of E-Allyl alcohol. The reaction is fully regio-selective and stereospecific and explains the formation of only E-allyl alcohol. Geometry of E-allyl selenium acid is retained during the hydrolysis.

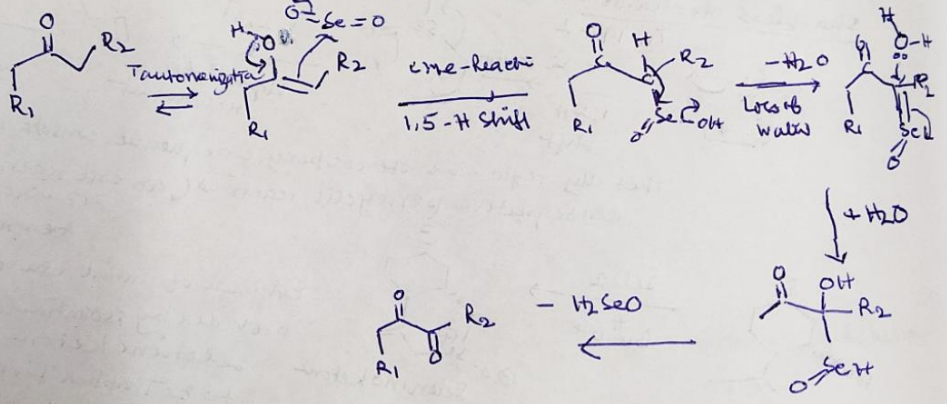
cyclic alkenes prefer to undergo allylic oxidation within the ring, rather than allylic position at the side chain. In the bridged ring system Bredt's rule is followed and bridgehead positions are not oxidized



The Riley oxidation is a selenium dioxide mediated oxidation of methylene groups adjacent to carbonyls and at the allylic position of olefins.



The oxidation of carbonyl α-methylene positions begins with attack by enol tautomer at the electrophilic selenium centre. Following rearrangement and loss of water, a second equivalent of water attacks at α-position. Selenic acid is liberated in the final step to give 1,2-dicarbonyl product

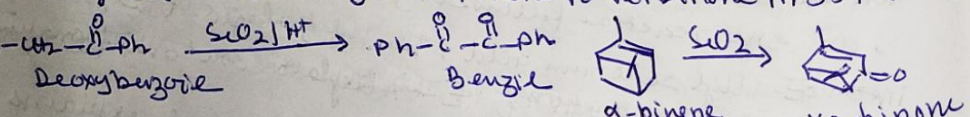


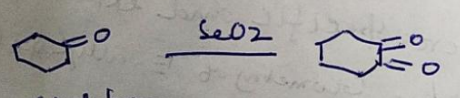
The Riley oxidations show high degree of regioselectivity based on the substitution pattern

The ketones with two available methylene group positions react more quickly at the least hindered position

Examples:

Deoxy benzoin is oxidized by SeO_2 in acedic medium to benzil in quantative yield. SeO_2 oxidizes α-pinene to verbinone in 35% yield





CrO_3, oxidising reagent

Synthesis of carbonyl compounds

(i) By oxidation of 1° and 2° alcohols:

1° and 2° amino alcohols are easily oxidized to aldehydes, ketones or carboxyl acids, depending upon the reaction conditions. The reagent most commonly used for oxidizing alcohols is chromic acid (H_2CrO_4) which is prepared by dissolving either Chromium (VI) oxide or potassium dichromate in aq sulphuric acid

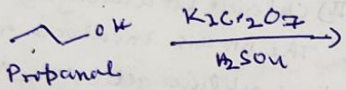
$$CrO_3 + H_2O \xrightarrow{H_2SO_4} H-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}-O-H \quad (H_2CrO_4)$$

Chromium (VI) oxide
Chromium trioxide

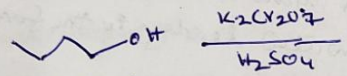
Chromic acid

$$K_2Cr_2O_7 \xrightarrow{H_2SO_4} H_2Cr_2O_7 \xrightarrow{H_2O} 2\,H-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Cr}}-O-H \quad 2(H_2CrO_4)$$

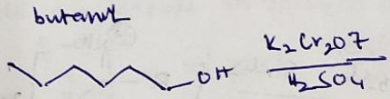
Chromic acid



Propanal — Propionaldehyde



butanol — Butyraldehyde

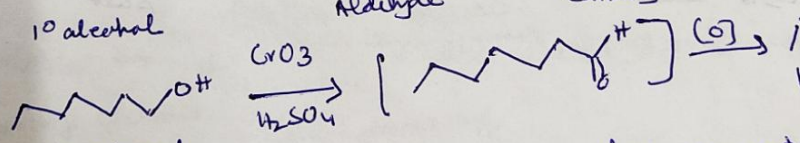


hexanol — hexanal

Primary alcohols are initially oxidized to aldehydes. However, if water is present in the reaction medium, the reaction cannot be stopped at the aldehyde stage as they are further oxidized by same reagent to carboxylic acid.

$$R-CH_2-OH \xrightarrow{[O]} R-\overset{\overset{O}{\|}}{C}-H \xrightarrow{[O]} R-\overset{\overset{O}{\|}}{C}-OH$$

1° alcohol — Aldehyde — Carboxylic Acid

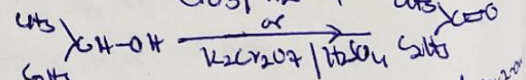


heptanal — heptanoic Acid

Secondary alcohols on oxidation yield ketones, which are not further oxidized

$$\begin{matrix} R \\ R \end{matrix}\!\!>\!CH-OH \xrightarrow{[O]} \begin{matrix} R \\ R \end{matrix}\!\!>\!C=O$$

2° alcohol — Ketone



Butan-2-ol — Butan-2-one

Ketone

$$\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>\!CH-OH \xrightarrow[H_2SO_4]{CrO_3} \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>\!C=O$$

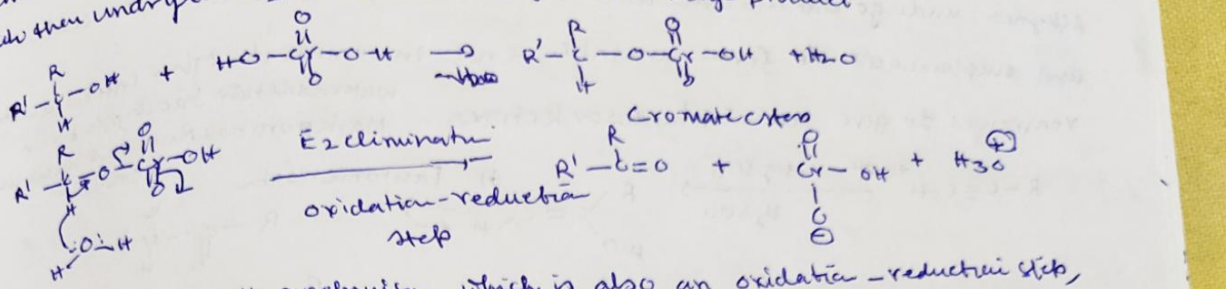
Pentan-3-ol — Pentan-3-one

Oxidation happens when – hydroxyl group is attached to carbon having hydrogen atom. Therefore, t-butyl alcohol does not oxidize or 3° alcohols do not oxidize

$$\begin{matrix} H_3C \\ \\ C_2H_5 \end{matrix}\!\!>\!\overset{\overset{CH_3}{|}}{C}-OH \xrightarrow[H_2SO_4]{CrO_3} \text{No reaction}$$

Mechanism

All chromium bearing oxidizing agent oxidize alcohols by first forming a chromate ester, which then undergoes E_2 elimination to yield carbonyl product



Chromate ester

oxidation-reduction step

The second step of the mechanism which is also an oxidation-reduction step, carbon undergoes a two electron oxidation whereas chromium (VI) undergoes a two electron reduction to chromium (IV) and eventually to chromium (III).

As the most organic compounds are insoluble in water. So reaction is carried out in acetone and then added stoichiometric amount of Jones reagent (sol^n of chromic acid in aq sulphuric acid

* number of chromium (VI) reagents are used for different oxidations are:

(a) collins reagent — Chromiumtrioxide in pyridine

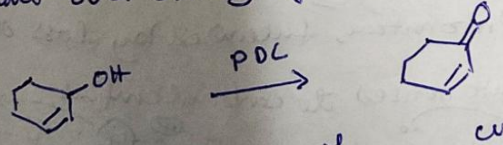
(b) Etard reagent — Chromylchloride (CrO_2Cl_2) in dichloromethane

(c) Pyridinium chlorochromate (PCC) — Chromiumtrioxide in pyridine in presence of HCl

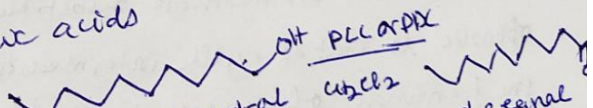
(d) Jones reagent: — 8N Chromicacid sol^n in aq H_2SO_4 acid.

(e) Pyridinium dichromate (PDC): Pyridin, potassium dichromate and HCl in dichloromethane

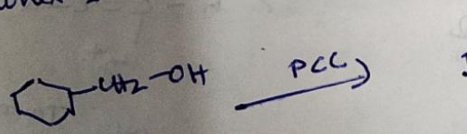
PDC and PCC are reagents of choice as they oxidize alcohols to aldehydes without over oxidizing it to carboxylic acids



cyclohex-2-ene-1-ol — cyclohex-2-ene-1-one

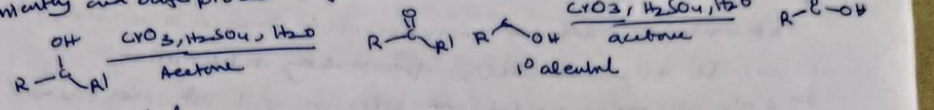


decan-1-ol — decanal



Jones oxidation : 8N chromic acid soln in Aq H_2SO_4 and

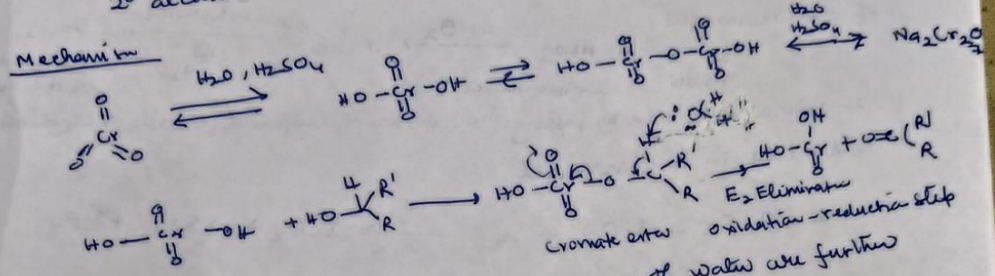
Jones oxidation allows a relatively inexpensive conversion of sec alcohol to ketones and primary alcohols to carboxylic acid Jones described for the first time a conveniently and safe procedure for chromium (VI) based oxidation



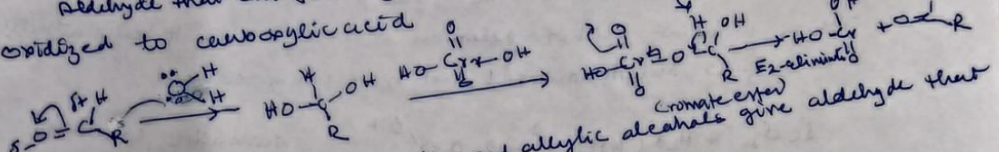
2° alcohol

1° alcohol

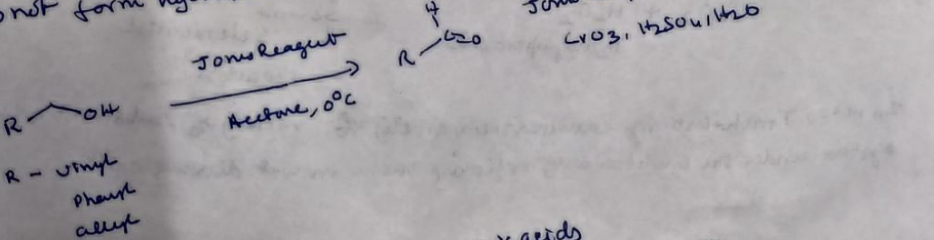
Mechanism



Aldehyde that can form hydrates in the presence of water are further oxidized to carboxylic acid

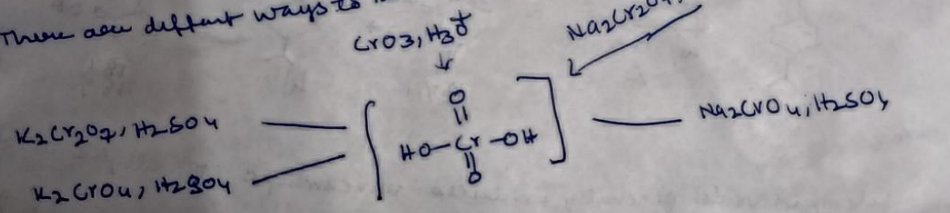


Some alcohols such as benzylic and allylic alcohols give aldehyde that do not form hydrates



R - vinyl
phenyl
allyl

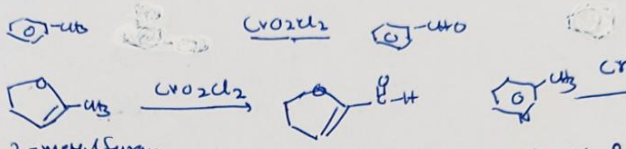
There are different ways to make cromic acids



Chromyl chloride oxidation

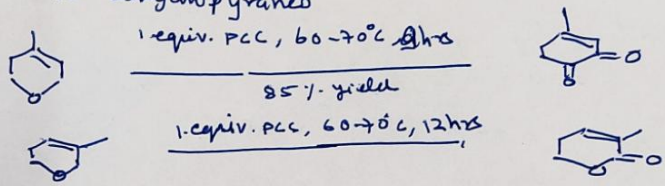
The transformation Ar-CH_3 into Ar-CHO can be accomplished by ETARD Reaction. A solution of two equivalent of Chromyl chloride CrO_2Cl_2 in carbon tetrachloride is added cautiously to the hydrocarbon with the control of temp 25-45°C. A molecular complex separates which on treatment with water decomposes give aldehydes and aq. salt of chromic acid and chromic chloride.

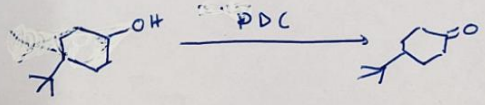
$$Ar-CH_3 + 2\,CrO_2Cl_2 \longrightarrow ArCH_3(CrO_2Cl_2)_2 \xrightarrow{H_2O} Ar-CHO$$



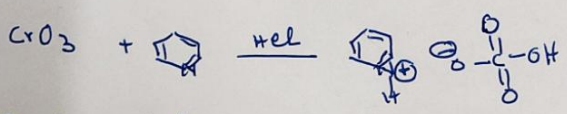
2-methylfuran

Pridinium chlorochromate has been shown to be a particular value in the allylic oxidation of compounds containing an activated methylene group such as 5,6-dihydropyranes



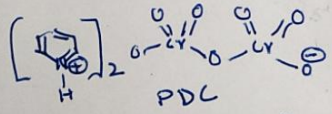


Pyridinium chlorochromate is made by the mixing of CrO_3 with pyridine and hydrochloric acid. The oxidising component of PCC is chlorochromate anion



Pyridinium dichromate (PDC) PCC

PDC



PDC

Orange salt