Unit 7
Oxidation–Reduction reactions

- Oxidation-reduction ("redox") reactions involve the transfer of electrons from one substance to another.
- Oxidized substances lose electrons and reduced substances gain electron.

For instance:

✓loses electrons in oxidation. (LEO) or (OIL)

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-}$$ (loss of electrons)

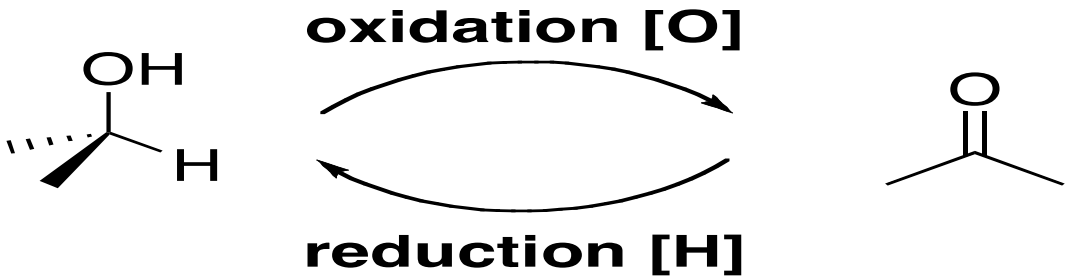
✓gains electrons in reduction. (GER) or (RIG)

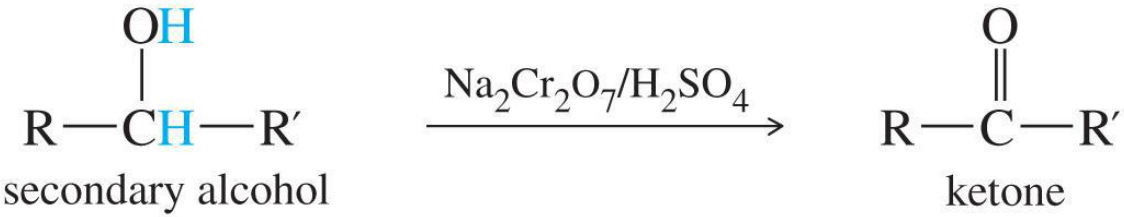
$$Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s)$$ (gain of electrons

Oxidation Reactions

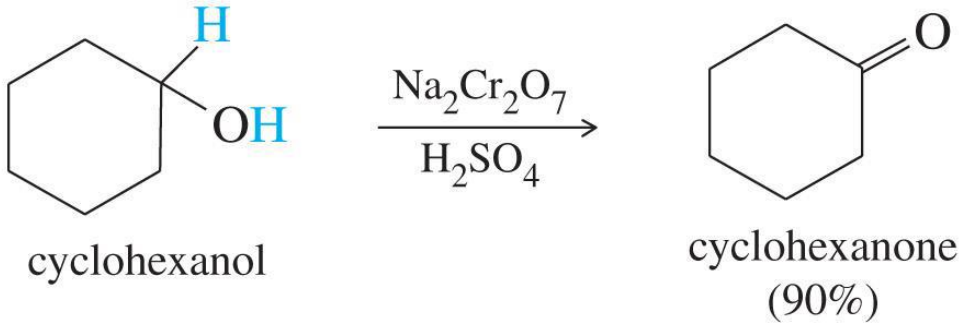
i) Oxidation of Alcohols

➢Primary and secondary alcohols are easily oxidized by a variety of reagents.





Example



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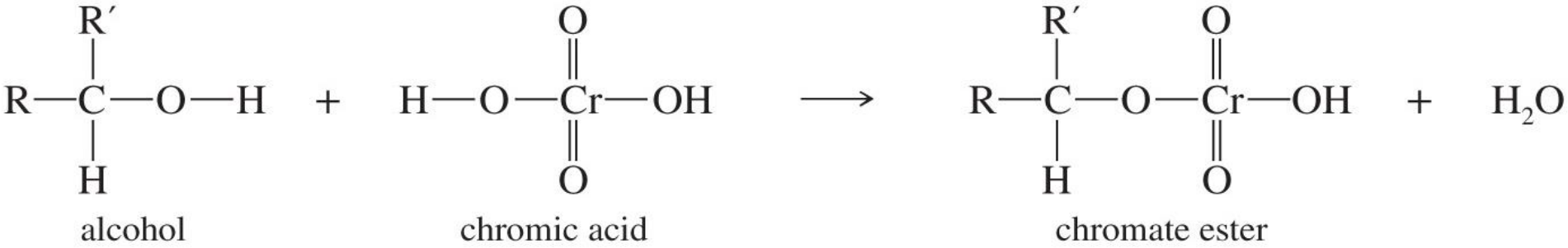
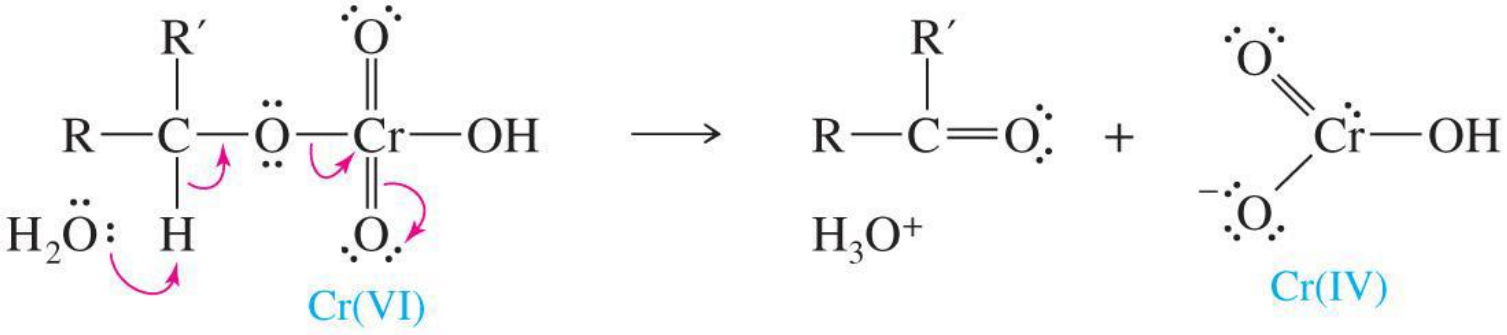
Mechanism of oxidation

- The alcohol and chromic acid produce a chromate ester, which then reductively eliminates the Cr species.
- The Cr is reduced (VI → IV), the alcohol is oxidized.





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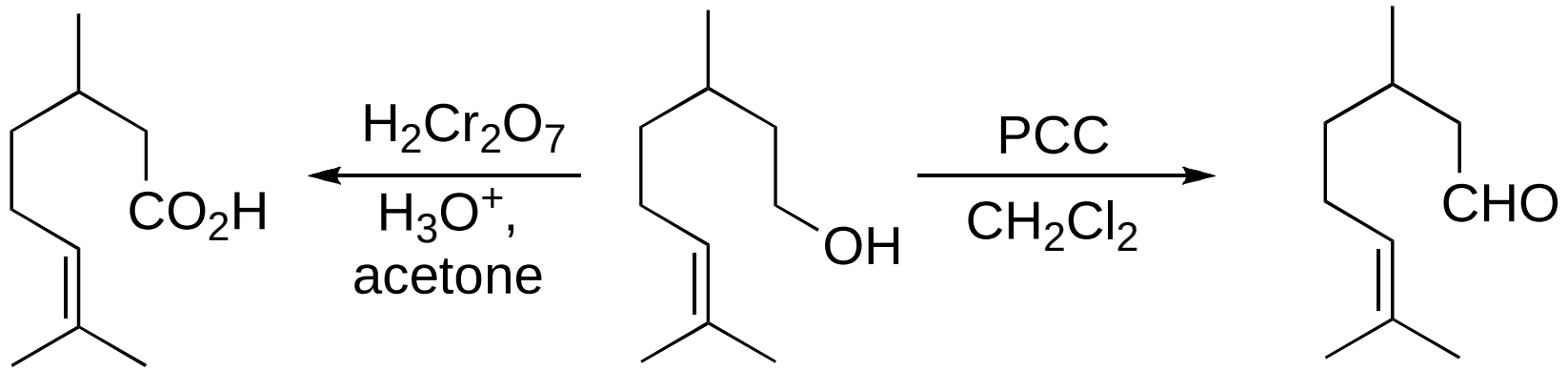
Oxidation of primary alcohols to aldehydes

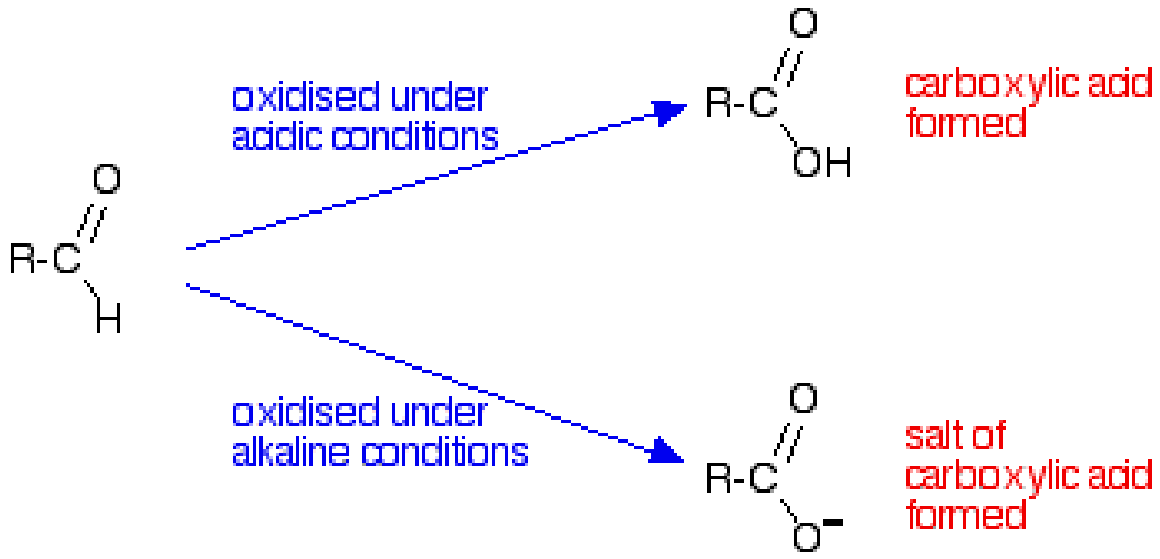
- Using Pyridinium Dichromate (PDC) and Pyridinium Chlorochromate (PCC);
- B/c both are soluble in *anhydrous* organic solvent; CH_2Cl_2.
- The oxidation of primary alcohols with PCC or PDC in anhydrous CH_2Cl_2 stops at the aldehyde



Carboxylic Acid **1° alcohol** **Aldehyde**

Oxidation Reactions of Aldehydes

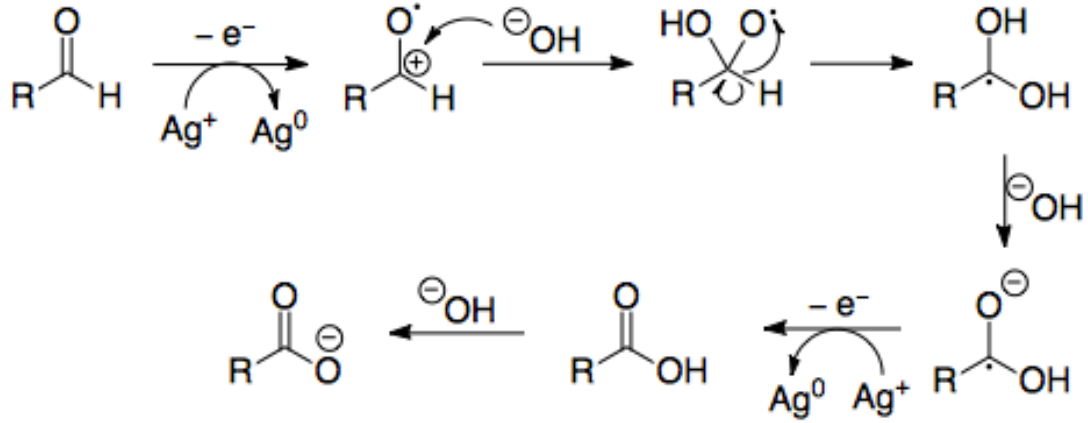
➢Aldehydes are readily oxidized to carboxylic acids by common oxidizing agents such as Chromic acid, Silver oxide and Permanganate.



➢In these oxidations aldehydes lose the hydrogen that is attached to the carbonyl carbon atom.

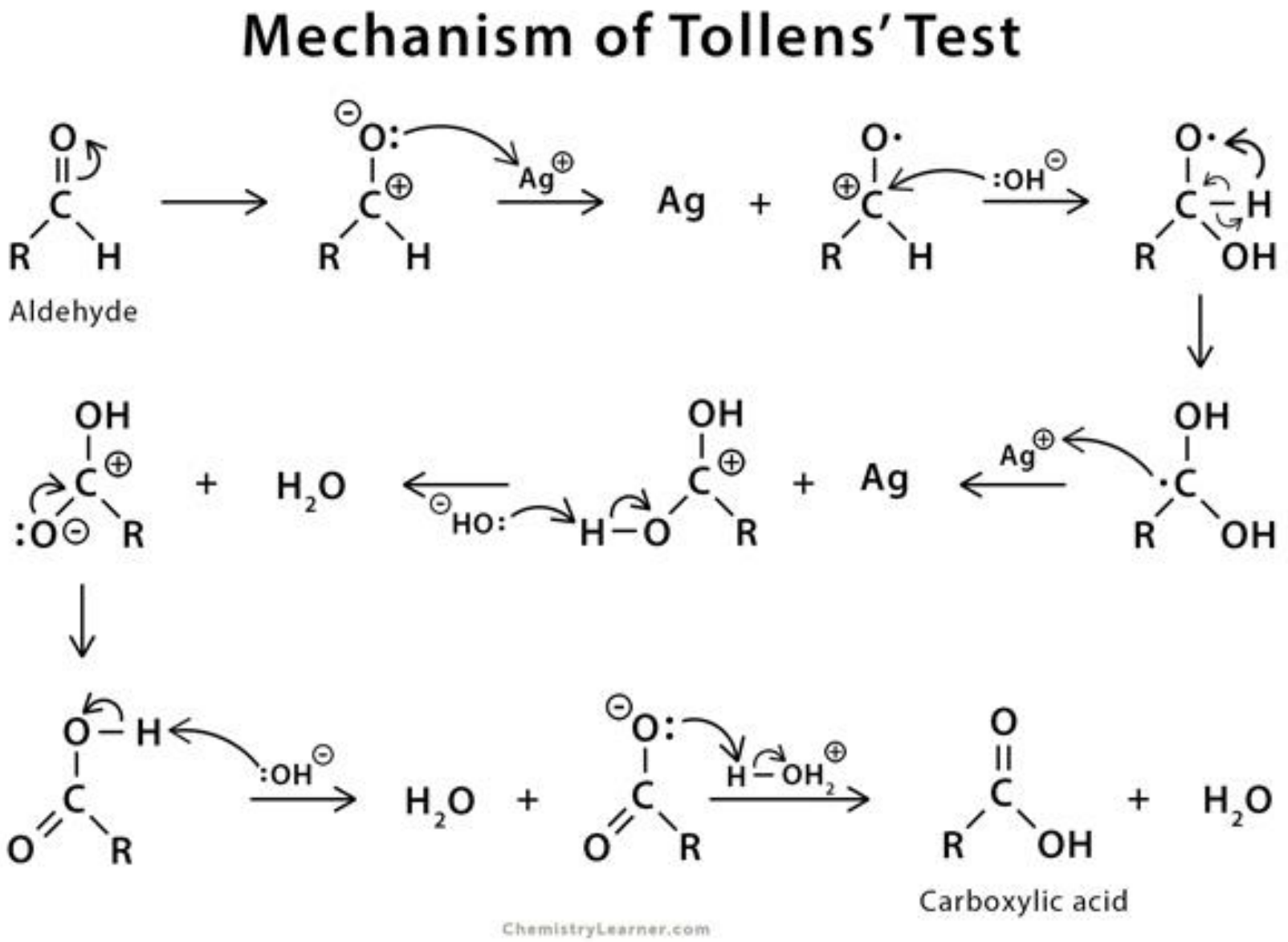
Tollens silver mirror test

➢Aldehydes are oxidized selectively in the presence of other functional groups using silver(I) oxide in aqueous ammonium hydroxide (Ag_2O in NH_4OH).



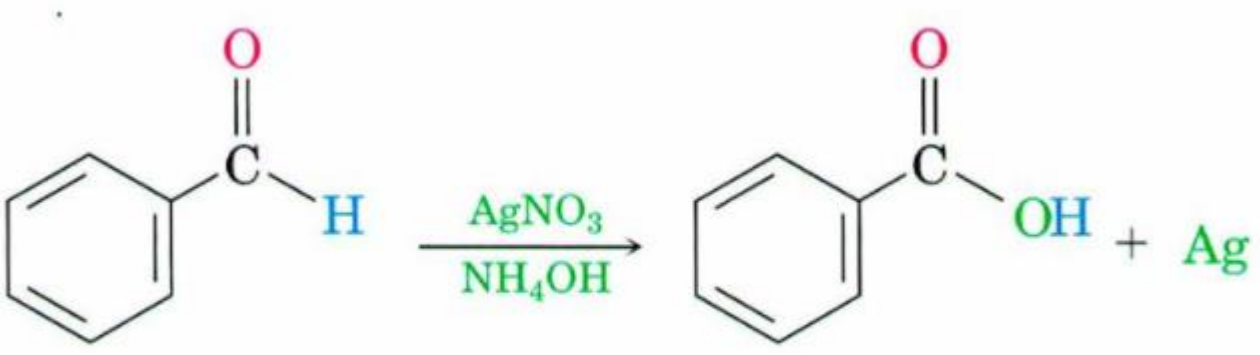
➢Oxidation with Tollens reagent provides a distinct color change, because the Ag^+ reagent is reduced to silver metal (Ag), which precipitates out of solution.

For instance

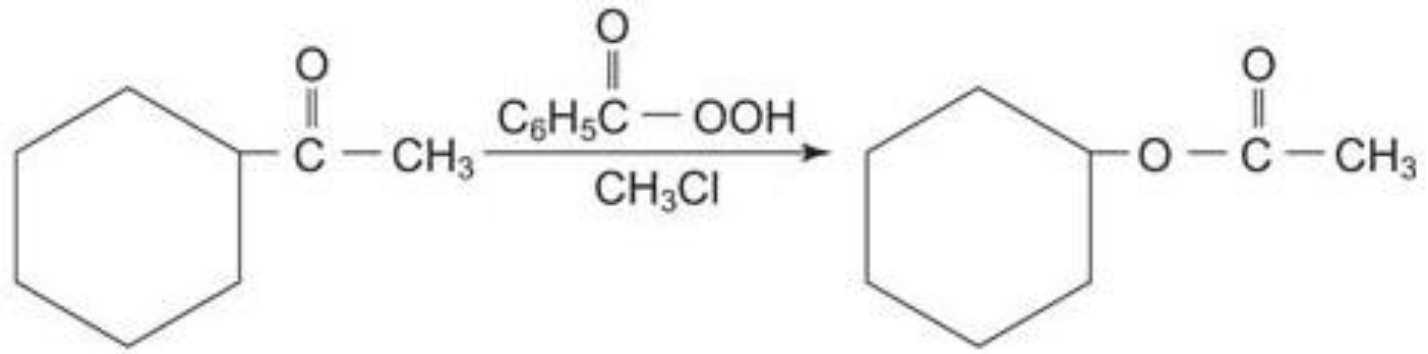


Exercise(1)

- Show the detail mechanism of the following reaction



Benzaldehyde **Benzoic acid**

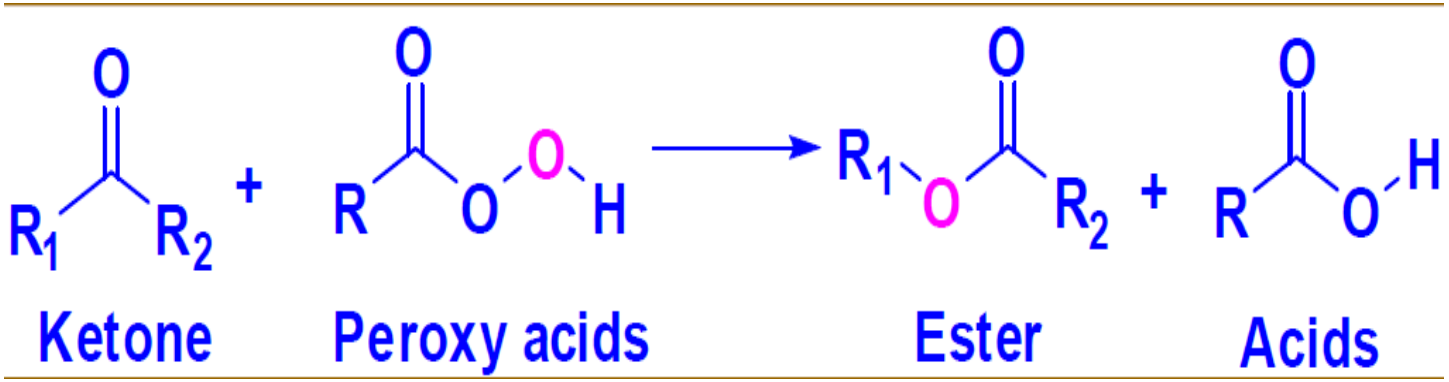


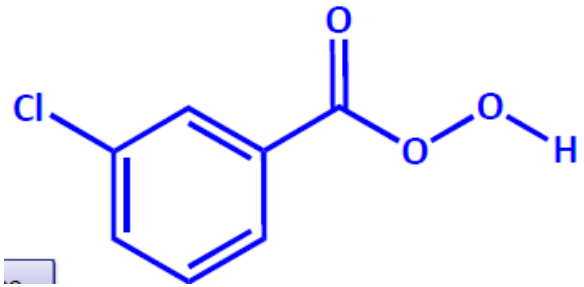
cyclohexylmethylketone cyclohexylacetate

Baeyer-Villiger Oxidation

➢It involves the insertion of an oxygen atom (derived from a peroxy acid, like *mchlorobenzoic* acid (*m-CPBA)) between the carbonyl* group of a ketone and one of the attached carbons to provide an ester.

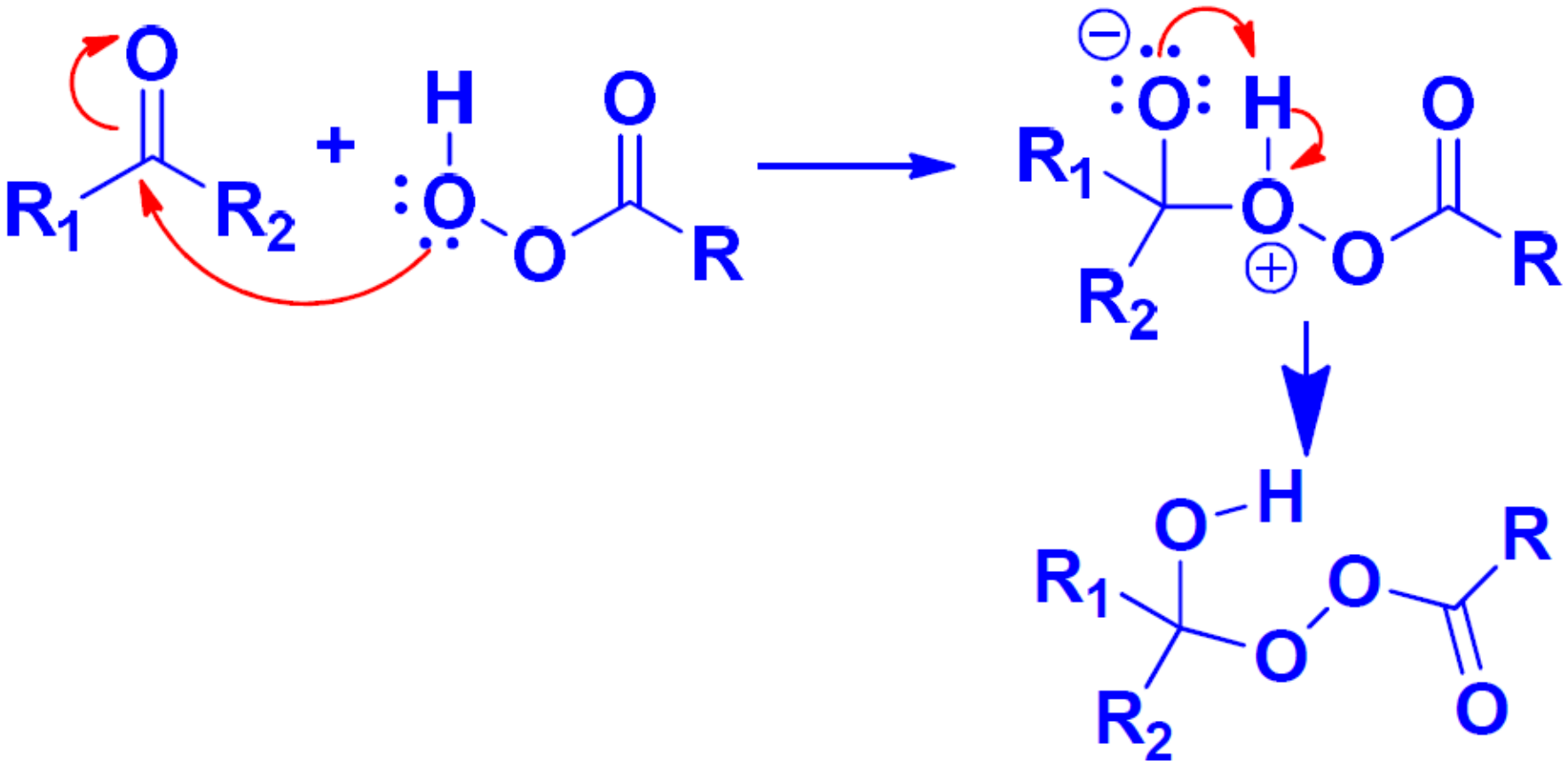
General Reaction





m-chlorobenzoic acid (*m*-CPBA)

Mechanism of the Baeyer-Villiger Oxidation



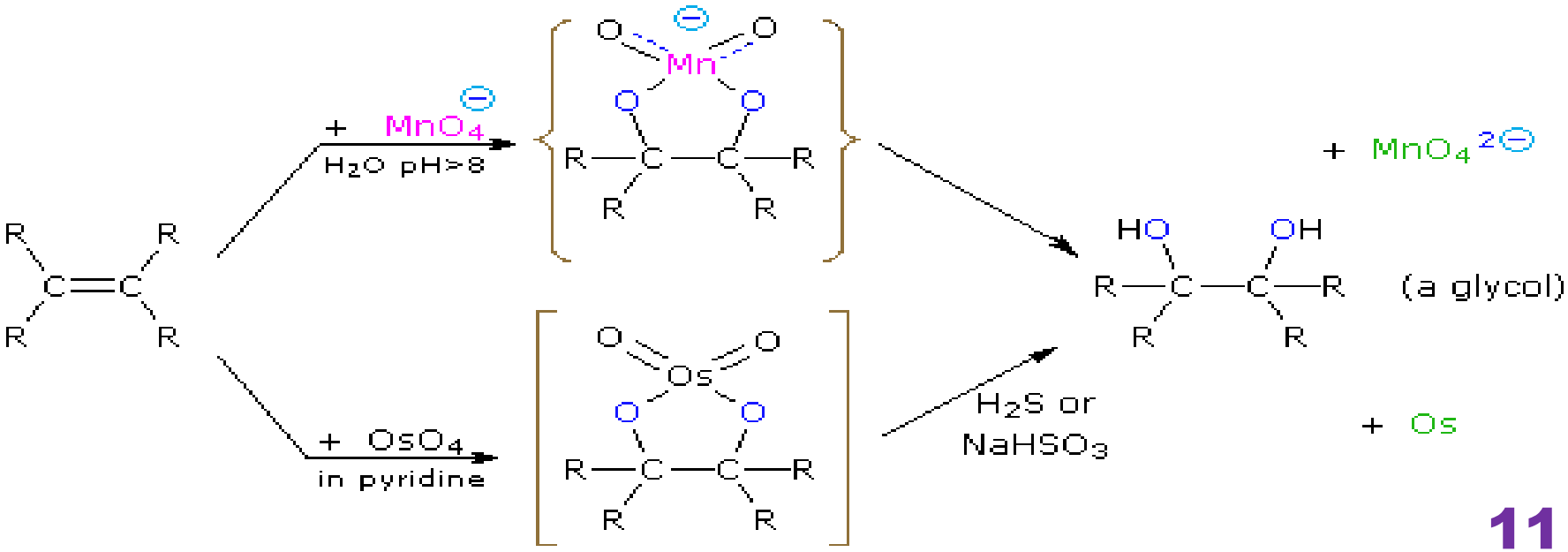
Peroxymonoester

Oxidations of double bond

✓Hydroxylation

❖Dihydroxylated products (glycols) are obtained by reaction with aqueous potassium permanganate (pH > 8) or osmium tetroxide in pyridine solution.

❖Both reactions appear to proceed by the same mechanism



Application of $KMnO_4$

- In basic solution the purple permanganate anion is reduced to the green manganate ion, providing a nice color test for the double bond functional group.

✓Epoxidation

✓Some oxidation reactions of alkenes give cyclic ethers in which both carbons of a double bond become bonded to the same oxygen atom.

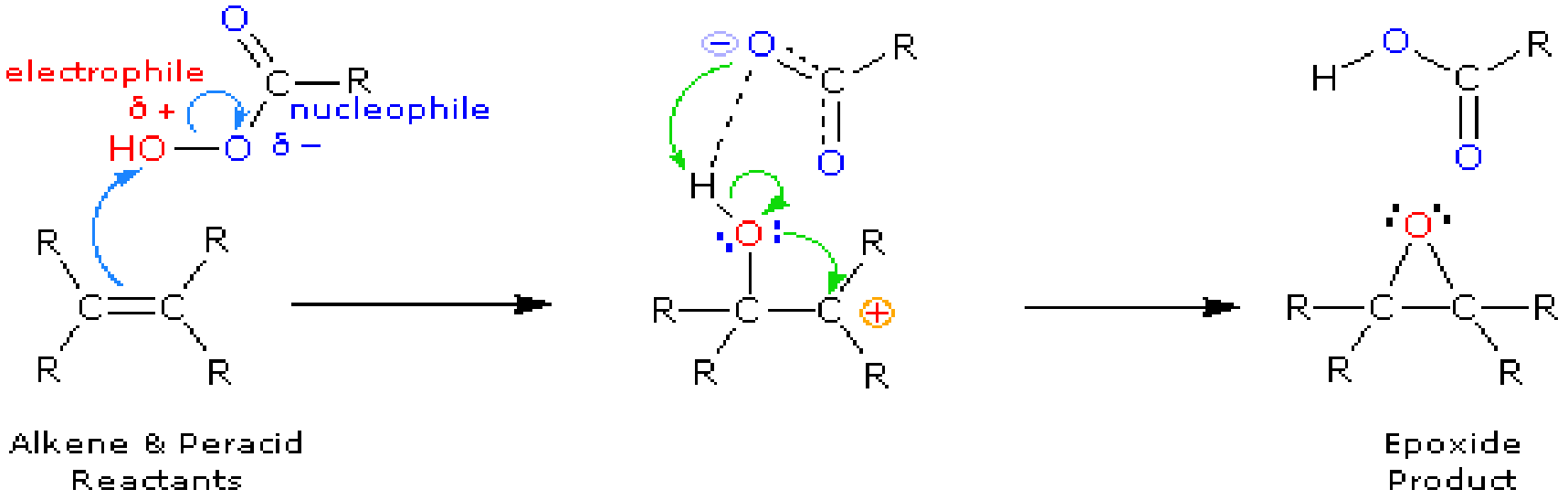
✓These products are called **epoxides** or **oxiranes**.

✓An important method for preparing epoxides is by reaction with peracids, RCO_3H

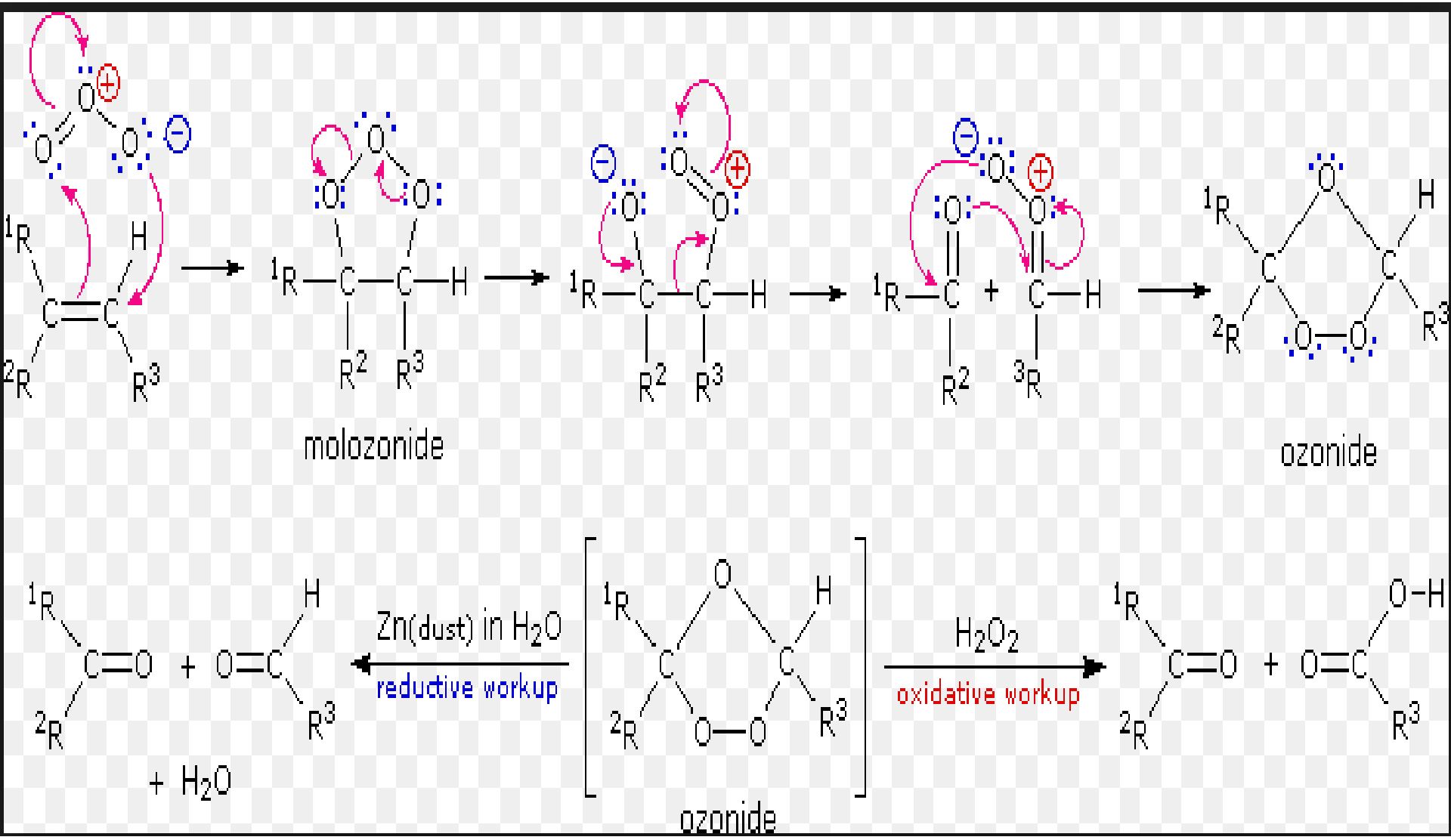
Cont'd…,

✓The oxygen-oxygen bond of such peroxide derivatives is not only weak (35 kcal/mole),

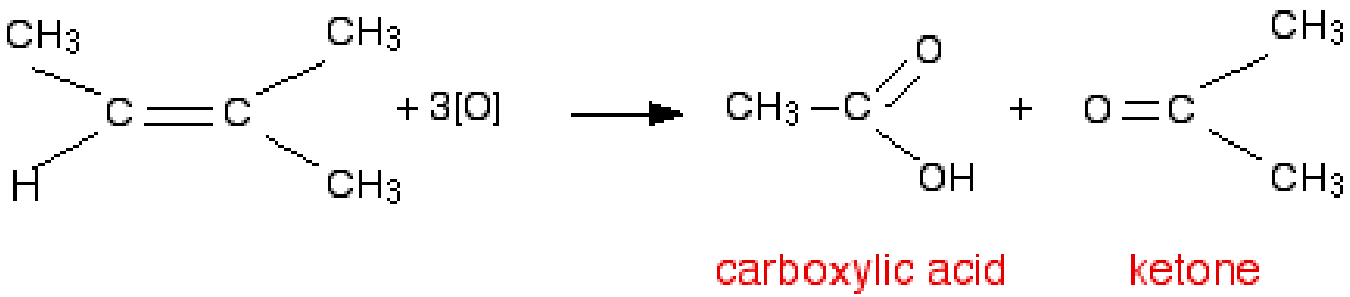
✓but in this case is polarized so that the acyloxy group is negative and the hydroxyl group is positive (recall that the acidity of water is about ten powers of ten weaker than that of a carboxylic acid



Possible Mechanism…,



Example



Conversion of alkylbenzenes to benzoic acids using $KMnO_4$



Alkylbenzene *Benzoic acid*

Key bonds formed	Key bonds broken
C–O(π)	C–H
C–O	C–H
C–OH	C–H

✓Oxidative Cleavage of Double Bonds

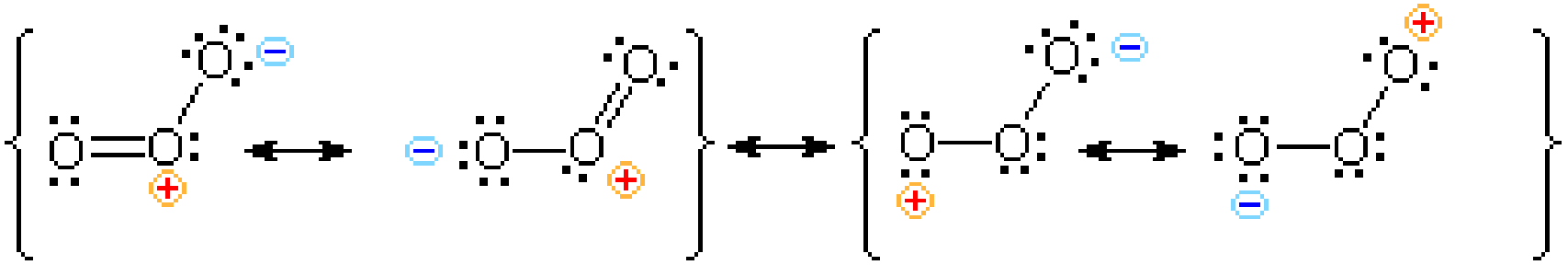
➢Ozonolysis

In determining the structural formula of an alkene, it is often necessary to find the location of the double bond within a given carbon framework.

✓One way of accomplishing this would be to selectively break the double bond and mark the carbon atoms that originally formed that bond.

✓If the double bond is cleaved and the fragments marked at the cleavage sites, the location of the double bond is clearly determined for each case.

The Mechanism of Ozonolysis



More Important

more bonds, less charge separation

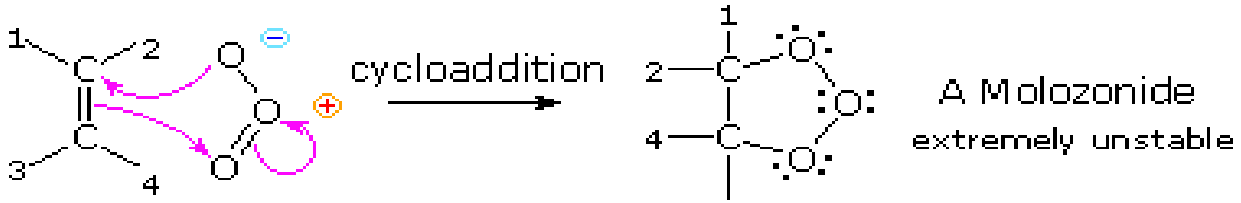
Less Important

fewer bonds, greater charge separation

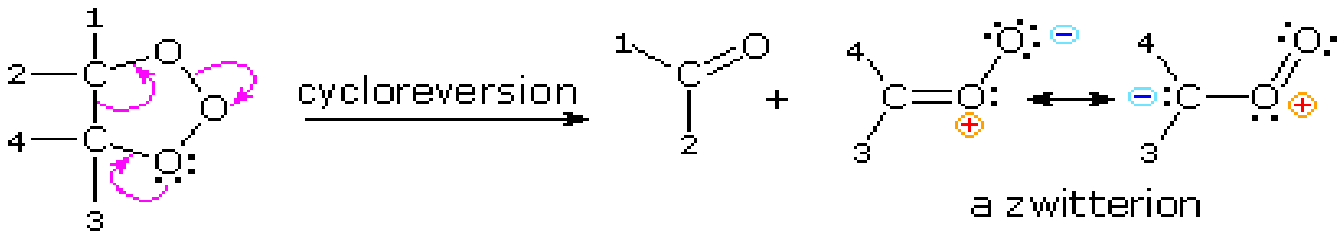
✓The initial product of ozone cycloaddition to an alkene is called a **molozonide**.

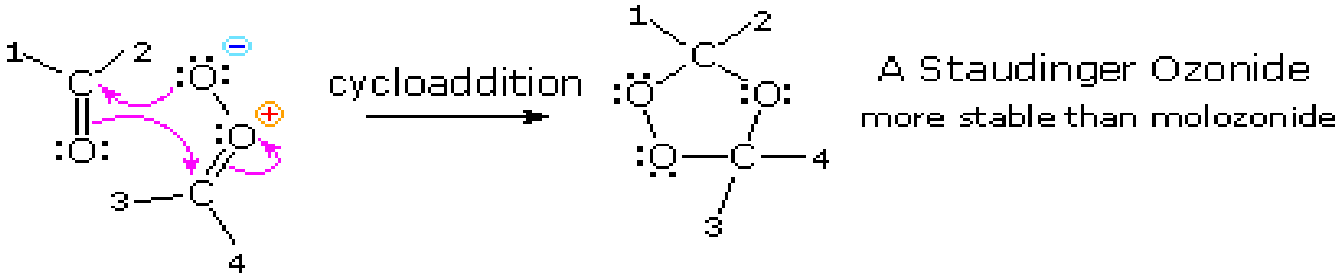
✓Molozonides are very unstable and rapidly decompose; nevertheless, spectroscopic evidence for the transient existence of a molozonide has been obtained at -100 ºC.

Possible reaction...,

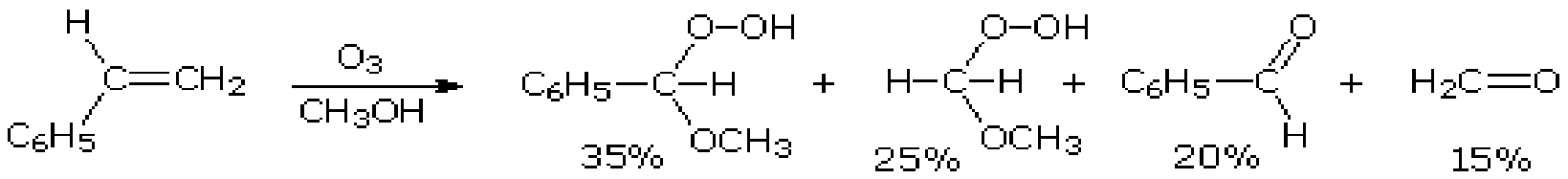


Molozonide Decomposition



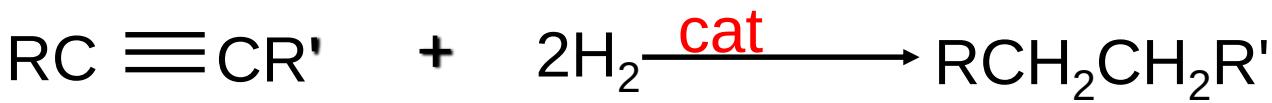


Trapping the Zwitterion Intermediate



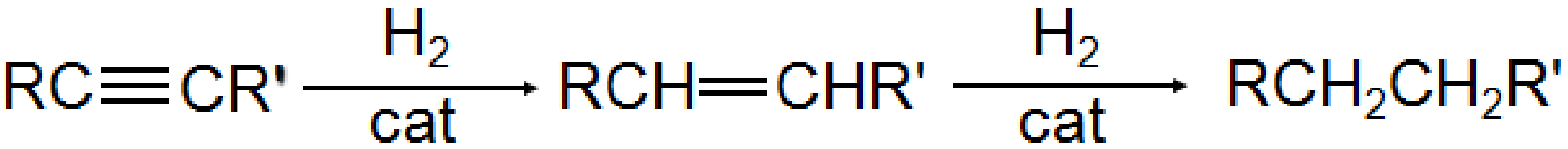
Addition Reactions of Alkynes

➢Hydrogenation of Alkynes



catalyst = Pt, Pd, Ni, or Rh; alkene is an intermediate

➢Partial Hydrogenation

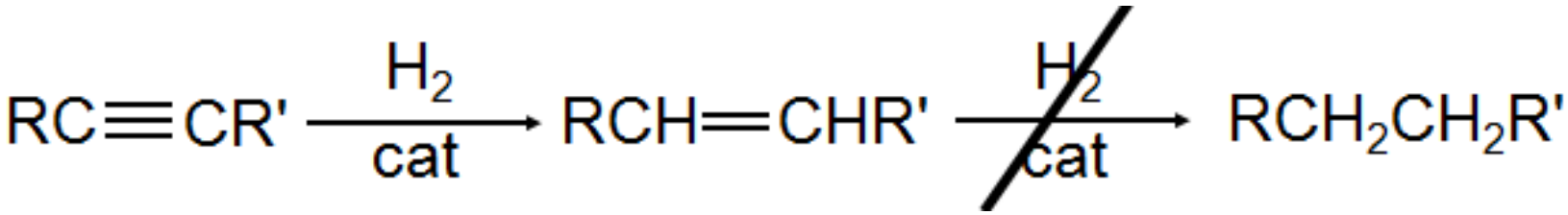


✓Alkenes could be used to prepare alkanes if acatalyst were Available;

✓Which is active enough to catalyze the hydrogenation of alkynes,

✓ but notactive enough for the **hydrogenation** of alkenes.

Lindlar Palladium

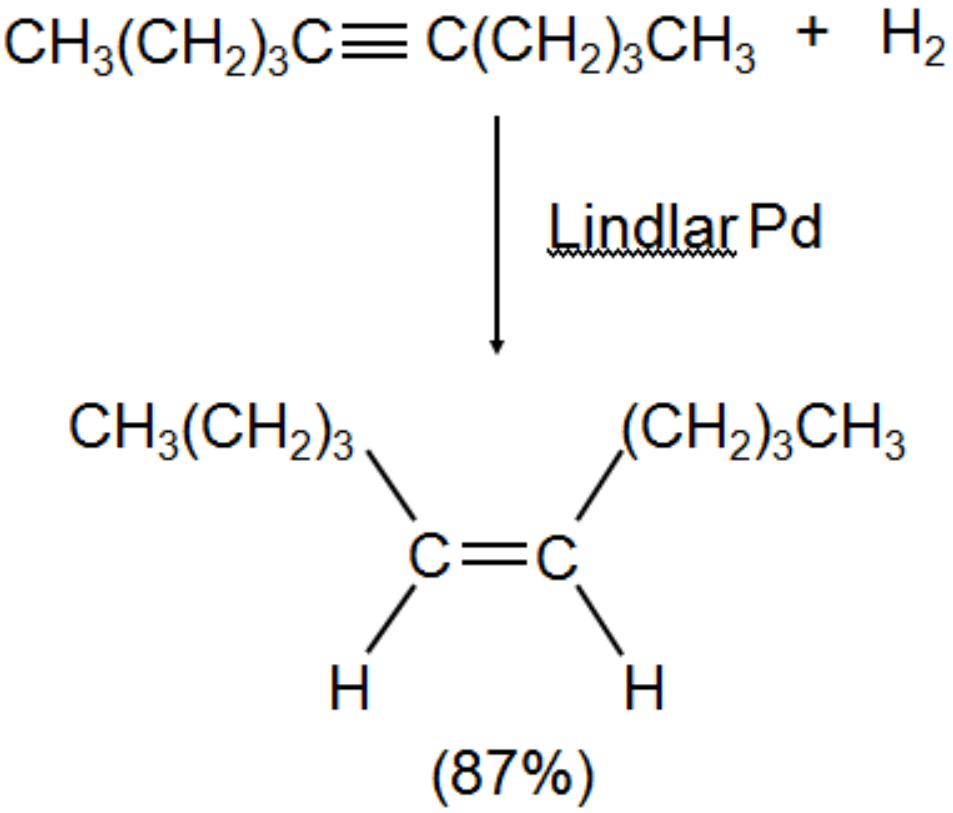


✓There is a catalyst that will catalyze the hydrogenation of alkynes to alkenes, but not that of alkenes to alkanes.

✓It is called the Lindlar catalyst and consists of palladium upported on $CaCO_3$, which has been poisoned with lead acetate and quinoline.

syn-Hydrogenation occurs; cis alkenes are formed.

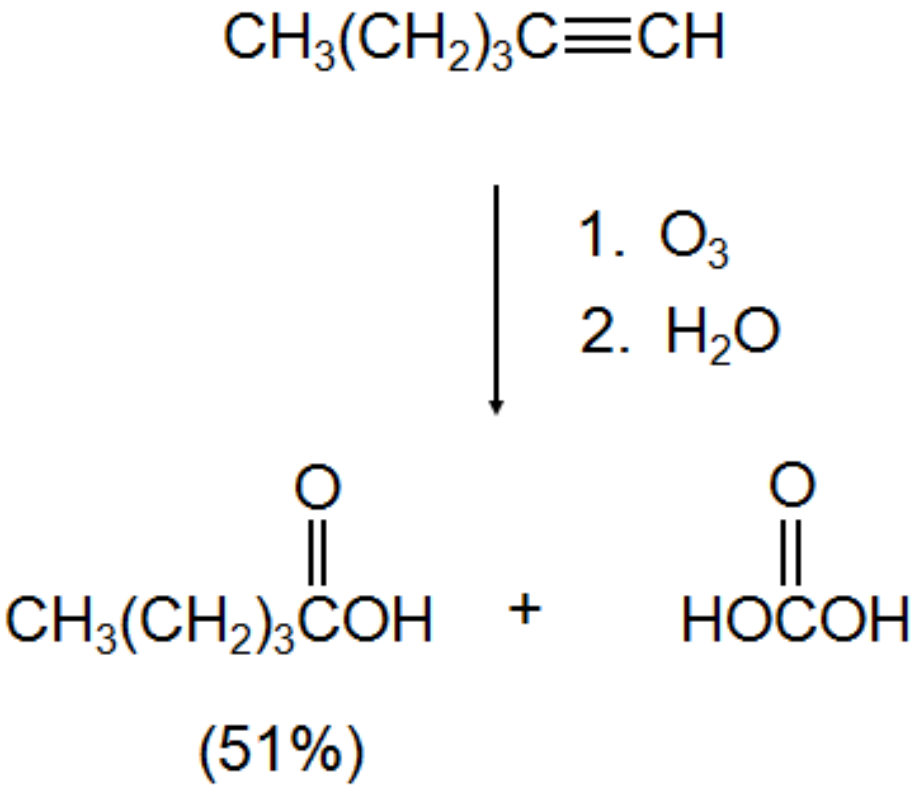
Example



Ozonolysis of Alkynes

- gives two carboxylic acids by cleavage of triple bond

Example



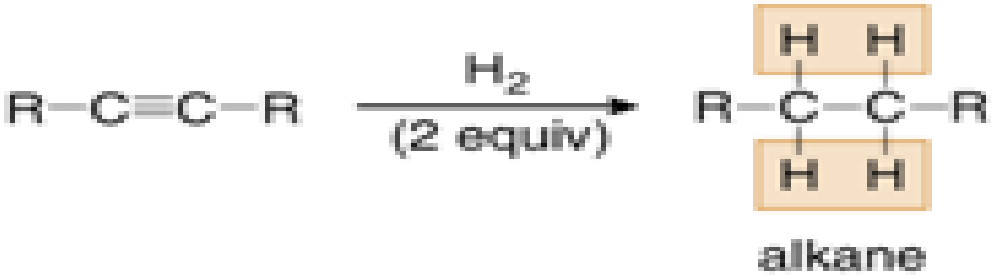
Reduction Reaction

✓Reduction of Alkynes

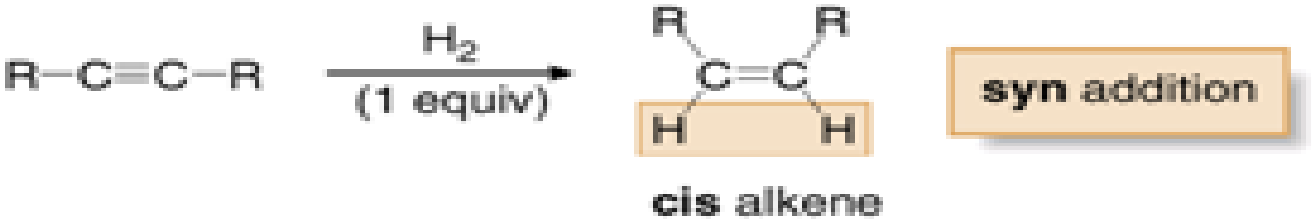
✓There are three different ways in which H_2 can add to the triple bond

For instance...,

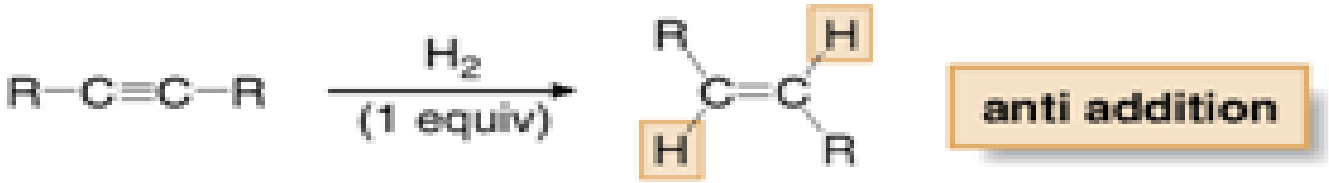
- Adding two equivalents of H_2 forms an alkane.



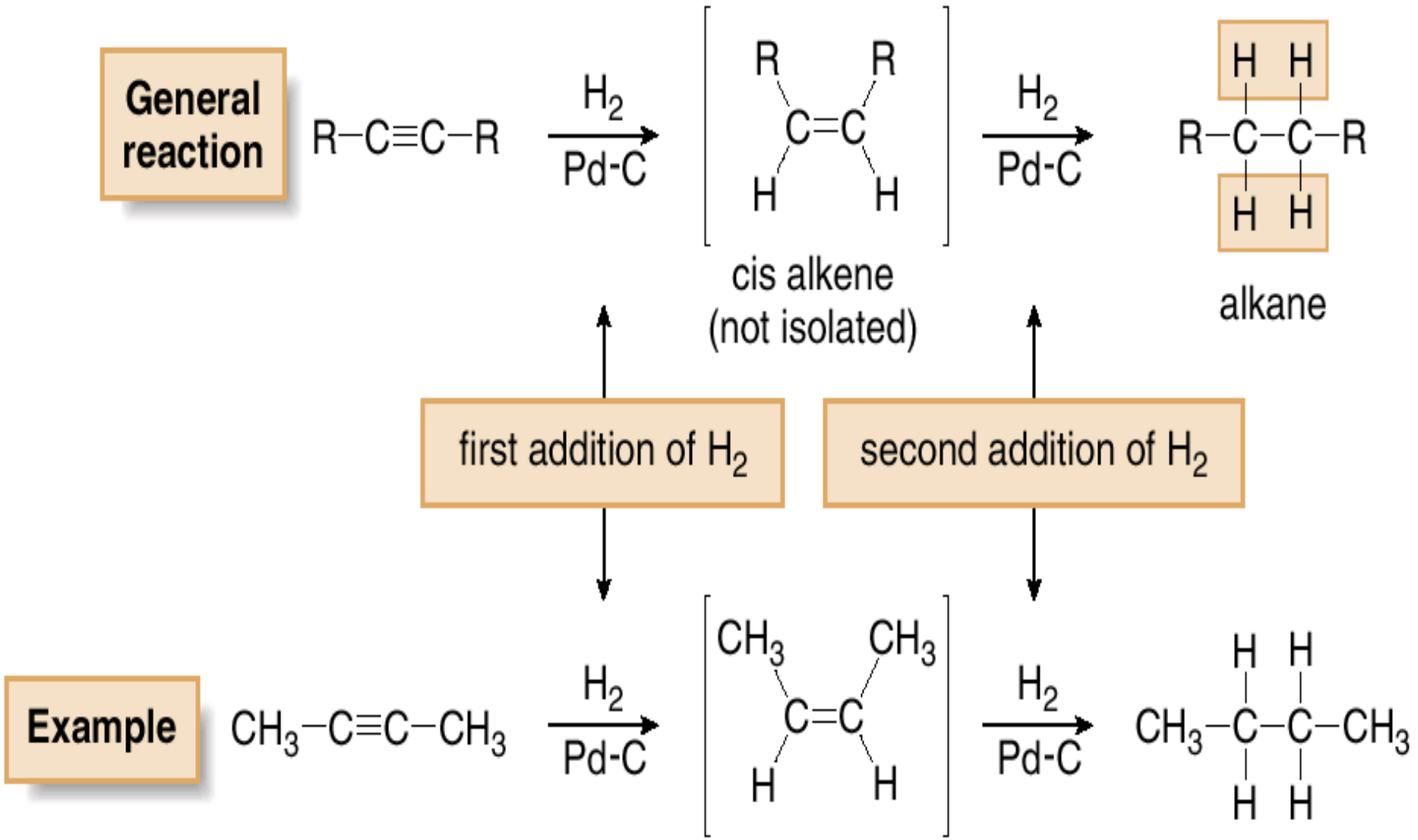
- Adding one equivalent of H_2 in a syn fashion forms a cis alkene.



- Adding one equivalent of H_2 in an anti fashion forms a trans alkene.



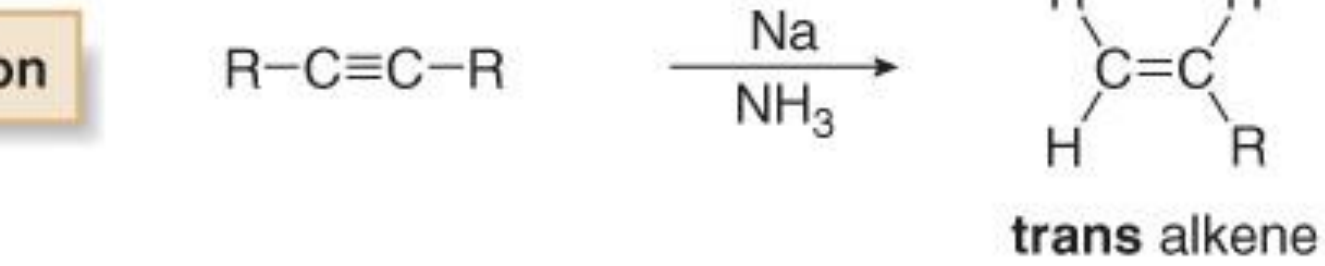
Reduction of an Alkyne to an Alkane



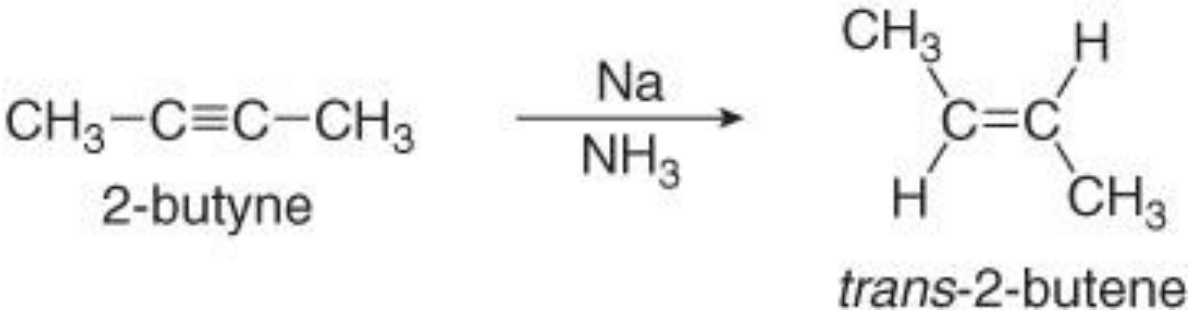
Reduction of an Alkyne to a Trans Alkene

- In a dissolving metal reduction (such as Na in NH_3),
- the elements of H_2 are added in an anti fashion to form a trans alkene

General reaction

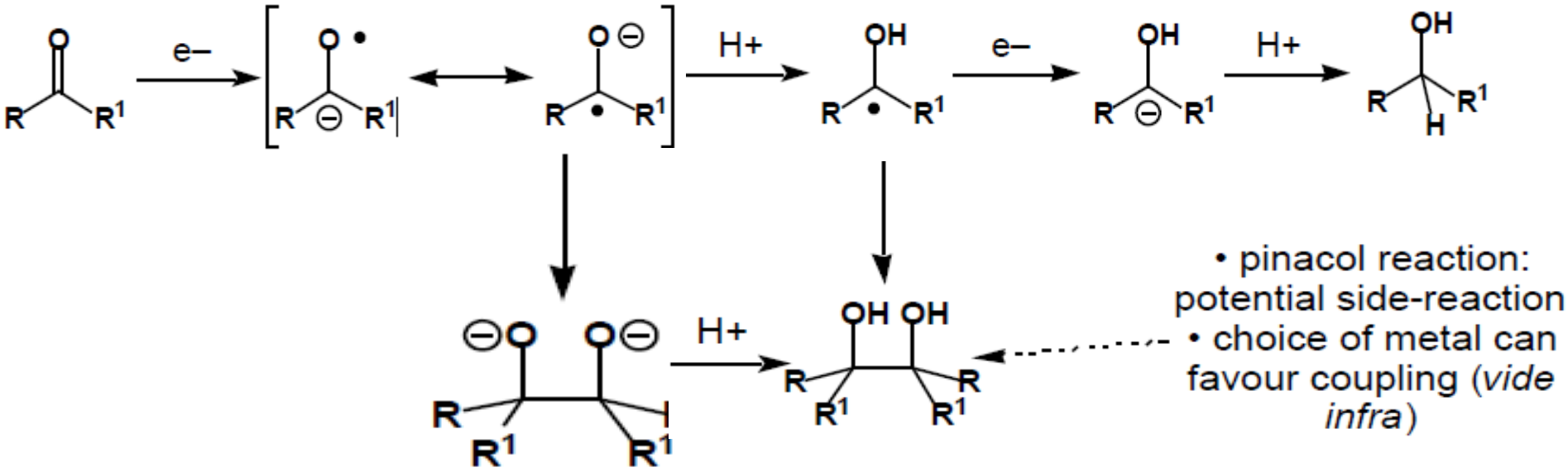


Example



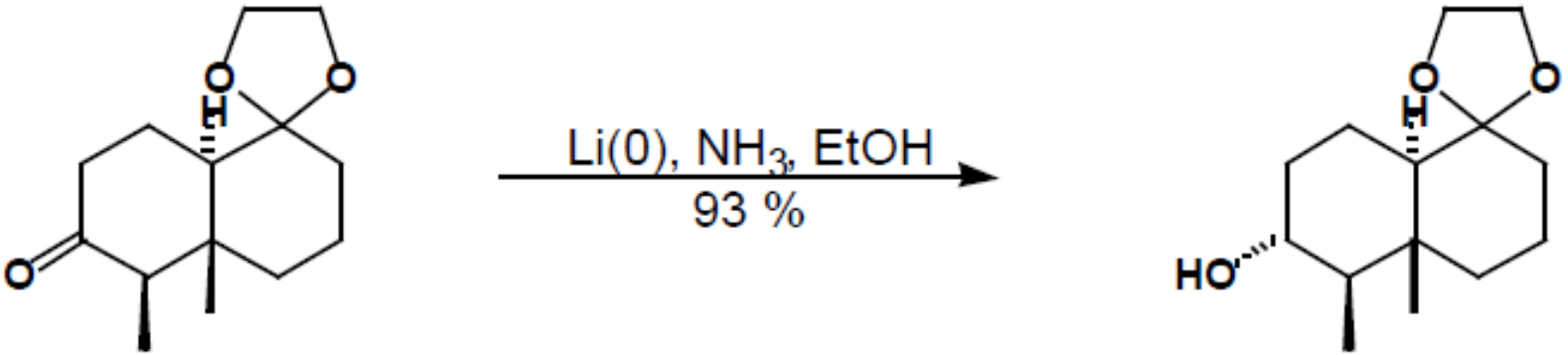
Reduction of Carbonyl Compounds

Mechanism



Selectivity

- Hydrogen normally adds to give the thermodynamic product

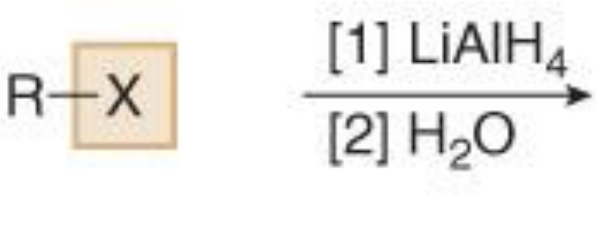


The Reduction of Polar C–X σ-bonds

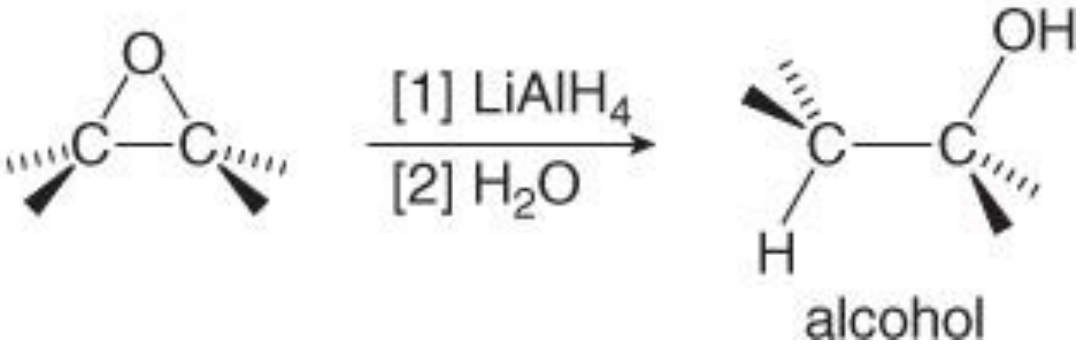
✓Alkyl halides and epoxides are reduced by the hydride reagent lithium aluminumhydride ($LiAlH_4$).

✓The reaction follows an S_N2 mechanism.

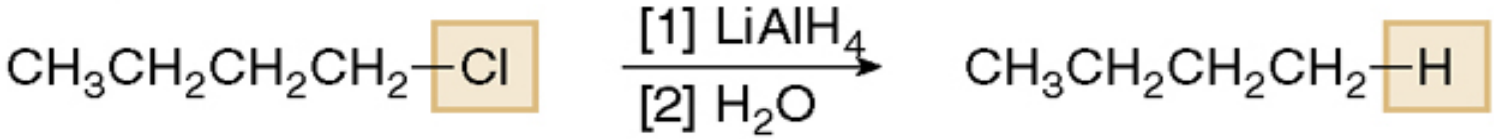
Reduction of alkyl halides

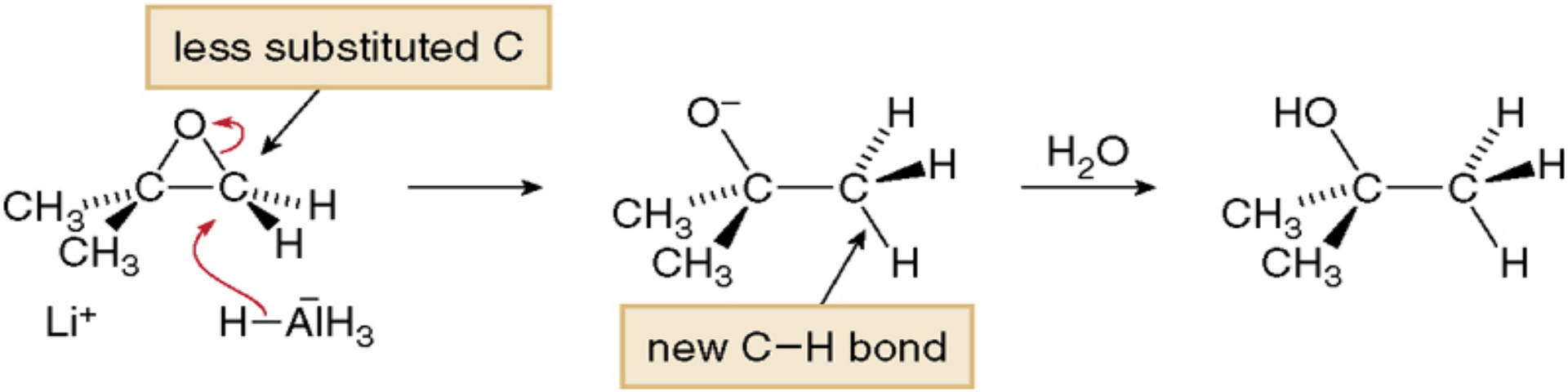


Reduction of epoxides

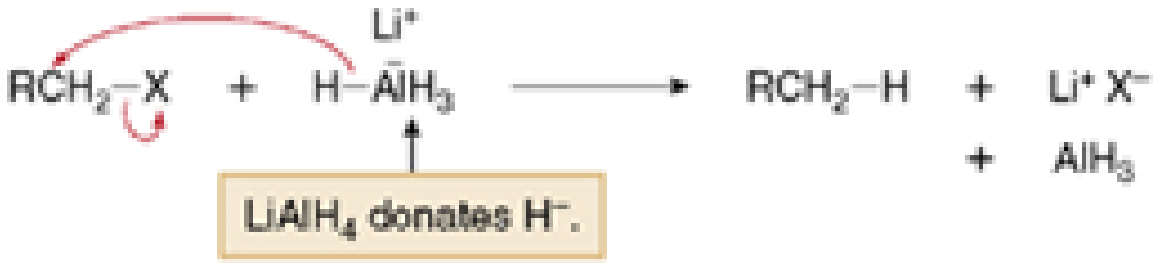


Examples...,





One step The nucleophile H^- substitutes for X^- in a single step.



Explanation...,

- This reaction follows an S_N2 mechanism.
- Unhindered CH_3X and 1° alkyl halides are more easily reduced than more substituted 2° and 3° halides.
- In unsymmetrical epoxides, nucleophilic attack of H^- (from $LiAlH_4$) occurs at the less substituted carbon atom.

Lithium Aluminum Hydride ($LiAlH_4$); reactivity

✓highly reactive, non-selective reducing agent

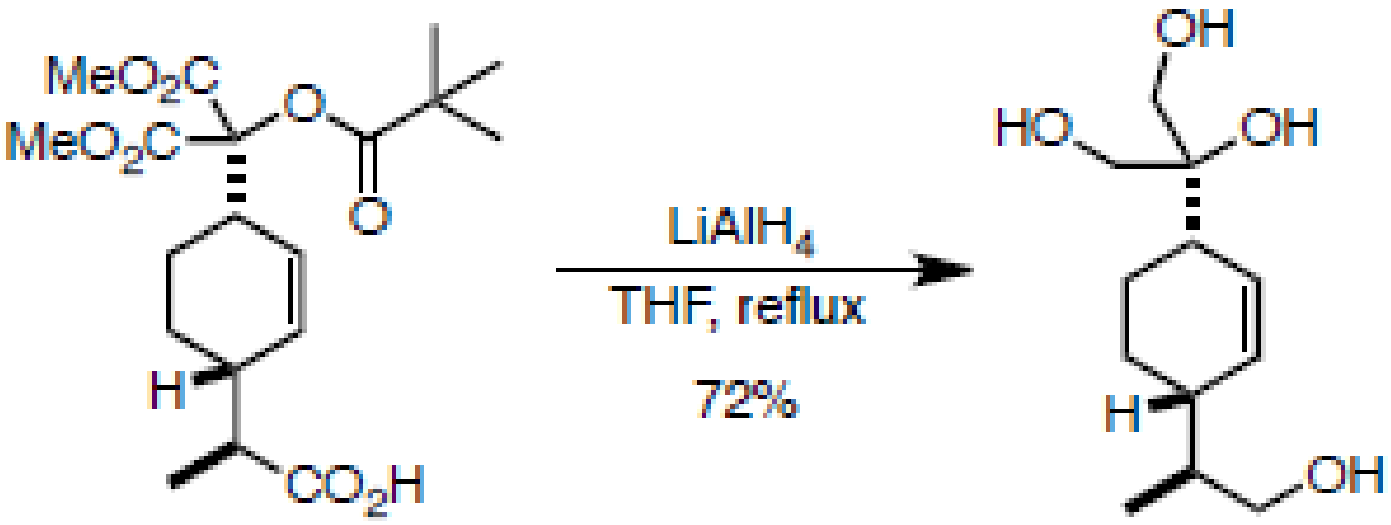
✓use with caution! Highly flammable solid!

✓one equivalent of LiAlH4 delivers 4 equivalents of hydride; still typically used in excess;

$LiAlH_4$...,

✓reduces carboxylic acids, esters, lactones, acid chlorides, anhydrides, aldehydes, ketones to give alcohols

✓reduces amides, lactams, nitriles, azides, aryl nitro groups to give amines.



For example
Hydride Reduction of Esters

✓Esters are easily reduced with $LiAlH_4$ to yield 1° alcohols;

➢Consider the possible mechanism

