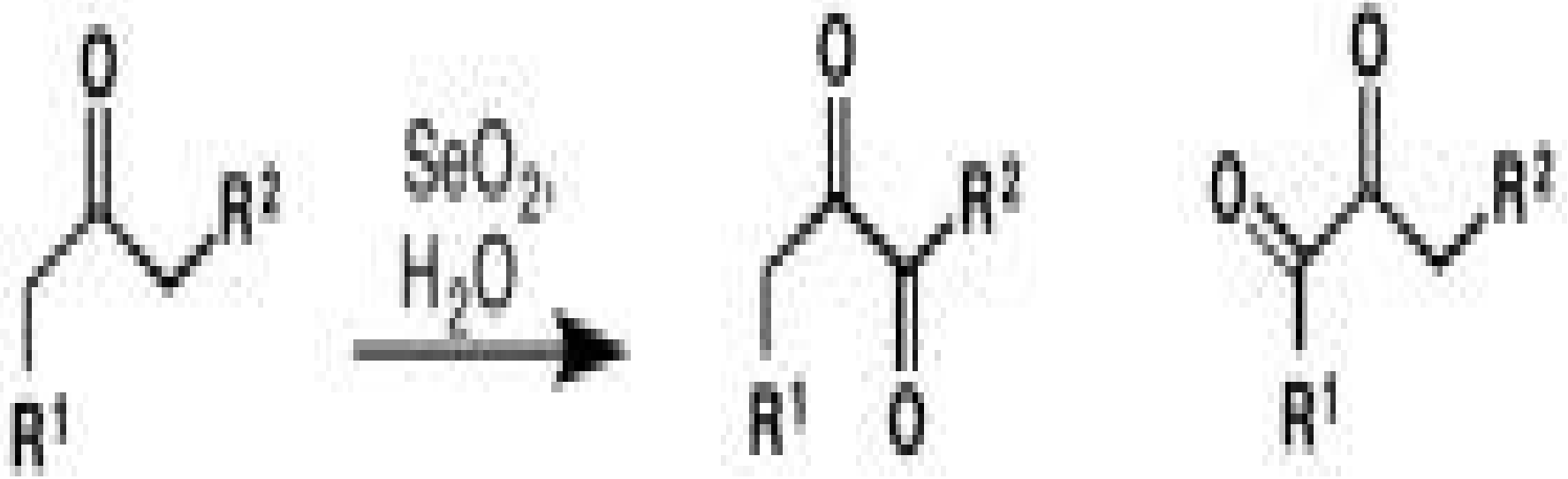
Allylic oxidation of olefins

- **The Riley oxidation is a selenium dioxide-mediated oxidation of** methylene **groups adjacent to carbonyls. It was first reported by Riley and co-workers in 1932. ... Today, selenium-dioxide-mediated oxidation of** methylene

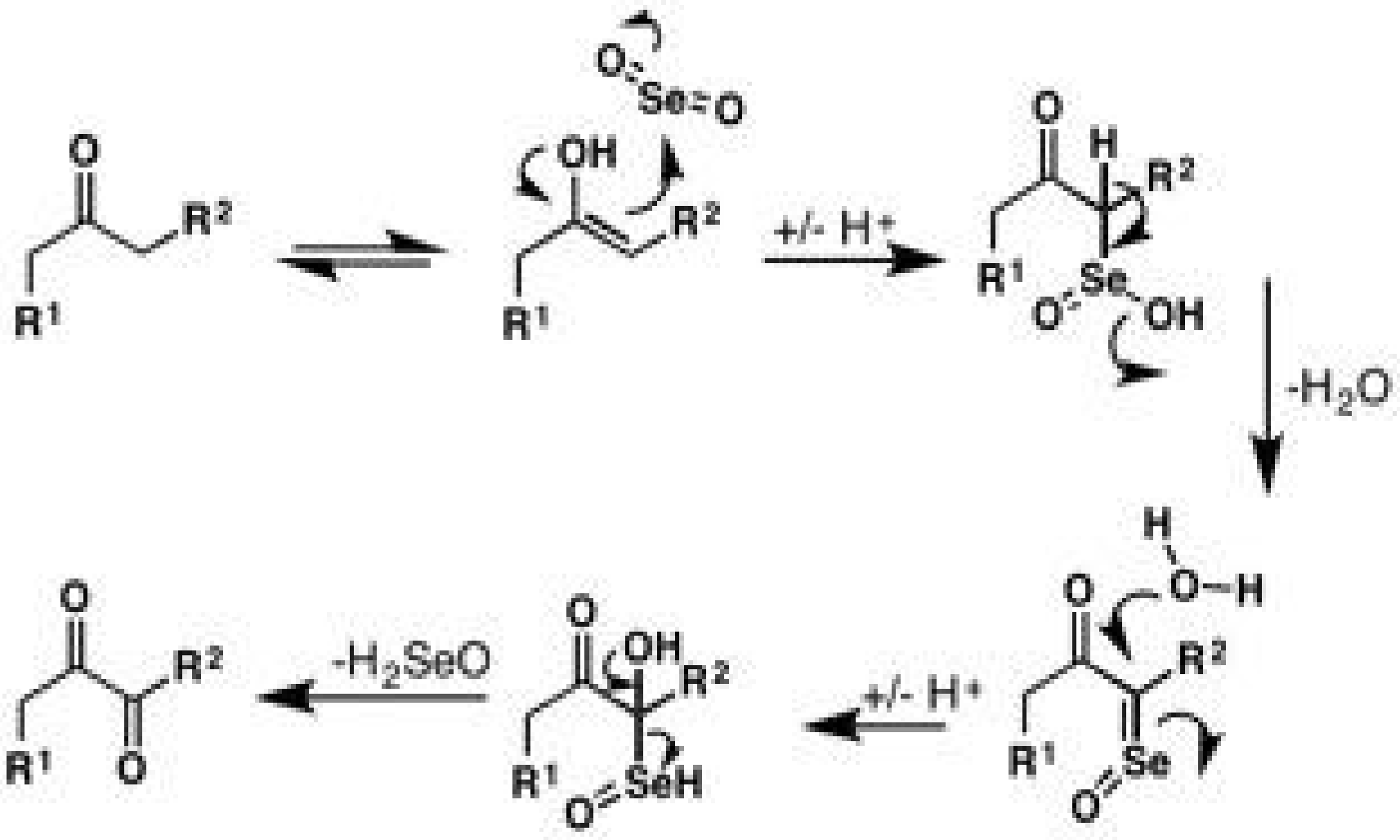

O
R2
R1
SeO2,
H2O
O
R2
R1
O
O
O
R2
R1

KETO

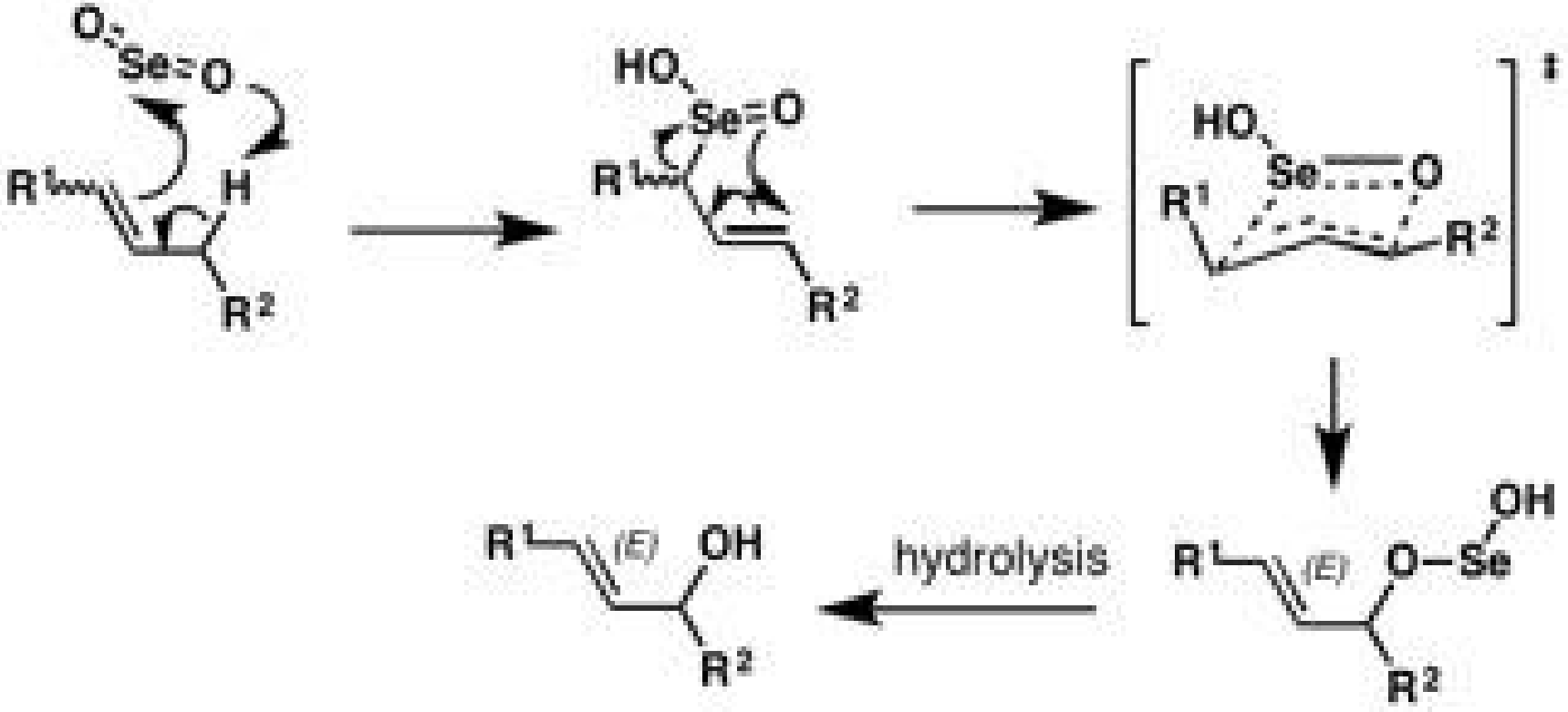
ENOL

MECHANISM

- The mechanism of oxidation of -CH2C(O)R group by SeO2 has been well investigated. The oxidation of carbonyl alpha methylene positions begins with attack by the enol tautomer at the electrophilic selenium center. Following rearrangement and loss of water, a second equivalent of water attacks the alpha position. Selenic acid is liberated in the final step to give the 1,2-dicarbonyl product.


O
R2
R1
O
Se=O
OH
R2
R1
+/- H+
O
H
R2
R1
Se
O
OH
-H2O
H
O
H
O
R2
R1
Se
O
+/- H+
O
OH
R2
R1
SeH
O
-H2SeO
O
R2
R1
O

- Allylic oxidation using selenium-dioxide proceeds via an ene reaction at the electrophilic selenium center. A 2,3-sigmatropic shift, proceeding through an envelope-like transition state, gives the allylselenite ester, which upon hydrolysis gives the allylic alcohol. The (E)- orientation about the double bond, a consequence of the


O
Se
O
H
R1
R2
HO
Se
O
R1
R2
HO
Se
O
R1
R2
‡
R1
(E)
O
Se
OH
R2
hydrolysis
R1
(E)
OH
R2

Application

- Selenium-dioxide mediated oxidation was used in the synthesis of the diterpenoid ryanodol.
- Selenium dioxide mediated allylic oxidation to access ingenol.

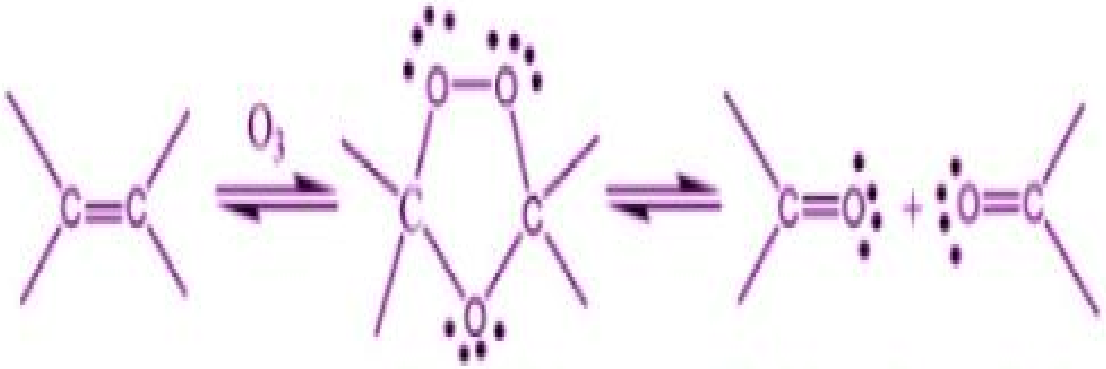
oxidative cleavage of double bonds

- **Ozonolysis** is a method of oxidatively **cleaving alkenes** or alkynes using ozone (O3), a reactive allotrope of oxygen. The process allows for carbon-carbon **double** or triple **bonds** to be replaced by **double bonds** with oxygen. This reaction is often used to identify the structure of unknown **alkenes**

- Ozone is a very reactive allotrope of oxygen. The reaction of ozone with alkenes and alkynes causes the oxidative cleaving of the alkene or alkyne. The carbon-carbon triple bonds are replaced with carbon-oxygen double bonds, giving the required carbonyl product as shown below.

Ozonolysis

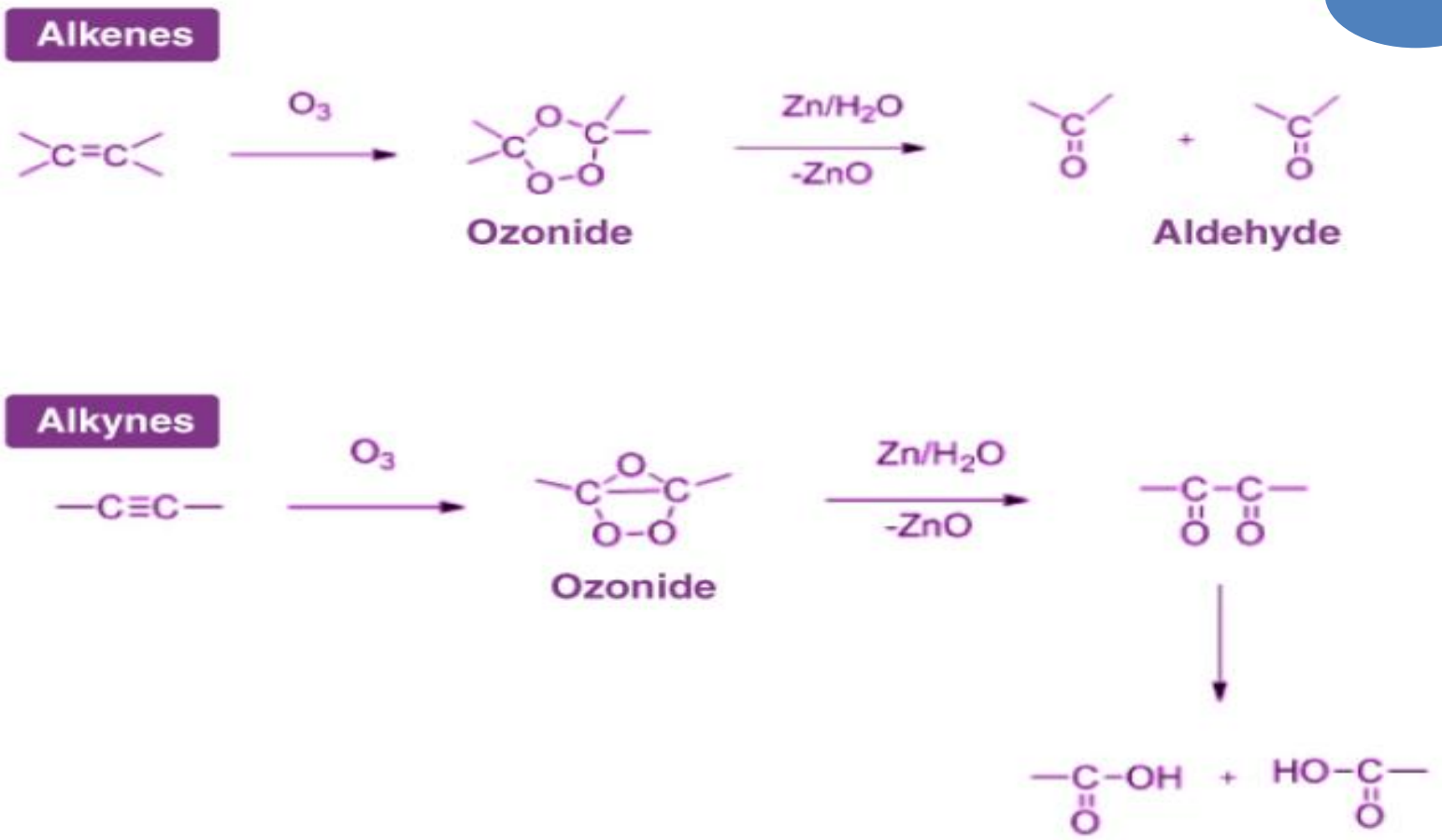
O3



Mechanism

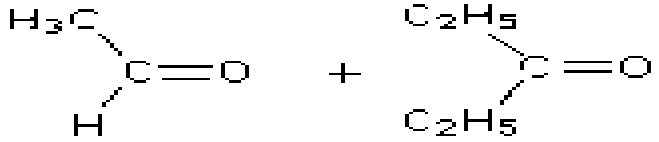
- Ozonolysis mechanism proceeds via an oxidative cleavage reaction.
- The ozone not only breaks the carbon pi bond but also the carbon-carbon sigma bond. It involves the attack of ozone on the given reactant to form an ozonide.
- To eliminate the oxygen in this intermediate stage, zinc dust is employed (since it forms zinc oxide with the oxygen).

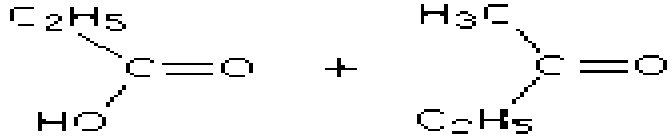
Mechanism


Alkenes
O3
Zn/H2O
-ZnO
Ozonide
Aldehyde
Alkynes
O3
Zn/H2O
-ZnO
Ozonide

- 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
- Since the overall change in ozonolysis is more complex than a simple addition reaction, its mechanism has been extensively studied. Reactive intermediates called ozonides have been isolated from the interaction of ozone with alkenes, and these unstable compounds may be converted to stable products by either a reductive workup (Zn dust in water or

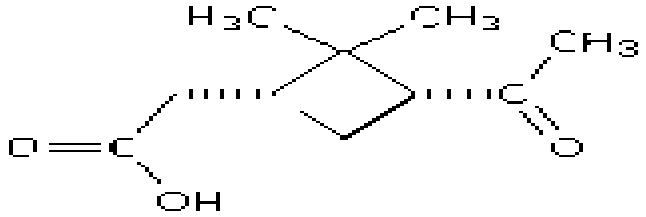
- From this analysis and the examples given here, you should be able to deduce structural formulas for the alkenes that give the following ozonolysis products

A C_7H_{14} — 1) O_3 in $CHCl_3$; 2) Zn dust → 

B C_7H_{14} Two Isomers — 1) O_3 in $CHCl_3$; 2) H_2O_2 → 

C C_8H_{14} — 1) O_3 in $CHCl_3$; 2) H_2O_2 or Zn dust → 

D $C_{10}H_{16}$ — 1) O_3 in $CHCl_3$; 2) H_2O_2 → 

E $C_{10}H_{16}$ — 1) O_3 in $CHCl_3$; 2) H_2O_2 → 

F C_8H_{12} — 1) O_3 in $CHCl_3$; 2) H_2O_2 or Zn dust →