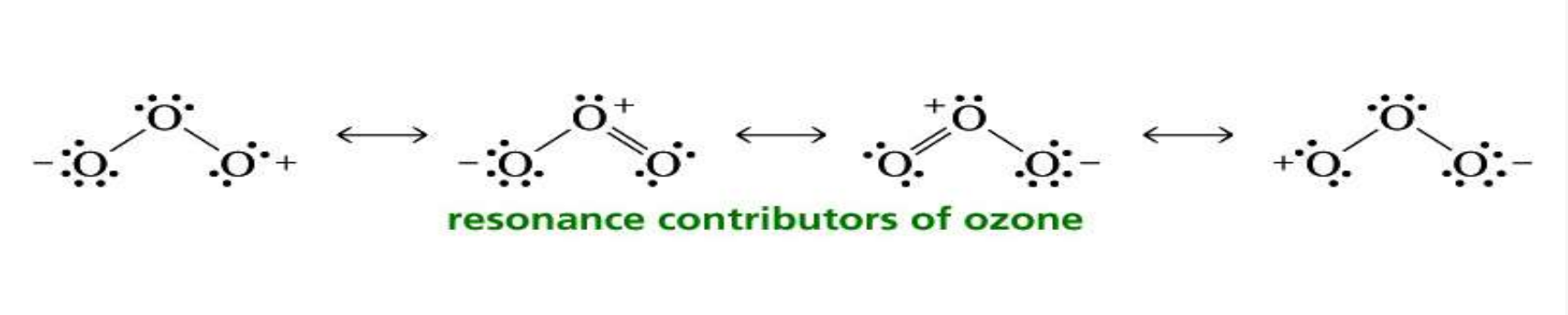
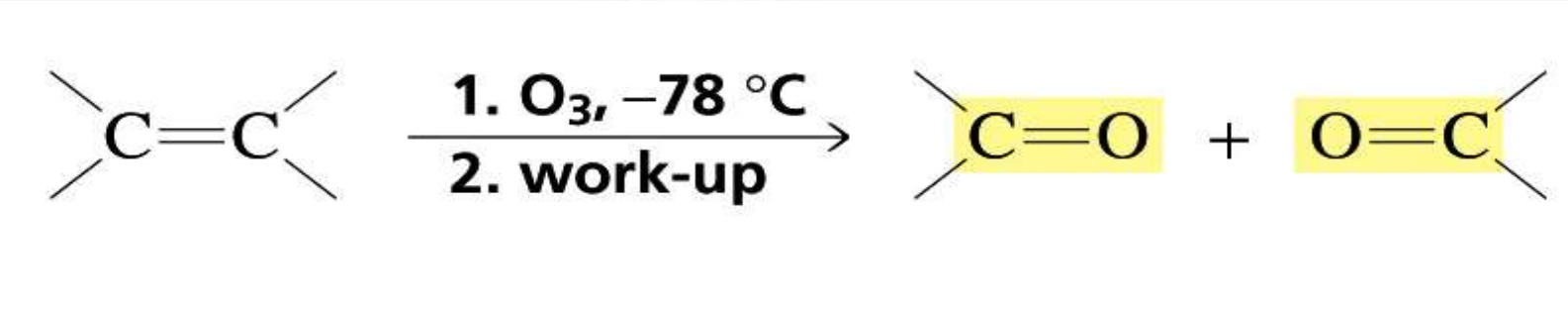
Oxidation Reactions: Ozonolysis and Bayer-Villiger Reaction

TOPICS TO BE COVERED

- Ozonolysis reaction
- Mechanism of Ozonolysis
- Epoxidation of alkene
- Baeyer–Villiger Oxidation and Mechanism
- Examples of Different Reaction

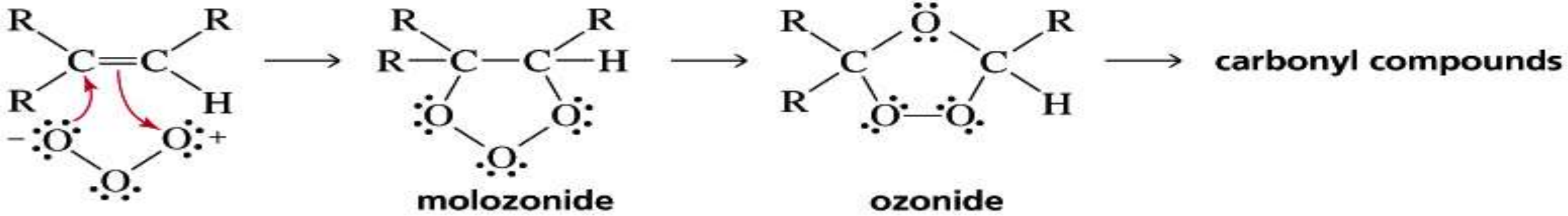
Oxidative Cleavage of Alkenes by Ozonolysis



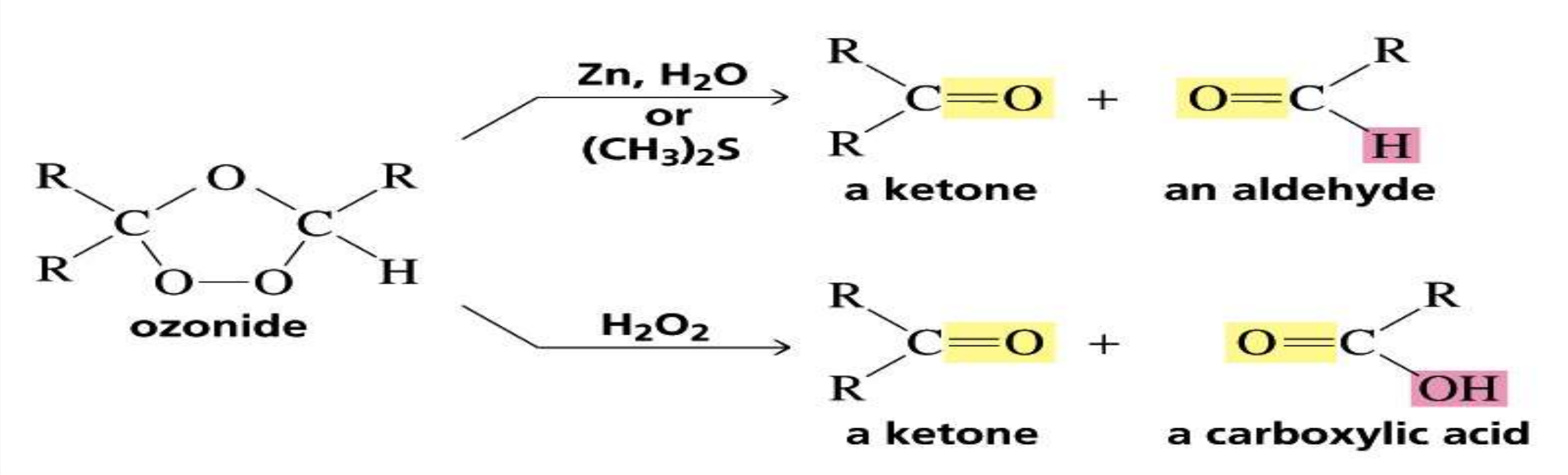


Mechanism of Ozonolysis

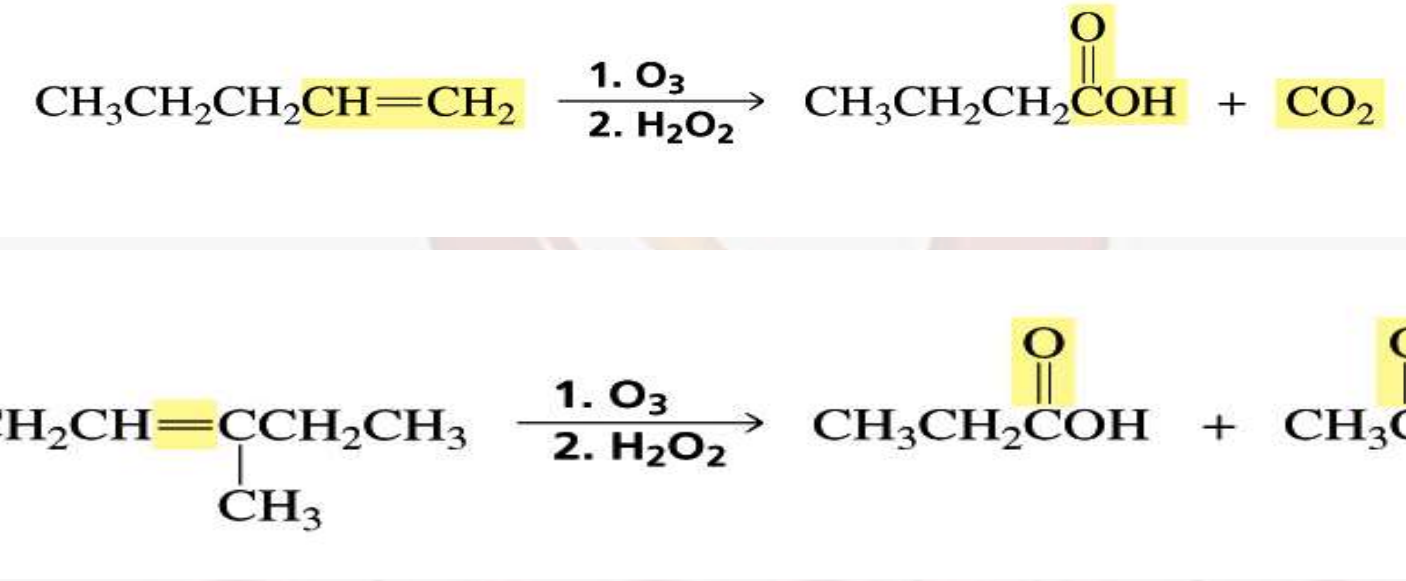
The alkene and ozone will undergo a concerted cycloaddition reaction to form molozonide. Molozonide is unstable as it has two O-O bonds, so rearranges to form stable ozonide.



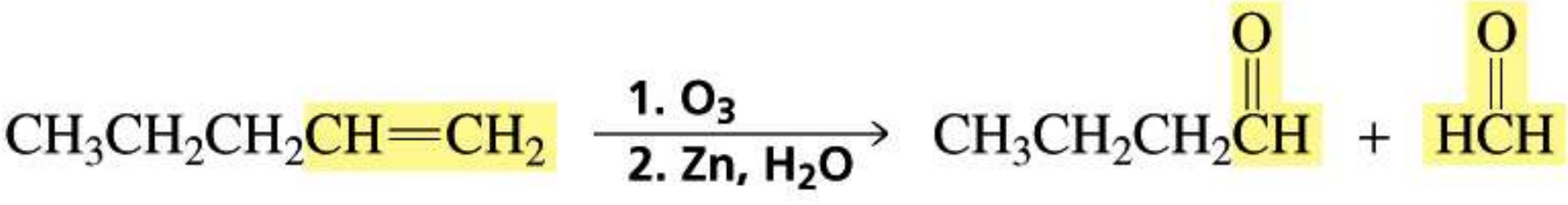
Ozonides can be cleaved to carbonyl compounds by oxidative cleavage in presence of H_2O_2 and reductive cleavage in presence of Zn/H_2O.

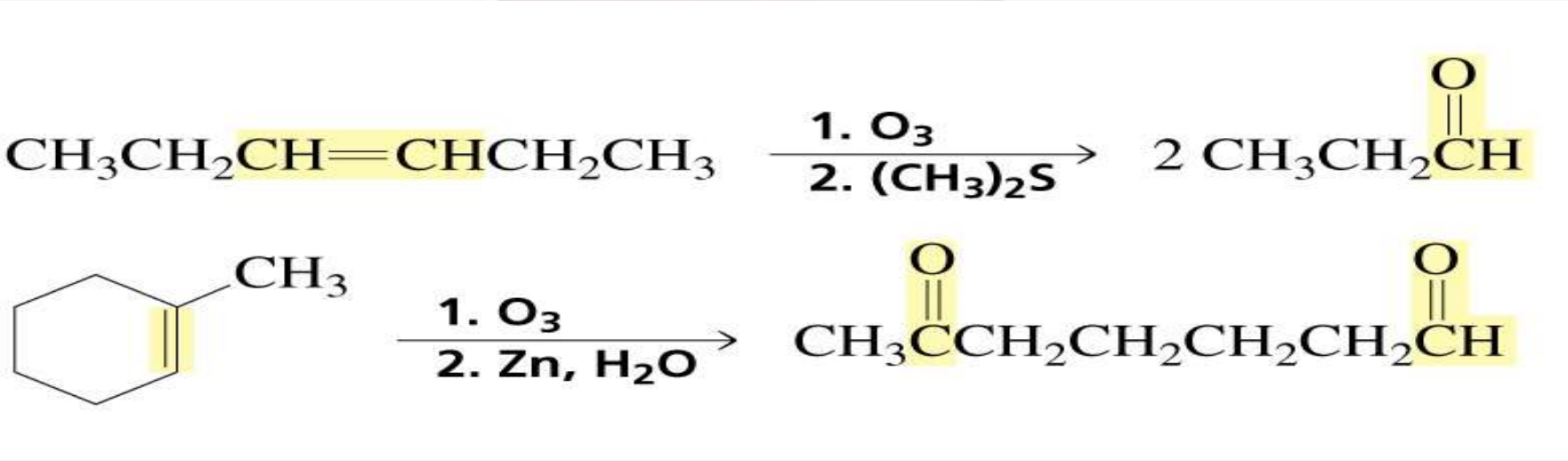


Examples of the Oxidative Cleavage of Alkenes by Ozonolysis

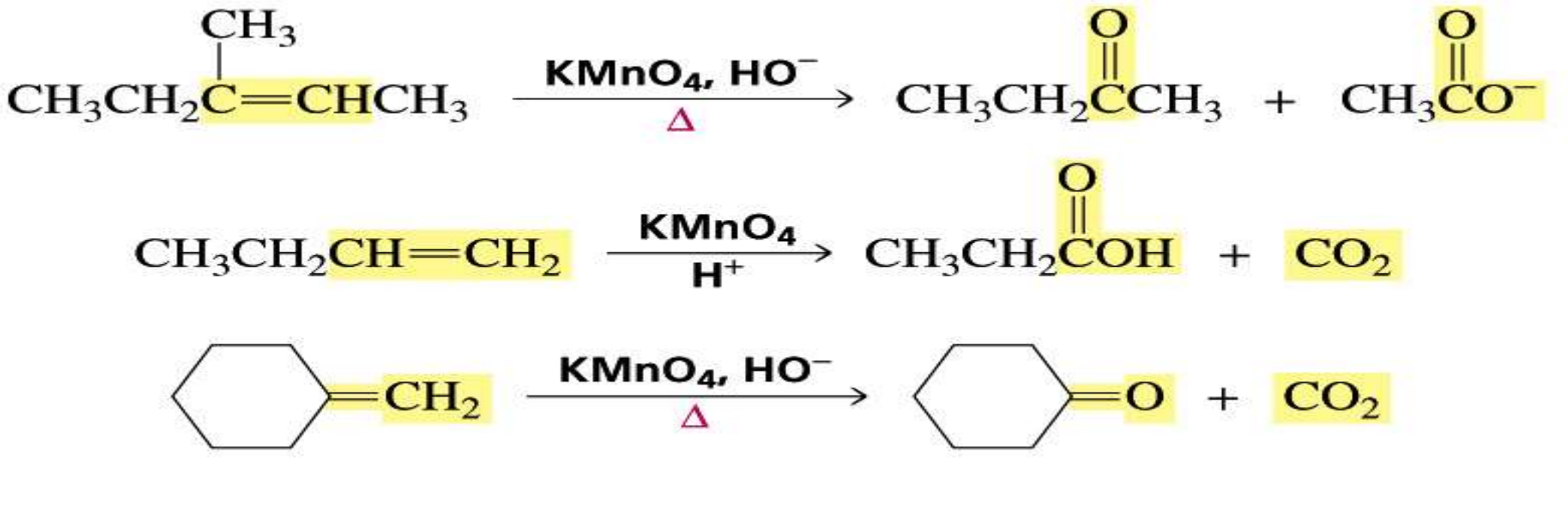


Examples of the Reductive Cleavage of Alkenes by Ozonolysis

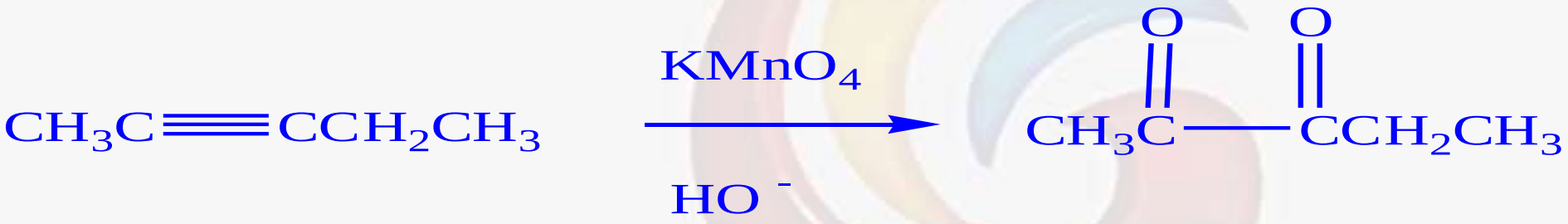


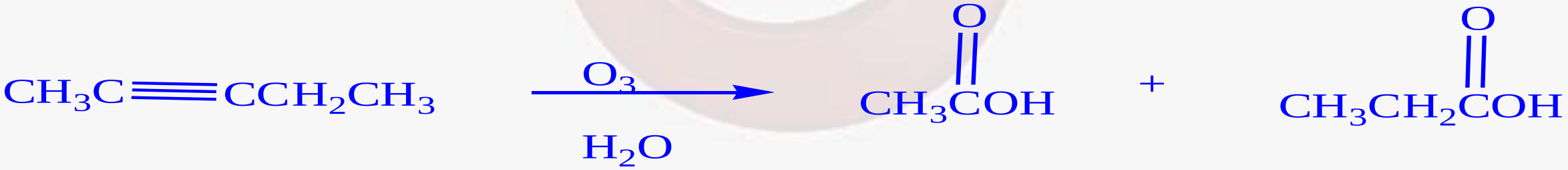


A peroxyacid, OsO_4, and (cold basic) $KMnO_4$ break only the p bond of the alkene. Ozone and acidic $KMnO_4$ break both the p bond and the s bond

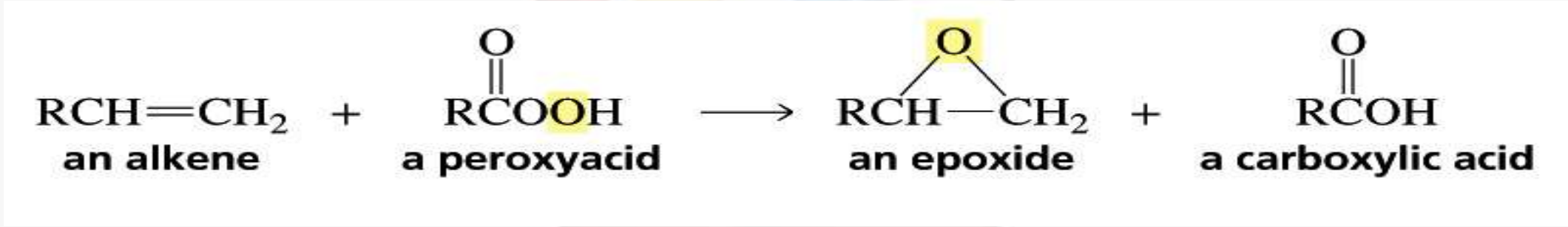


Oxidative Cleavage of Alkynes

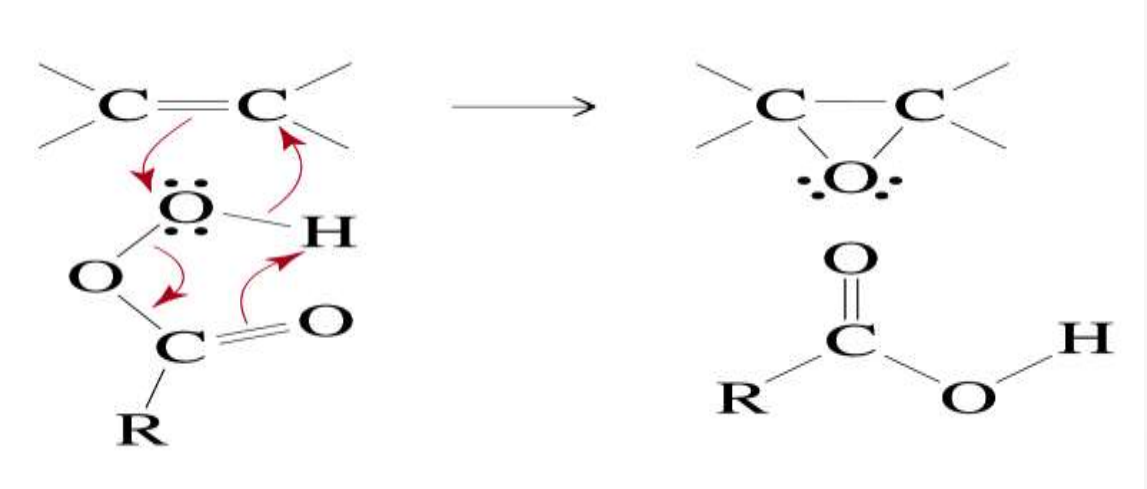




Oxidation of Alkenes with Peroxyacids

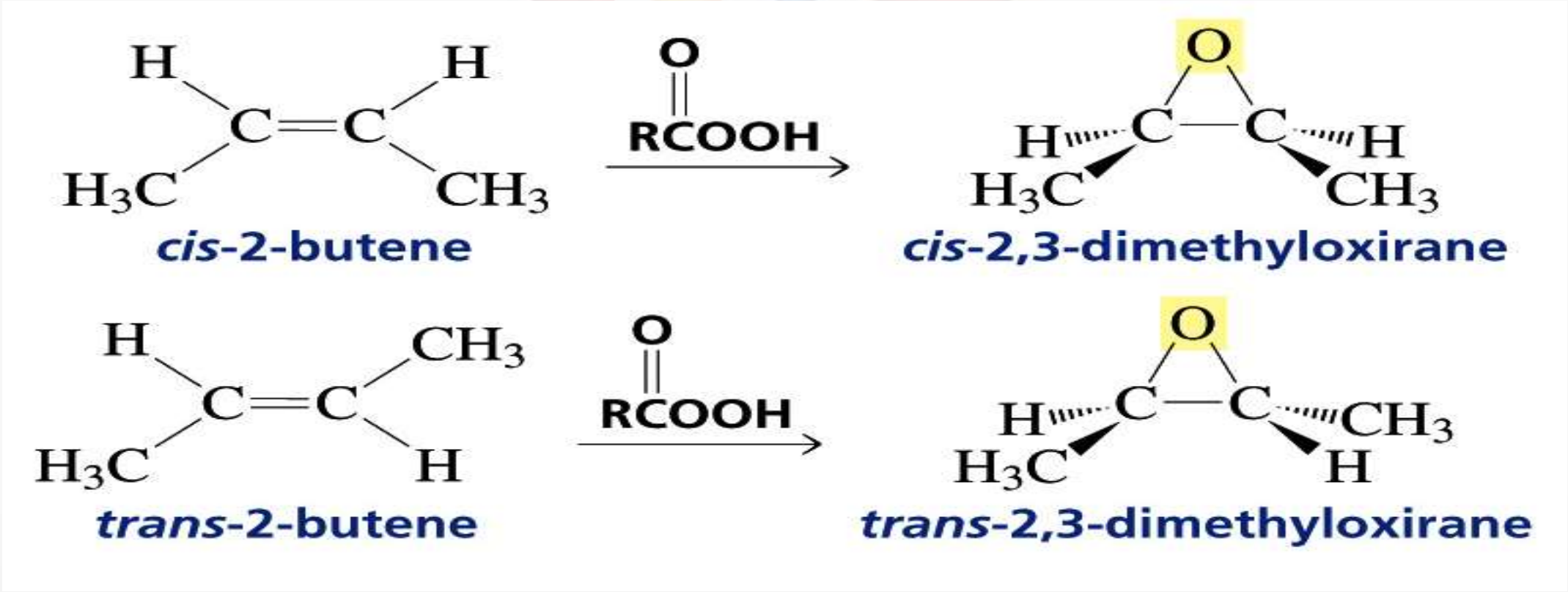


Mechanism of Epoxidation of an Alkene



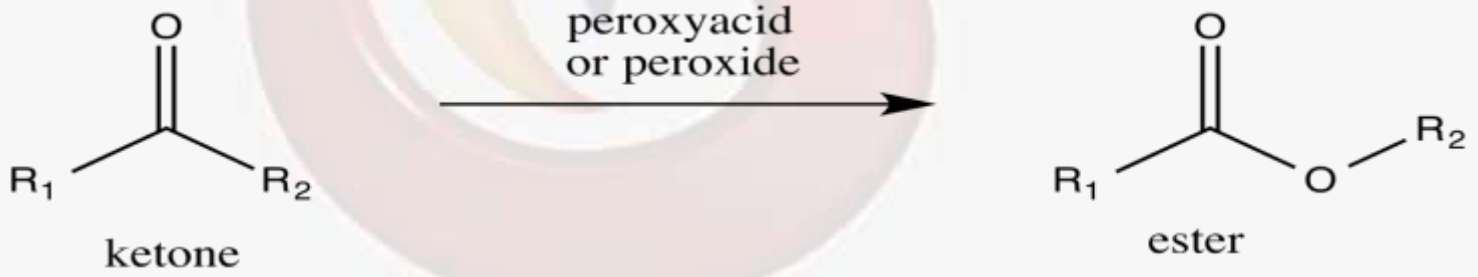
Stereochemistry of Epoxidation of alkene

The addition of oxygen to an alkene is a stereospecific reaction.

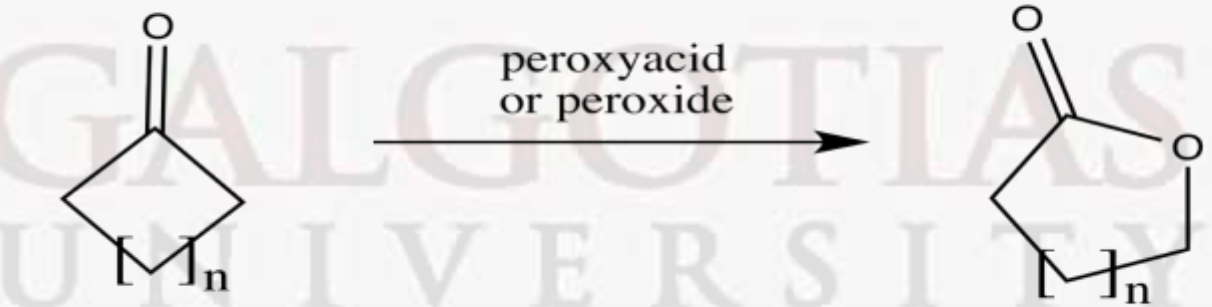


Baeyer–Villiger Oxidation

Ketones on oxidation with peracids converted into esters and cyclic ketones into lactones. This reaction was discovered by Bayer and Villiger in 1899.



ketone ester



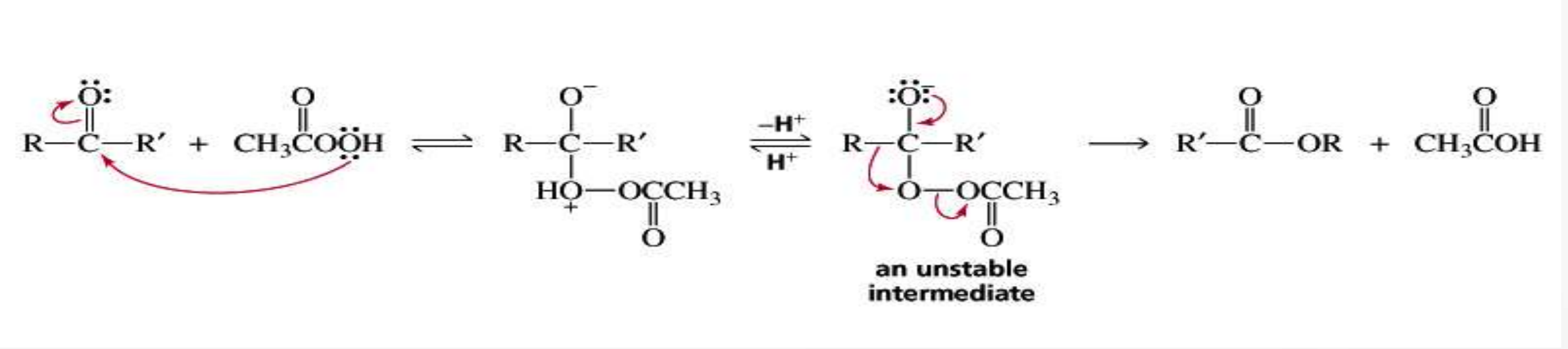
cyclic ketone lactone

Mechanism of Baeyer–Villiger Oxidation

Reagents used to carry out this reaction is peracetic acid, perbenzoic acid and m-CPBA.

The oxygen of peracid behaves as anucleophile and adds to the carbonyl carbon of ketone.

This reaction proceeds by a concerted intramolecular process involving migration of a group from carbon to electron deficient oxygen.



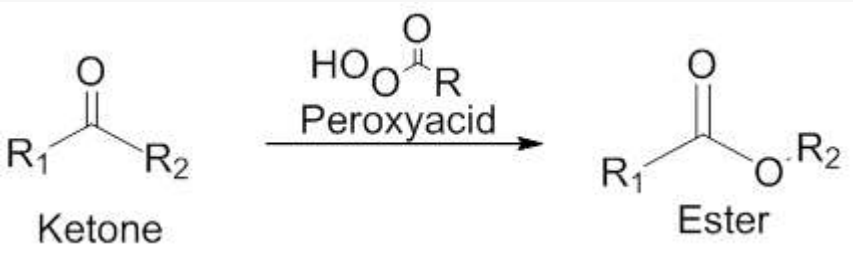
Migratory ability of groups in Baeyer–Villiger Oxidation

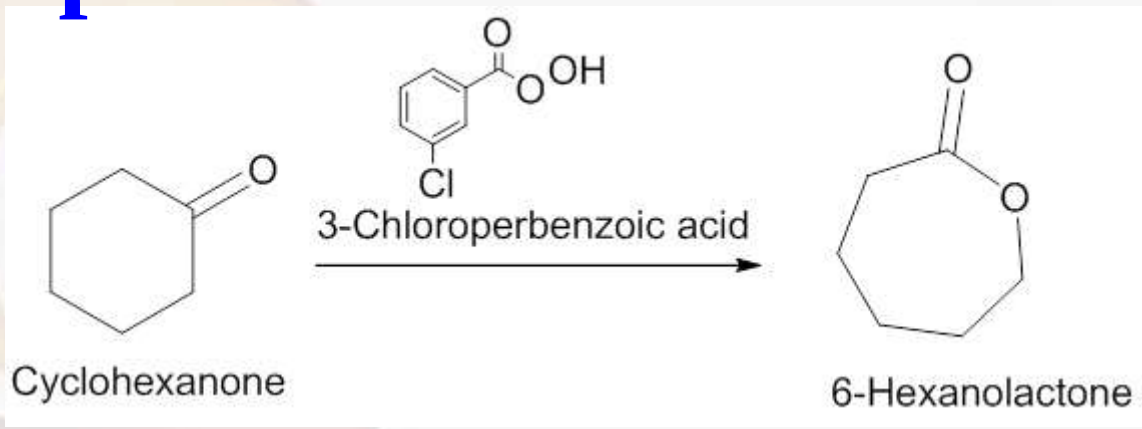
An unsymmetrical ketone may give two different products due to migration of different groups. But the group with highest migratory ability will migrate fast to give predominant product.

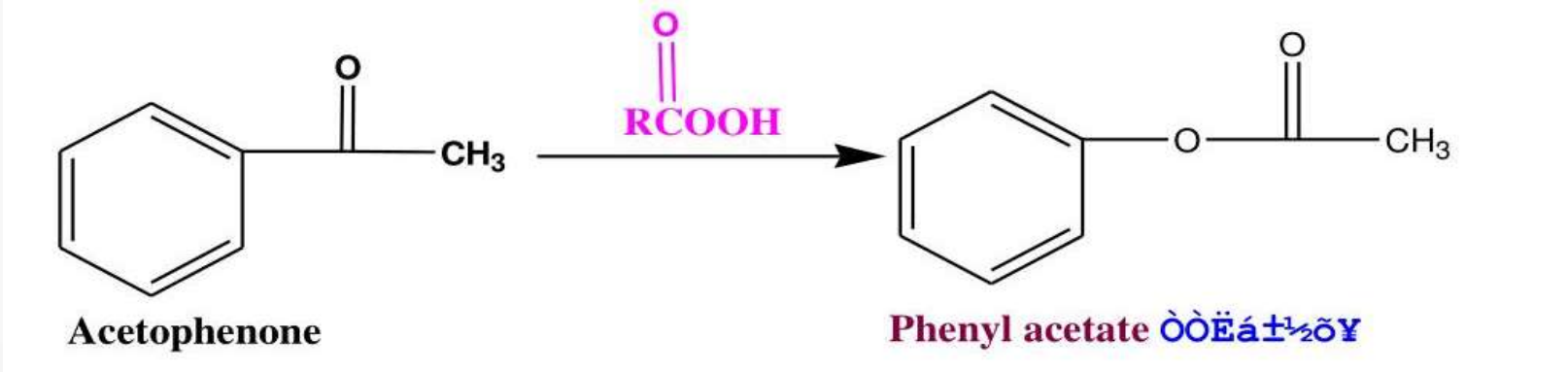
relative migration tendencies

H > *tert*-alkyl > *sec*-alkyl = phenyl > primary alkyl > methyl

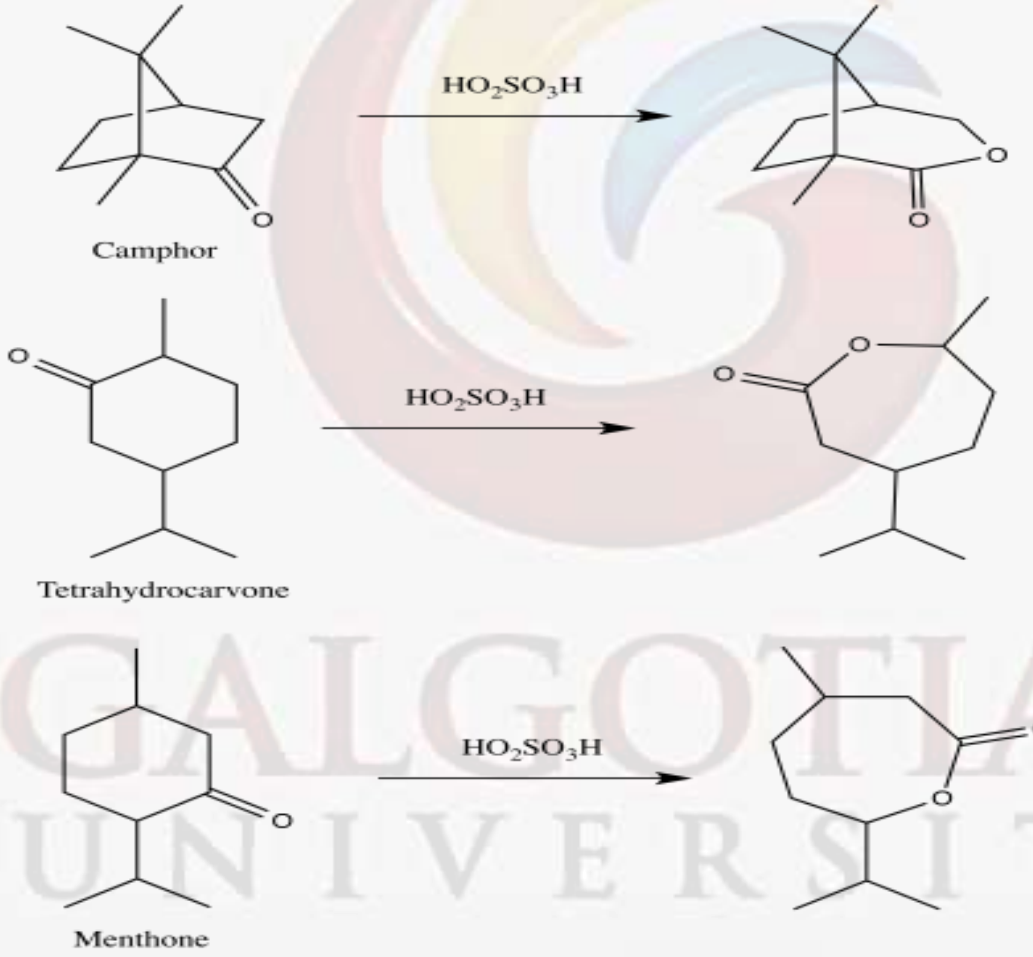
Examples


O
R1
R2
Ketone
HO
O
O
R
Peroxyacid
O
R1
O
R2
Ester

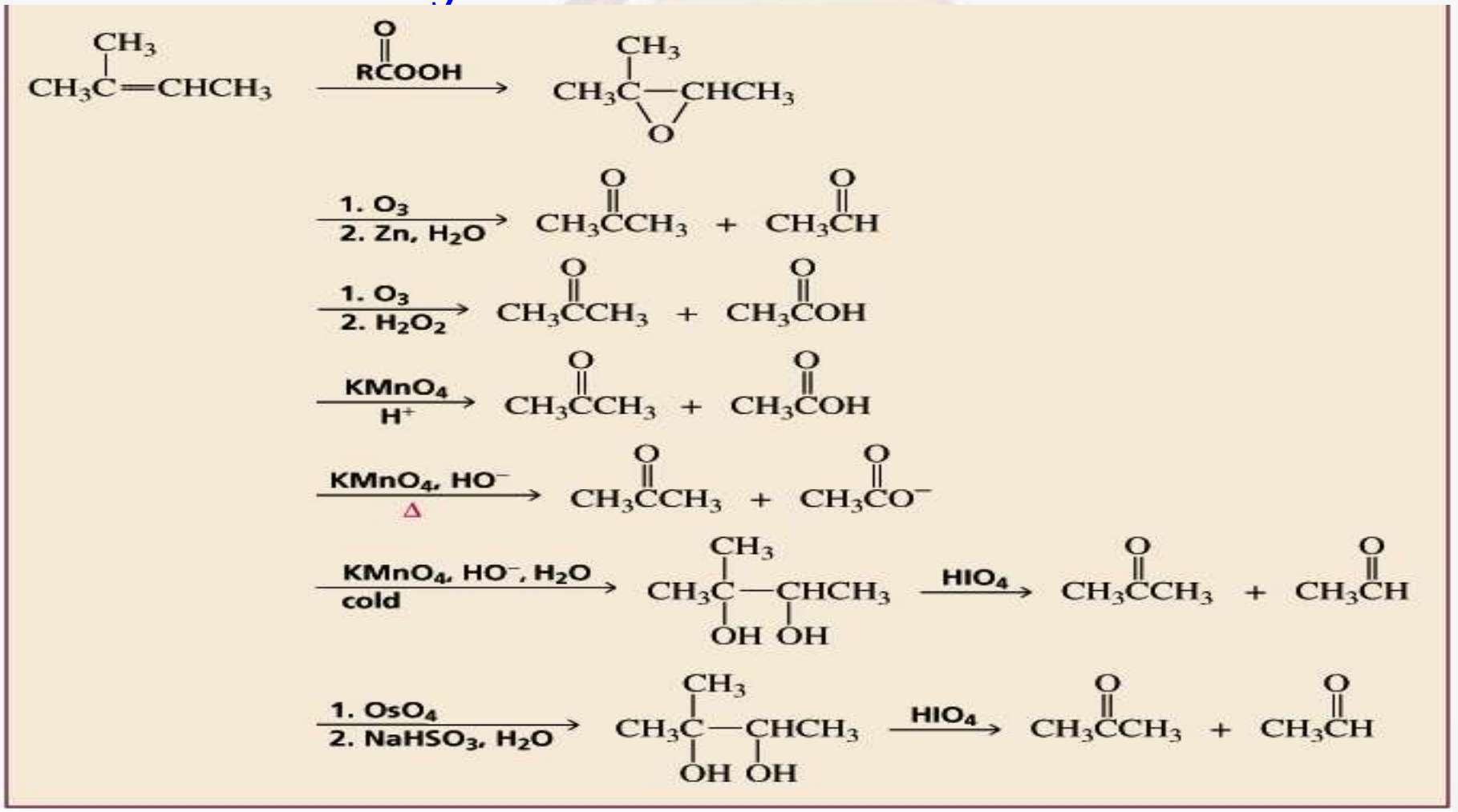

O
Cyclohexanone
O
OH
O
Cl
3-Chloroperbenzoic acid
O
O
6-Hexanolactone


O
CH3
Acetophenone
O
RCOOH
O
O
CH3
Phenyl acetate ÒÒËá±½õ¥

Examples


HO2SO3H
Camphor
HO2SO3H
Tetrahydrocarvone
HO2SO3H
Menthone

Summary of Oxidation of Alkenes



References

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- J. Clayden, N. Greeves and S. Warren, Organic Chemistry, Oxford University Press, 2nd edition, 2012.
- T.L. Gilchrist, Heterocyclic Chemistry, 3rd edition, Addison-Wesley Longman Ltd., England, 1997.

- https://www.google.com/search?q=baeyer-villiger+oxidation+ppt&source=lmns&bih=625&biw=1366&rlz=1C1CHBD_enIN920IN920&hl=en&sa=X&ved=2ahUKEwiV-r3UoZ3sAhUtJLcAHQXNBAUQ_AUoAHoECAEQAA