

## Module 1

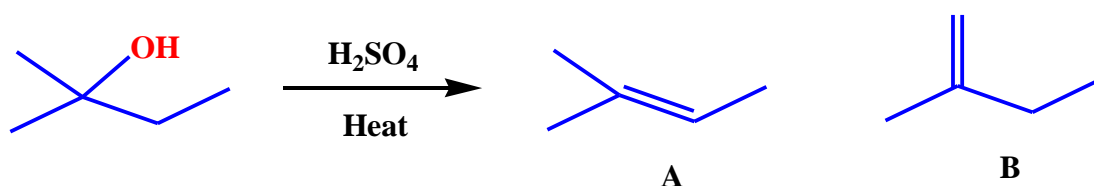
# Regioselective, Regio-specific and Chemoselective reactions

### 1. Regioselective and Regiospecific reactions

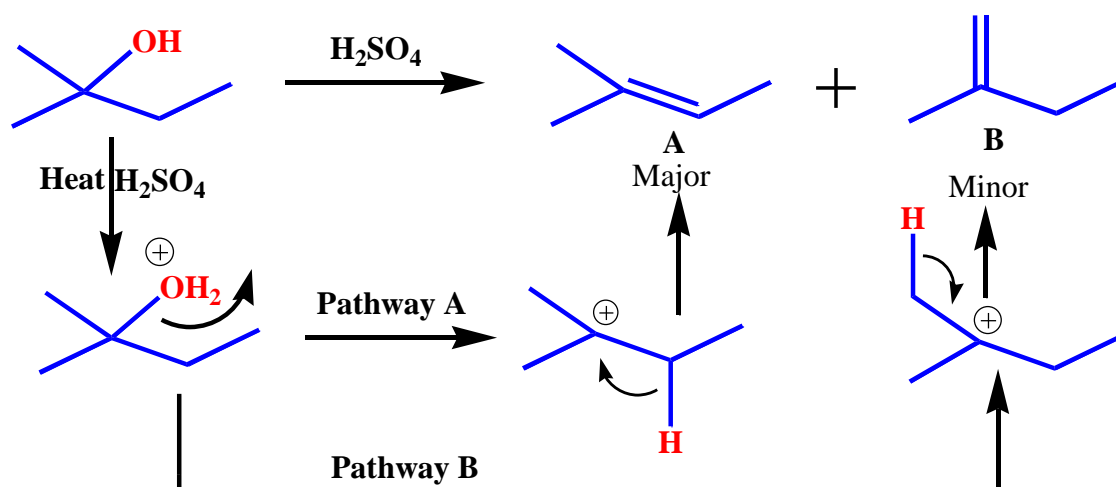
Suppose, you are walking 100 metre distance in a straight path and you suddenly find two different routes A and B from the same starting point. After walking 100 metres on route A, you find the house of your friend A and after walking 100 metres on route B, you find the house of your friend B. If you analyze the situation, then you are providing the same physical effort and energy to walk 100 metres in two different routes, and you are getting two targets, houses of friend A and friend B.

For chemical reactions, you can start with the same starting materials and reaction conditions, and the reactants can react with each other via different pathways. Each pathway will lead us to different product.

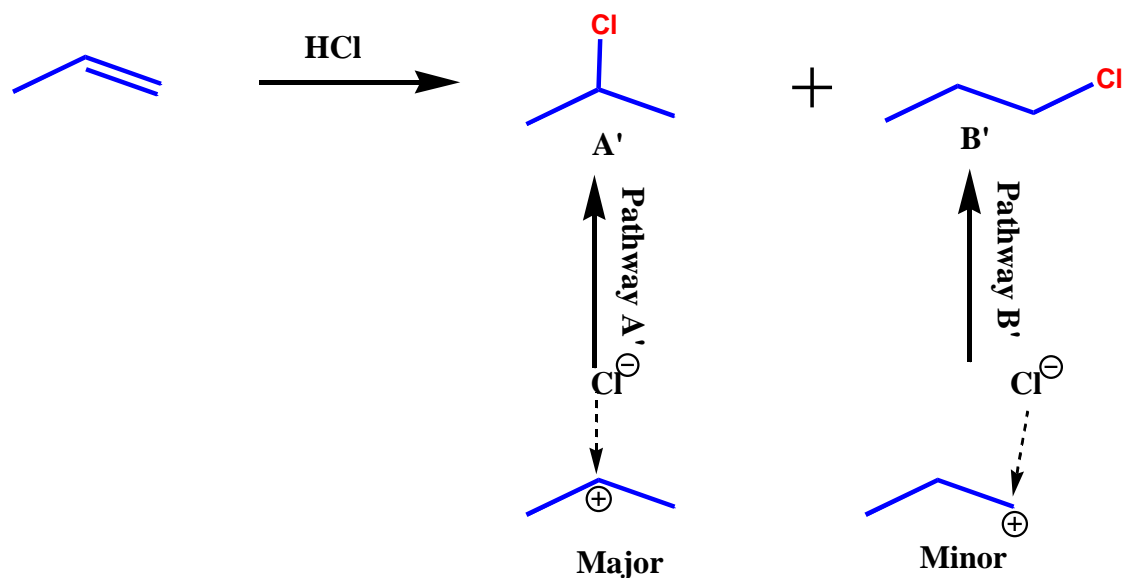
Let us take the following example:



In the above reaction after heating the alcohol with sulphuric acid, we get two products A and B, which have different position of double bonds. Product A, which is the tri-substituted alkene is the major product and Product B is the minor product. They differ by the position of double bond and are generated by two different pathways, Pathway A and Pathway B as shown below:

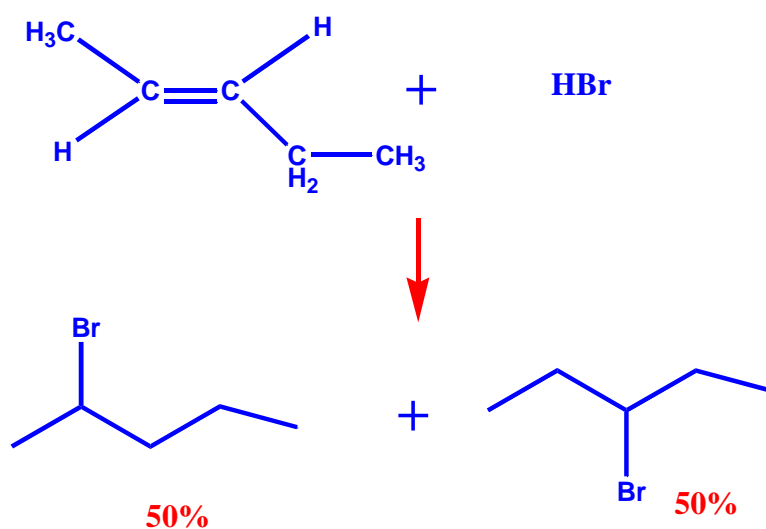


Let us take another example as shown below:



In the second example, 2-chloropropane, A' is the major product. Here, pathway A' involves a secondary carbocation, which is more stable than the primary carbocation formed in pathway B'. So, we get two different products A' and B', by two different pathways and product A' is formed in greater proportion than product B'. If a reaction takes place on an unsymmetrical compound and more than one reacting pathways are possible due to site selectivity of one functional group in a reaction, then the reaction is called **regiochemical reaction**.

Now, all regiochemical reactions are not regioselective. For example, consider the following reaction:



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In this case, the reaction is regiochemical as it can occur by two different pathways. But, the reaction is not regioselective as the two products are formed in equal proportions and no product is major product for this reaction.

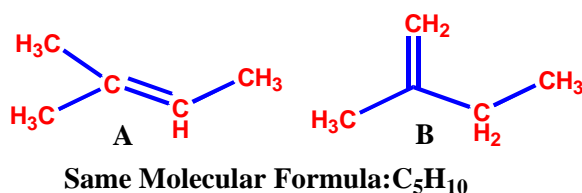
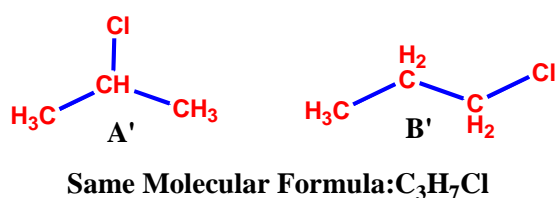
Thus, If out of the several pathways, one pathway predominates, then the reaction is called **regioselective reaction**. In regioselective reactions, if only one product is formed exclusively, then the reaction is called **regiospecific reaction**.

**Regiochemistry** is the study of different pathways that two reactants can take during a reaction.

In the first example, products A and B are called regioisomers and in the second example, products A' and B' are regioisomers of each other. Now why these are called regioisomers? It is because, they are formed by two different pathways of a regiochemical reaction. Now, let us study what is the nature of isomerism present in case of regioisomers.

Do you remember the term **constitutional isomers**?

**Constitutional isomers** are compounds that have the same molecular formula and different connectivity. Regioisomers are constitutional isomers. So, regioisomers will be generated from the same chemical reaction, they will have the different bond connectivity and the same chemical formula.



It is clearly evident that A and B have the same molecular formula, but different bond connectivity, and they are formed by two different pathways of one chemical reaction. Hence, they are regioisomers of each other. Similarly, A' & B' are also the regioisomers.

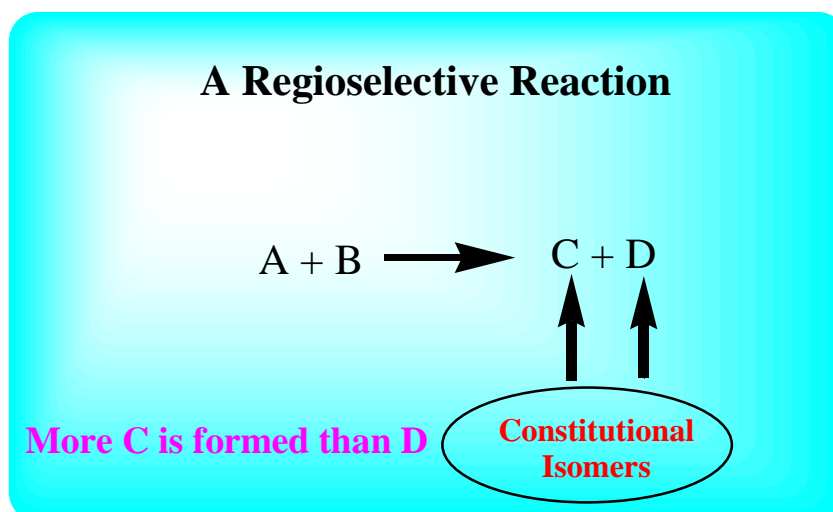
We can define regioselectivity as follows:

*Regioselectivity is a type of substrate selectivity in which substrates have the capability to react at more than one centre but react at one centre at a higher rate than the other. For example, 2-methylcyclohexanone on base induced alkylation gives mostly 2,2-dimethylcyclohexanone and only small amount of 2,6-dimethylcyclohexanone.*

Thus, If we add a non-symmetrical reagent (i.e. A-B where A is not equal to B) to non-symmetrical starting materials (think an alkene, where the groups at each end of the double bond are different), then two isomeric products that are constitutional isomers can be obtained. The reaction is regiochemical reaction. If one product predominates over the other, then it is called regioselective.

According to IUPAC Gold Book,

"A regioselective reaction is one in which one direction of bond making or breaking occurs preferentially over all other possible directions. Reactions are termed completely (100%) regioselective if the discrimination is complete, or partially (x%), if the product of reaction at one site predominates over the product of reaction at other sites."



### Self Check Exercise

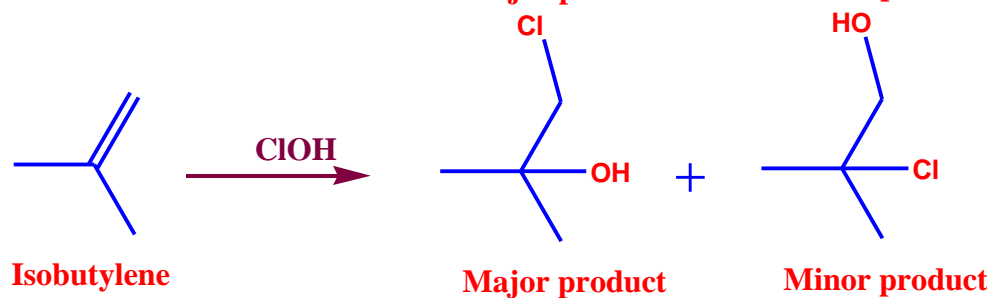
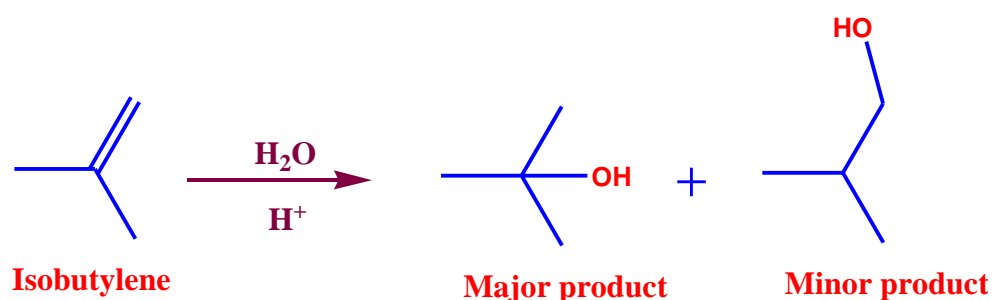
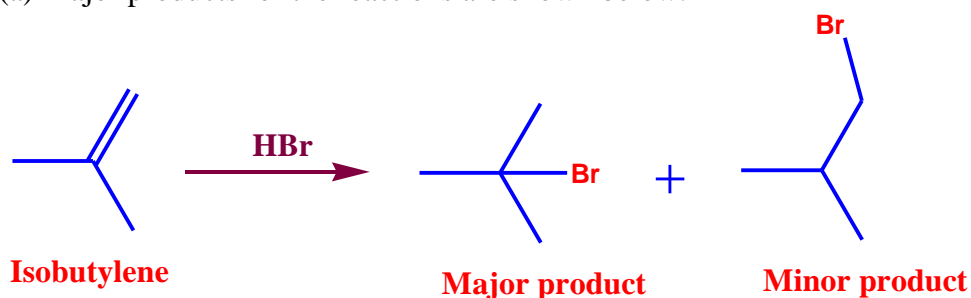
**1.(a) Write the major product from the reaction of an unsymmetrical alkene, such as isobutylene, with the following unsymmetrical addenda:**

(i) HBr, (ii) H<sub>2</sub>O(H<sup>+</sup>) and (iii) ClOH

(b) State the rule for getting the correct answers to part (a)

(c) Give the general name for the reactions that give one of several possible products.

Ans: (a) Major products for the reactions are shown below:



(b) Answers to part (a) were obtained according to Markownikoff's rule. The rule states that E<sup>+</sup> will be added to the double bonded carbon that has more hydrogens. This will be followed by addition of the Nu<sup>-</sup> to the carbon having less hydrogens.

(c) The general name of reactions which provide only one of the several possible products is regioselective reaction. If the reaction provides one major product and other minor products, then the reaction is called regioselective reaction.

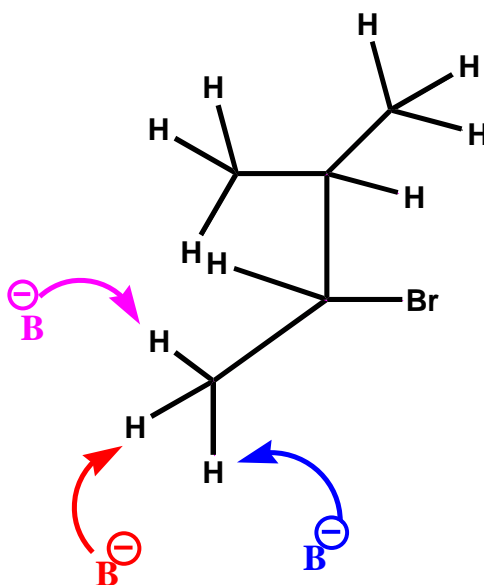
**E2 reaction is regioselective in nature. Let us explain how?**

Generally, in a E2 reaction, we have a halide and a proton to be removed and form a double bond. Now, if there are option of two protons to be removed, then the two options might lead to two different products. Thus, such reactions can have different regiochemical outcomes, which means the reaction can occur at two different places of the molecule.

The removal of proton in E2 generally leads to the most-substituted alkene as the major product. However, steric factor is also important for removal of proton.

If the hydrogen leading to more substituted double bond is crowded and not easy to approach, then the base approaches other proton more easily which is less crowded.

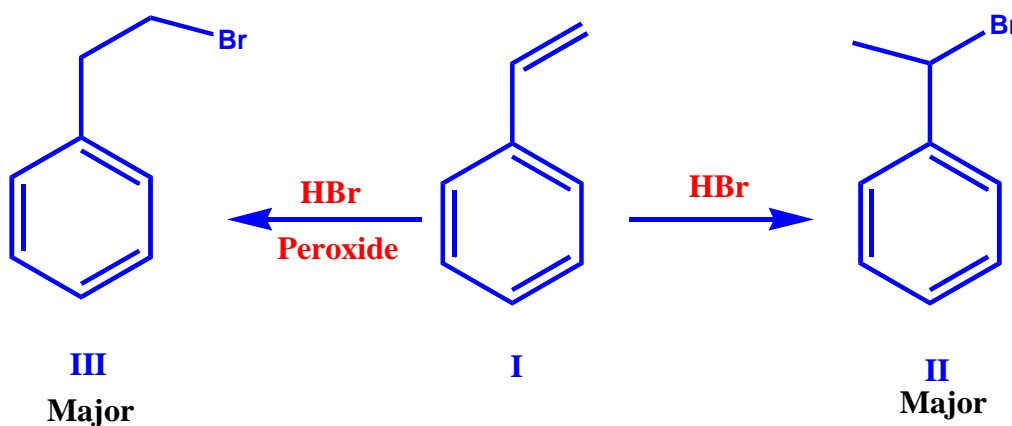
If the bases have a bulky structure, then in some cases, the least substituted alkene is formed as the major product.



Now, let us study regioselectivity observed in some commonly known reactions such as addition reactions, hydration, epoxidation, electrophilic substitution, Diels Alder reaction and 1,3-Dipolar cycloaddition reactions.

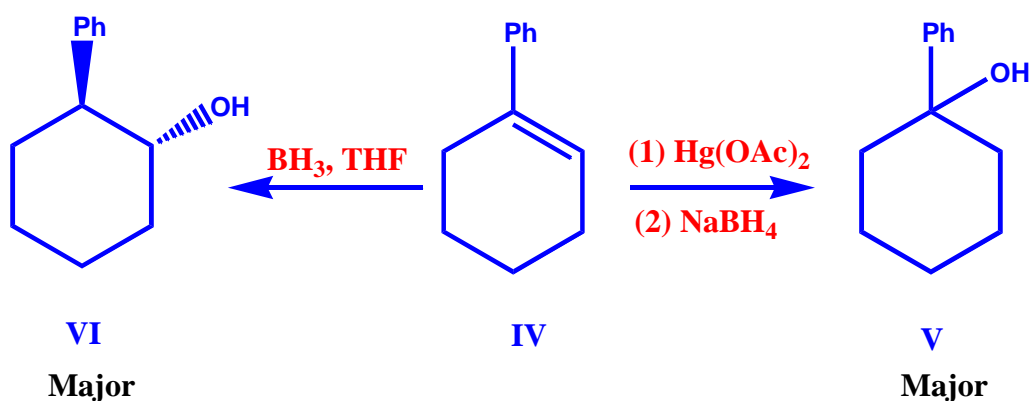
*(a) Addition of HBr to alkenes*

When compound I reacts with HBr, it gives II as the major product and when compound I reacts with HBr in presence of peroxide, it gives III as the major product. Both these reactions are regioselective. **In case of regioselective reactions, there is preferential reactivity of one site over the other of the same functional group, which is the olefinic double bond in this case.**



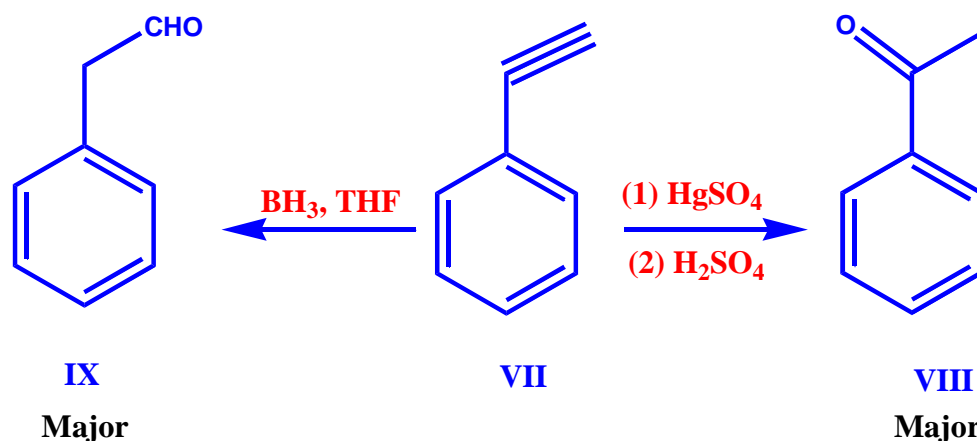
*(b) Hydration of alkenes*

When compound IV reacts with  $\text{Hg}(\text{OAc})_2$  followed by  $\text{NaBH}_4$ , it gives V as the major product and when compound IV reacts with  $\text{BH}_3 \cdot \text{THF}$ , it gives VI as the major product. Both these reactions are regioselective. **In case of regioselective reactions, there is preferential reactivity of one site over the other of the same functional group, which is the olefinic double bond in this case.**



*(c) Hydration of alkynes*

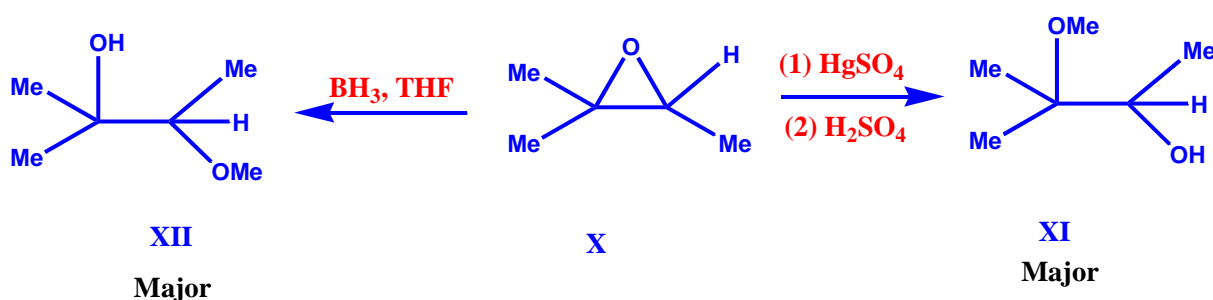
When compound VII reacts with  $\text{HgSO}_4/\text{H}_2\text{SO}_4$ , it gives VIII as the major product and when compound VII reacts with  $\text{BH}_3\cdot\text{THF}$  followed by  $\text{NaOH}/\text{H}_2\text{O}_2$ , it gives IX as the major product. Both these reactions are regioselective. **In case of regioselective reactions, there is preferential reactivity of one site over the other of the same functional group, which is the alkyne functional group in this case.**



*(c) Epoxide Opening*

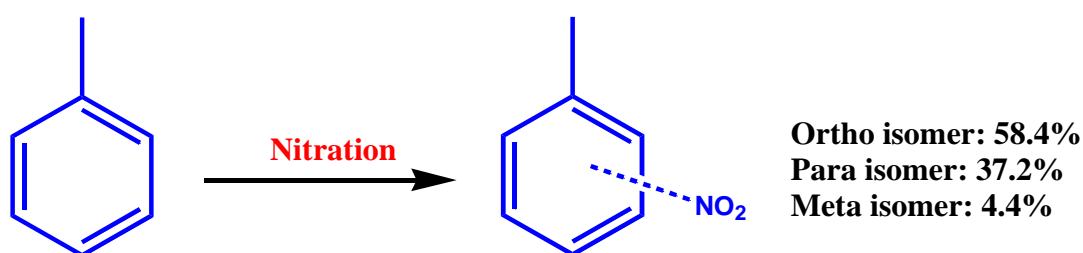
When compound X reacts under acidic condition, it gives XI as the major product and when it reacts under alkaline condition, it gives XII as the major product. **In case of regioselective reactions, there is preferential reactivity of one site over the other of the same functional group, which is the epoxide functional group in this case.**





#### (d) Aromatic Electrophilic substitution

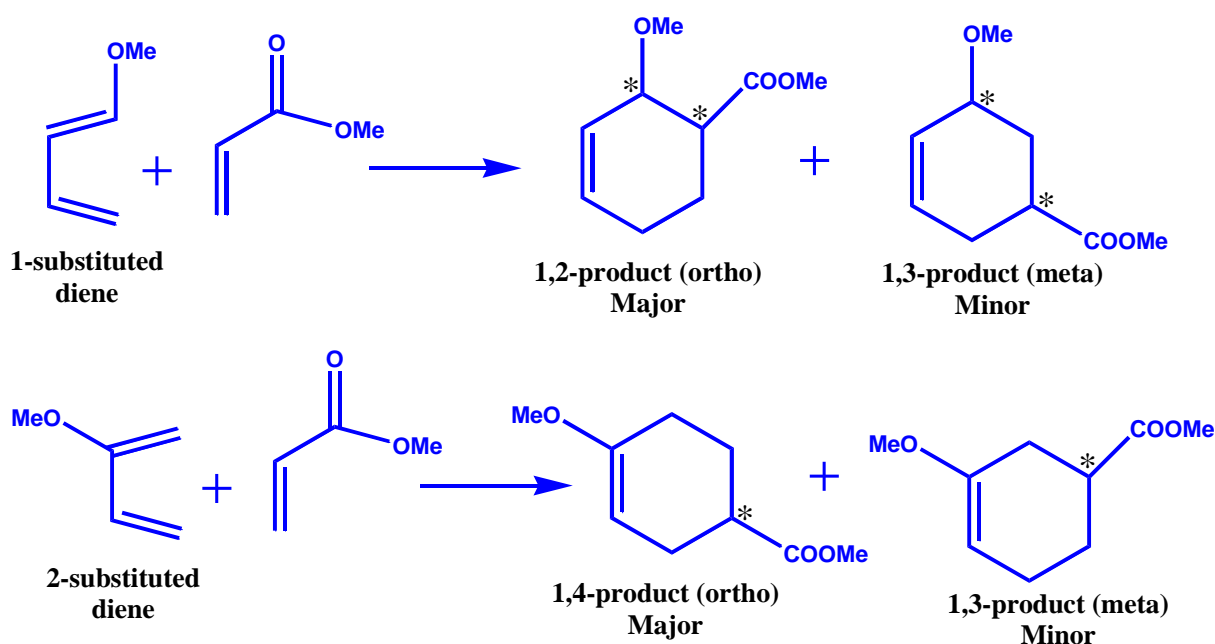
When benzene undergoes nitration, it gives *ortho* and *para* products as the major products. In case of regioselective reactions, there is preferential reactivity of one site over the other of the same functional group, which is the benzene ring in this case.



Similarly, Friedel Crafts Reaction, Baeyer Villiger Oxidation, Diels Alder Reactions and several other organic reactions show regioselectivity in many cases

**How can you explain regioselectivity in Diels Alder reactions?**

Consider the following Diels alder reactions:

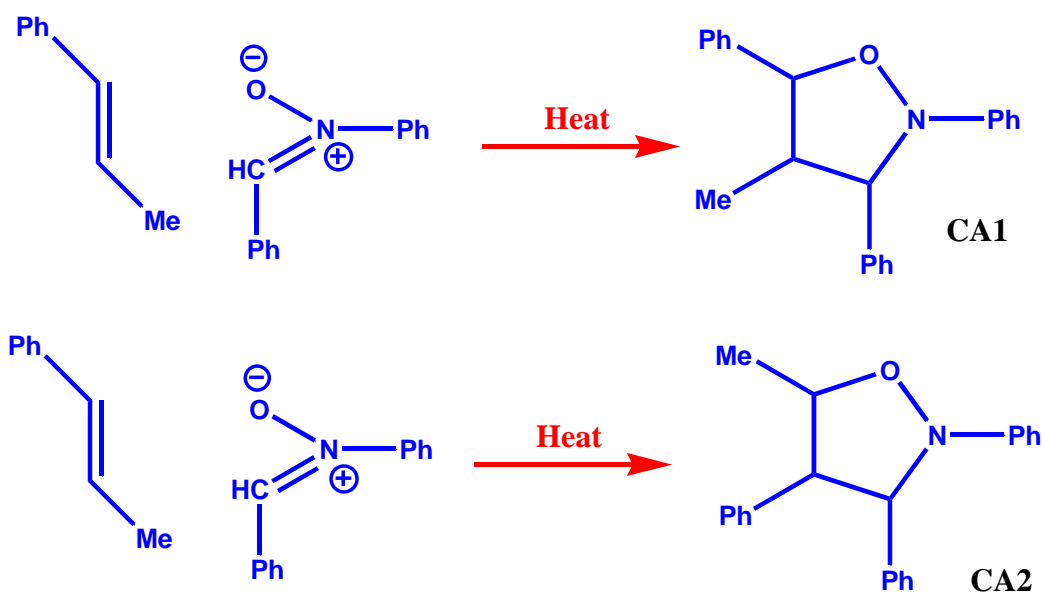


So far we have discussed that if we add a non-symmetrical reagent to non-symmetrical starting materials (think an alkene, where the groups at each end of the double bond are different), then two isomeric products that are constitutional isomers can be obtained. The reaction is regiochemical reaction.

In the above cases of Diels Alder reaction, we can see that the chiral centres are generated in the products of these reactions and they have some stereochemistry. However, the stereochemistry of the chiral centres in the products are exactly same. Here, only the bond connectivity is different. 1,2-product and 1,4-product are obtained as the major products and 1,3-product as the minor product. So, for the first Diels Alder reaction, 1,2-product and 1,3-product are regioisomers and for the second Diels Alder reaction, 1,4-product and 1,3-product are the regioisomers and both the reactions are regioselective.

### How can you explain regioselective dipolar cycloadditions?

Suppose, we have a simple dipolar cycloaddition reaction as shown below:



Here, the stereochemistry of the reacting alkene is trans in both cases and also the stereochemistry of the reacting 1,3-dipole is same in both cases, where Ph substituent on the carbon and Ph substituent on the nitrogen are cis to each other.

In this reaction, two pathways are shown, one in which methyl substituent of the diene gets attached to carbon centre of the dipole and in another pathway, methyl substituent of the diene gets attached to the oxygen centre of the dipole. These two pathways give rise to two products, **CA1** and **CA2**, which are constitutional isomers, having same molecular formula, but different connectivity of bonds. Thus, **CA1** and **CA2** are regioisomers of each other and the reaction is a regiochemical reaction.

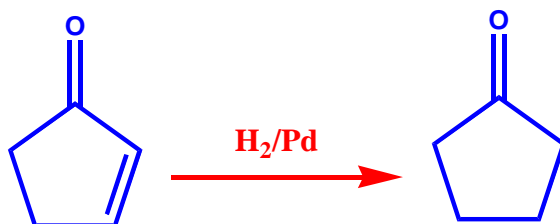
## 2. Chemoselective reactions

In the previous section, we studied about regioselectivity where there is preferential reactivity of one site over the other of the same functional group. Now, let us discuss another type of selectivity observed in chemical reactions which is known as chemoselectivity. In a chemoselective reaction, out of the two functional groups present in a reactant, one of the functional groups is attacked by a reagent. Hence, there are two different functional groups with unequal reactivity. However, in a regioselective reaction, there is only one functional group with different reactivity of its two sites.

Let us explain chemoselectivity observed in some common reactions such as reduction, oxidation, epoxidation, alkylation etc

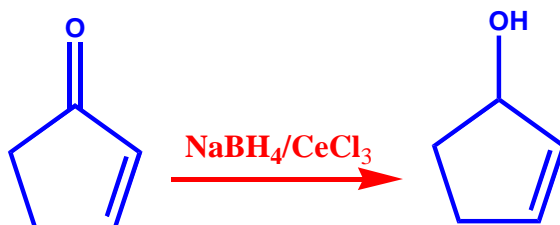
### (a) Chemoselective reduction of C=C over C=O:

In the following reaction, cyclopentenone has two functional groups, the olefinic double bond and the carbonyl group. When it is subjected to reduction by  $H_2/Pd$ , then carbonyl group remains unaffected and the olefinic double bond is reduced. **Thus, in this reaction, out of the two functional groups, the reagent attacks only one functional group. Hence, the reaction is chemoselective.**



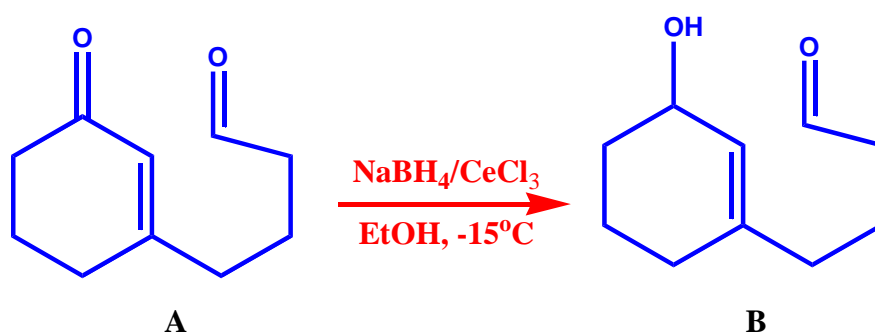
**(b) Chemoselective reduction of  $C=O$  over  $C=C$ :**

In the following reaction, cyclopentenone has two functional groups, the olefinic double bond and the carbonyl group. When it is subjected to reduction by  $NaBH_4/CeCl_3$ , then olefinic double bond remains unaffected and the carbonyl group is reduced. **Thus, in this reaction, out of the two functional groups, the reagent attacks only one functional group, which is the carbonyl group. Hence, the reaction is chemoselective.**



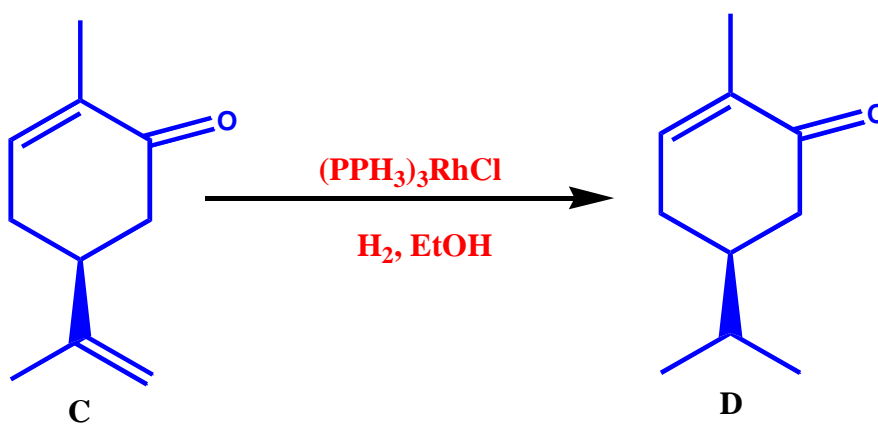
**(c) Chemoselective reduction of  $\alpha,\beta$ -unsaturated ketones over allylic alcohols:**

In the following reaction, compound A undergoes reduction in presence of  $NaBH_4/CeCl_3$  at low temperature.  $\alpha,\beta$ -saturated ketone undergoes reduction, but the allylic alcohol remains unaffected. **Thus, in this reaction, out of the two functional groups, the reagent attacks only one functional group, which is  $\alpha,\beta$ -saturated ketonic group. Hence, the reaction is chemoselective.**



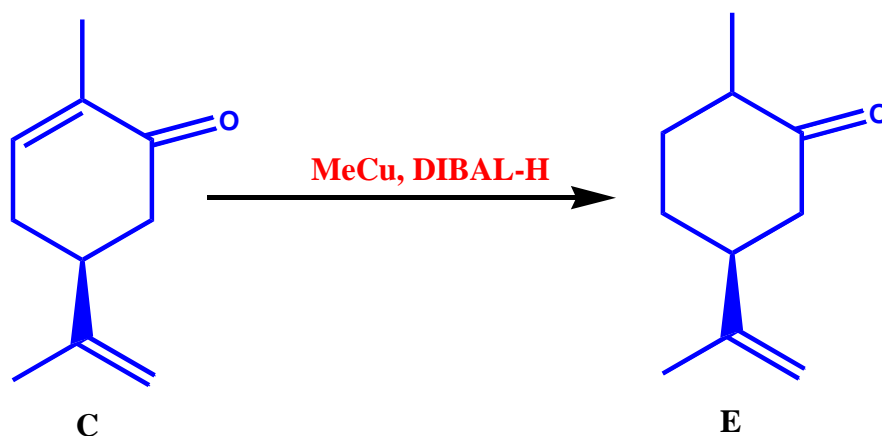
*(d) Chemoselective reduction of alkenes over alkenones:*

In the following reaction, compound C undergoes reduction in presence of  $(\text{PPh}_3)_3\text{RhCl}/\text{H}_2, \text{EtOH}$ . The olefinic double bond gets reduced in the compound, but the alkenone group remains unaffected. **Thus, in this reaction, out of the two functional groups, the reagent attacks only one functional group, which is alkene double bond. Hence, the reaction is chemoselective.**



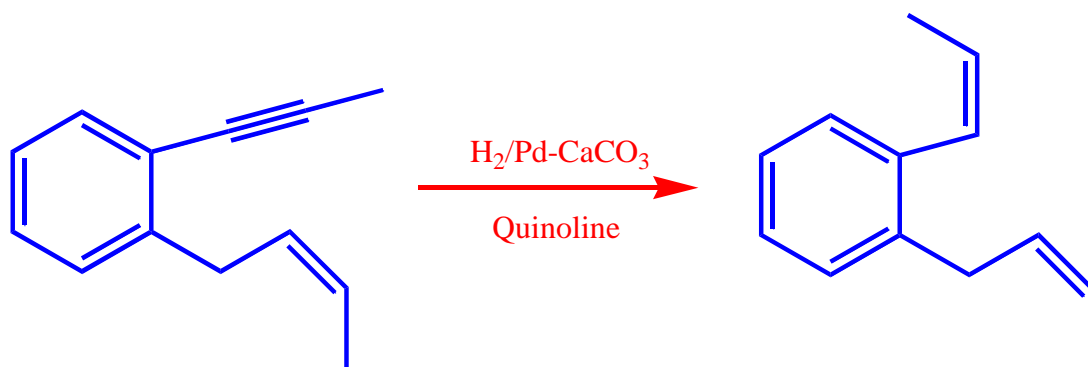
(e) *Chemoselective reduction of alkenones over alkenes:*

In the following reaction, compound C undergoes reduction in presence of MeCu, DIBAL-H. The alkenone group gets reduced and the alkene group remains unaffected. **Thus, in this reaction, out of the two functional groups, the reagent attacks only one functional group, which is alkenone group. Hence, the reaction is chemoselective.**



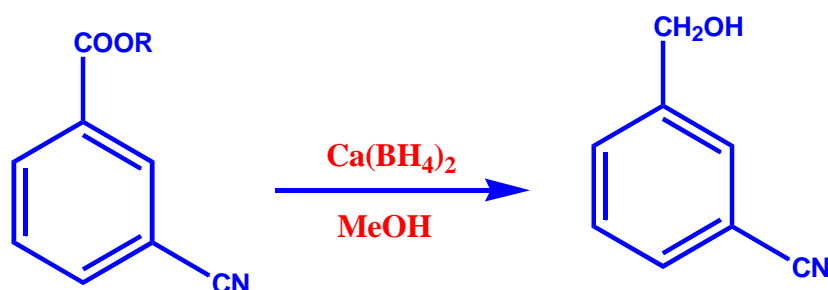
(f) *Chemoselective reduction of alkynes over alkenes:*

In the following reaction, we observe the chemoselective reduction of alkyne group over alkene group. Here, when we undergo hydrogen/palladium reduction ( $H_2/Pd-CaCO_3$ ) to the starting material, then only the alkyne group is reduced in this case and the alkene group remains unaffected. **Thus, in this reaction, out of the two functional groups, the reagent attacks only one functional group, which is alkyne group. Hence, the reaction is chemoselective.**



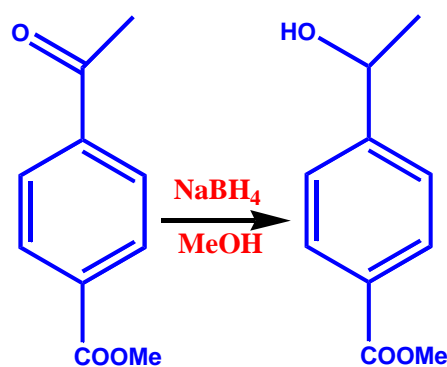
**(g) Chemoselective reduction of COOR over CN:**

In the following reaction, we observe the chemoselective reduction of carboxylic group over cyano group. Here, when we add  $\text{Ca}(\text{BH}_4)_2$  (in methanol) to the starting material, then only the carboxylic group is reduced to alcohol and the cyano group remains unaffected. **Thus, in this reaction, out of the two functional groups, the reagent attacks only one functional group, which is carboxylic group. Hence, the reaction is chemoselective.**

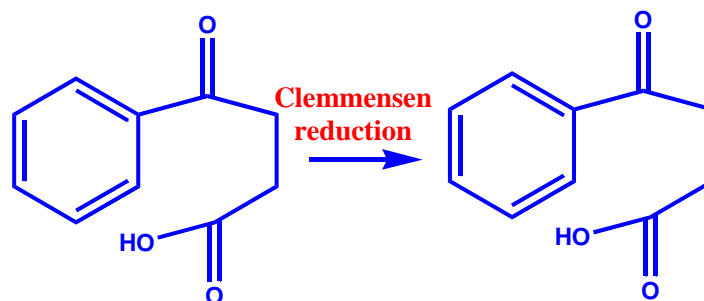


**(h) Chemoselective reduction of C=O over COOR:**

In the following two reactions, we observe the chemoselective reduction of carbonyl group over the carboxylic group. In Reaction 1, sodium borohydride ( $\text{NaBH}_4$ ) in methanol reacts with the starting compound and in the product, only the carbonyl group is reduced to alcohol, while the carboxylic group remains unaffected. Reaction 2 is the Clemmensen reduction [ $\text{Zn}(\text{Hg}), \text{HCl}$ ]. Here, the carbonyl group is reduced and the carboxylic acid is unaffected. **Thus, in these reactions, out of the two functional groups, the reagent attacks only one functional group, which is carbonyl group. Hence, the reaction is chemoselective.**



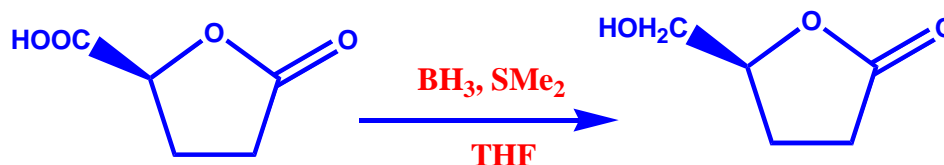
Reaction 1



Reaction 2

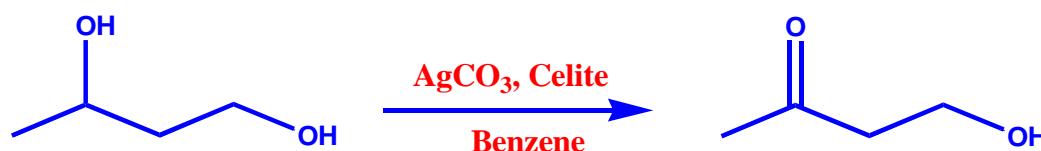
**(i) Chemoselective reduction of carboxylic acids in presence of esters, nitro and cyano groups:**

In the following reaction, we observe an example of chemoselective reduction of carboxylic group over esters, nitro and cyano groups. When we add  $\text{BH}_3, \text{SMe}_2$  (in THF) to the starting material, then only the carboxylic group is reduced to alcohol and the cyano, esters and nitro groups remains unaffected. **Thus, in this reaction, out of the two functional groups, the reagent attacks only one functional group, which is carboxylic group. Hence, the reaction is chemoselective.**



**(j) Chemoselective oxidation of secondary alcohols over primary alcohols:**

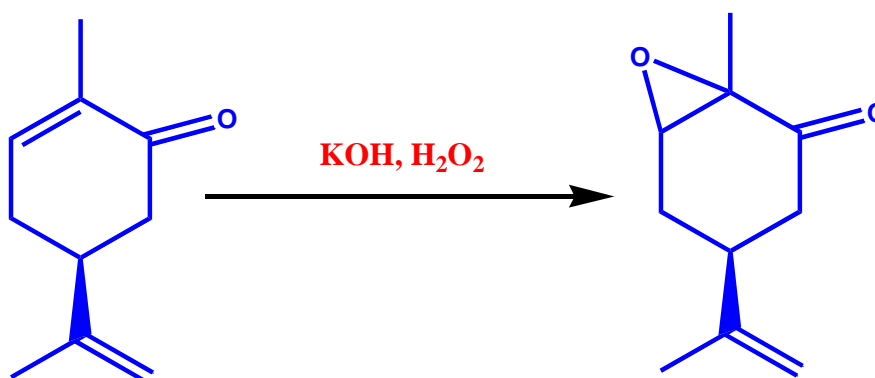
In the following reaction, we observe an example of chemoselective oxidation of secondary alcohols over primary alcohols. When we add silver carbonate ( $\text{AgCO}_3$ ), Celite in Benzene to the starting material, then only the secondary alcohol group is oxidized and the primary alcohol remains unaffected. **Thus, in this reaction, out of the two functional groups, the reagent attacks only one functional group, which is secondary alcohol group. Hence, the reaction is chemoselective oxidation.**





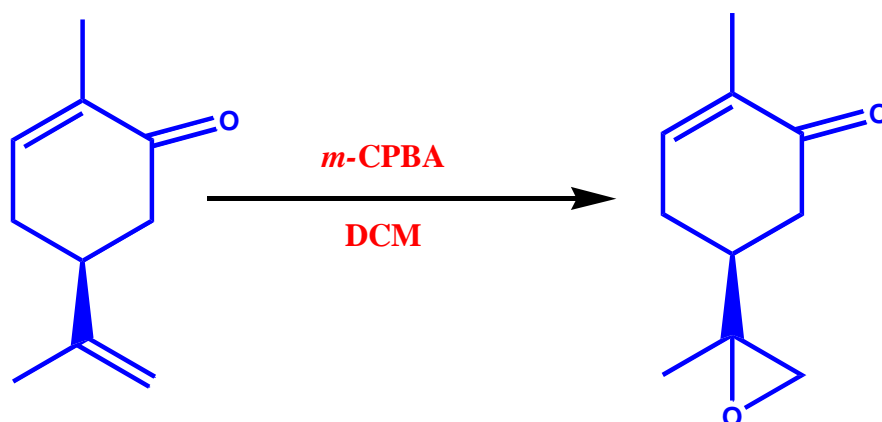
**(k) Chemoselective epoxidation of  $\alpha,\beta$ -unsaturated ketones over alkenes:**

In the following reaction, we observe an example of chemoselective epoxidation of  $\alpha,\beta$ -unsaturated ketone over alkene group. When we add potassium hydroxide and hydrogen peroxide to the starting material, then only the  $\alpha,\beta$ -unsaturated ketone is epoxidized and the alkene group remains unaffected. **Thus, in this reaction, out of the two functional groups, the reagent attacks only one functional group, which is  $\alpha,\beta$ -unsaturated ketonic group. Hence, the reaction is chemoselective epoxidation.**



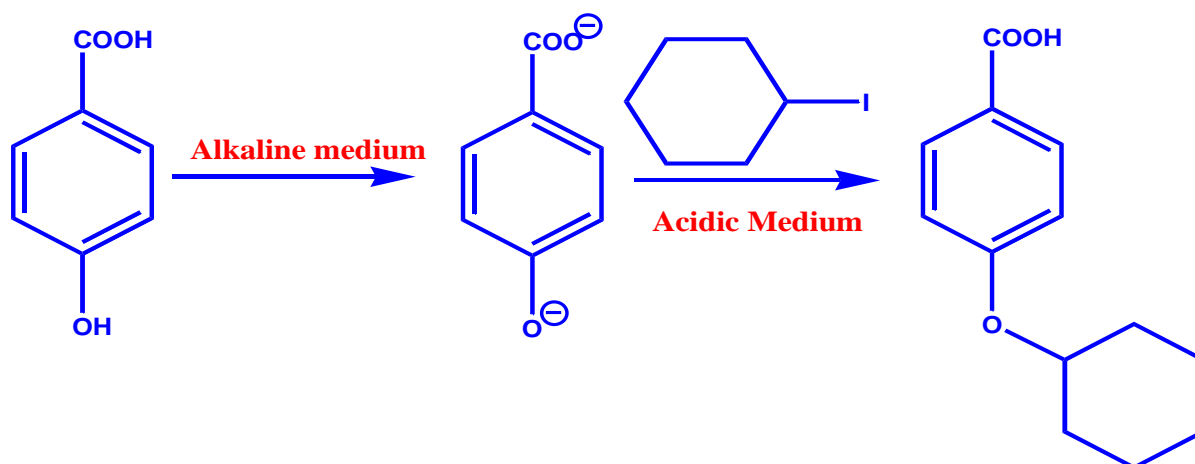
**(l) Chemoselective epoxidation of alkenes over  $\alpha,\beta$ -unsaturated ketones:**

In the following reaction, we observe an example of chemoselective epoxidation of alkene over  $\alpha,\beta$ -unsaturated ketone group. When we add *m*-chloroperbenzoic acid in dichloromethane to the starting material, then only the alkene group is epoxidized and the  $\alpha,\beta$ -unsaturated ketonic group remains unaffected. **Thus, in this reaction, out of the two functional groups, the reagent attacks only one functional group, which is alkene group. Hence, the reaction is chemoselective epoxidation.**



***(m) Chemoselective alkylation of phenols over carboxylic acids:***

In the following reaction, we observe an example of chemoselective alkylation of phenolic OH group over carboxylic acid group. When we add alkyl halide in acidic medium to the starting material, then only the phenolic OH is alkylated and the carboxylic acid group remains unaffected. **Thus, in this reaction, out of the two functional groups, the reagent attacks only one functional group, which is phenolic OH group. Hence, the reaction is chemoselective alkylation.**



Thus, we have learnt from the above examples, that chemoselectivity is observed when a reagent has preferable reactivity for one functional group over the other functional group. In some cases, chemoselectivity is also observed when the same functional group is present twice or thrice in a compound and the reaction occurs at only one of them. Let us consider the following example in this context.



In this case, there are two nitro groups present in 1,3-dinitrobenzene. However, only one nitro group is reduced in presence of NaSH in MeOH and the other nitro group remains unaffected in presence of the reagent. This is also an example of chemoselectivity.

### Conclusion

In this module, we have discussed the regioselective, regiospecific and chemoselective reactions. Regioselective reactions are those which involve preferential reactivity of one site over the other in the same functional group. When this preferential selectivity is 100% and only one product is obtained, then the reaction is called regiospecific reaction. Chemoselective reactions are those which involve preferential attack of a reagent on one functional group over the other functional group in a compound. In chemoselectivity, there is presence of two or more functional groups and hence it specifies chemical selectivity of the reagent. But, in case of regioselectivity, there is presence of only one functional group and the preference of the reagent is on a particular site of the functional group. Hence, it specifies regio-specific selectivity and hence is called regioselectivity.

### Books/Materials for further reading:

- 1) E.L. Eliel, S.H. Wilen and L.N. Mander, Stereochemistry of Organic Compounds, John Wiley & Sons, New York, 1994.
- 2) S. Sengupta, Basic Stereochemistry of Organic Molecules, 2009.
- 3) D. Nasipuri, Stereochemistry of Organic Compounds, 2nd Edn., Wiley Eastern, New Delhi, 1993.
- 4) Schaum's Solved Problem Series, 3000 solved problems in Organic Chemistry, Volume 1, McGraw Hill International Editions.
- 5) J. March, Advanced Organic Chemistry: Reactions, Mechanisms and Structure, 5th Edn., John Wiley, New York, 1999.
- 6) F.A. Carey and R.J. Sundberg, Advanced Organic Chemistry Part A and Part B, 4th Edn., Plenum Press, New York, 2001.
- 7) NPTEL course on NOC-Stereochemistry:  
<https://nptel.ac.in/courses/104105086/>

Department of Chemistry; Durgapur Government College;  
Level: Undergraduate; Semester-VI (Honours); Paper: Dynamic  
Stereochemistry (DSE); Unit: General Introduction;  
Module: 1, Dr. Nivedita Acharjee

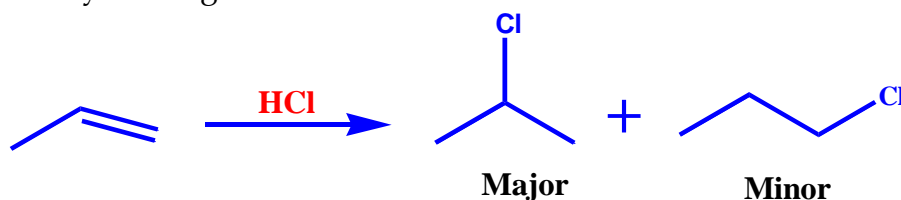
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## Assignments

### Module 1

### Regioselective, Regio-specific and Chemoselective reactions

1. The reaction below produces a major and a minor product. What type of selectivity is being observed in this reaction?



- a) Regioselectivity
- b) Stereoselectivity
- c) Chemoselectivity
- d) None of the above

Ans: \_\_\_\_\_

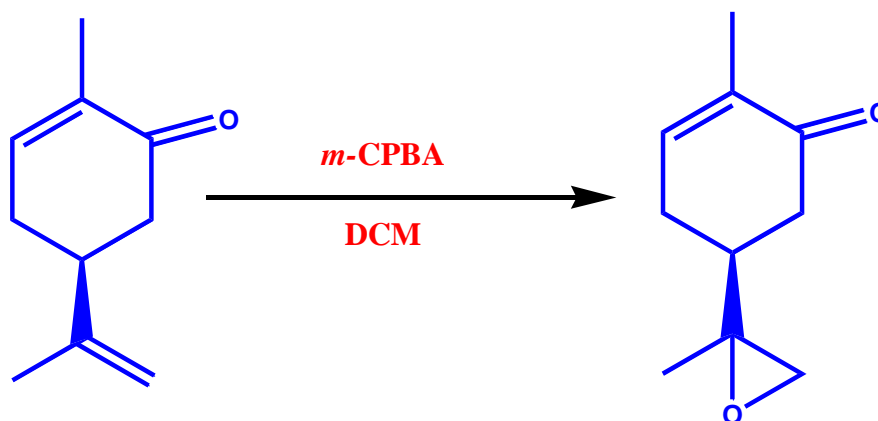
2. The reaction below produces a single product. What type of selectivity is being observed in this reaction?



- a) Regioselectivity
- b) Stereoselectivity
- c) Chemoselectivity
- d) None of the above

Ans: \_\_\_\_\_

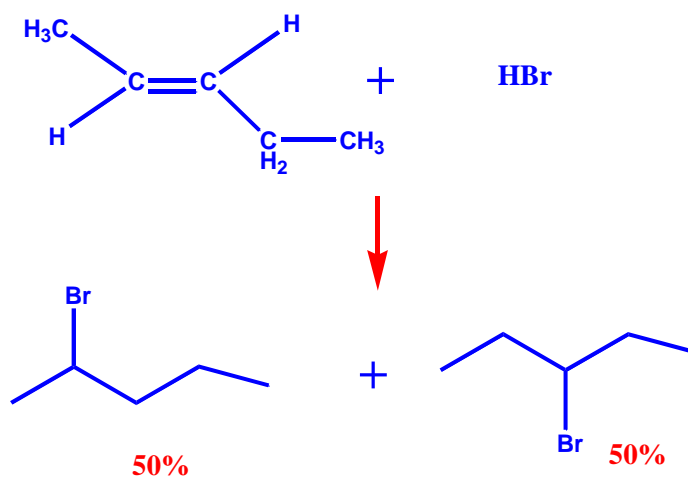
3. The reaction below produces a single product. What type of selectivity is being observed in this reaction?



- a) Regioselectivity
- b) Stereoselectivity
- c) Chemoselectivity
- d) None of the above

Ans: \_\_\_\_\_

4. The reaction below produces two products, each of 50% yield. What type of selectivity is being observed in this reaction?



- a) Regioselectivity
- b) Stereoselectivity
- c) Chemoselectivity
- d) None of the above

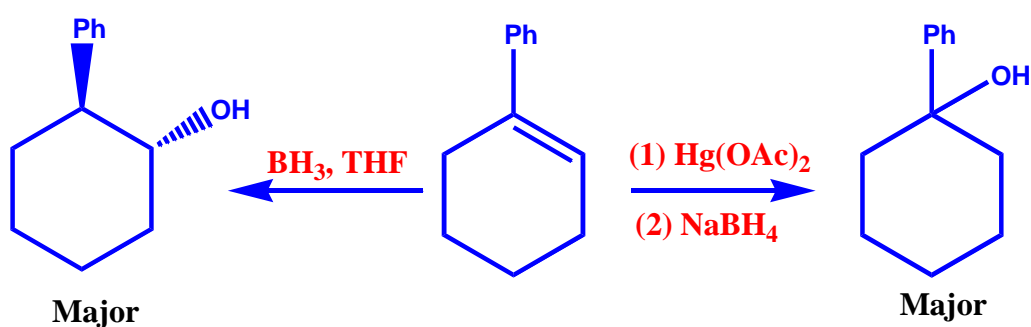
Ans: \_\_\_\_\_

5. Regioisomers are

- a) Constitutional isomers
- b) Conformational isomers
- c) Enantiomers
- d) None of the above

Ans: \_\_\_\_\_

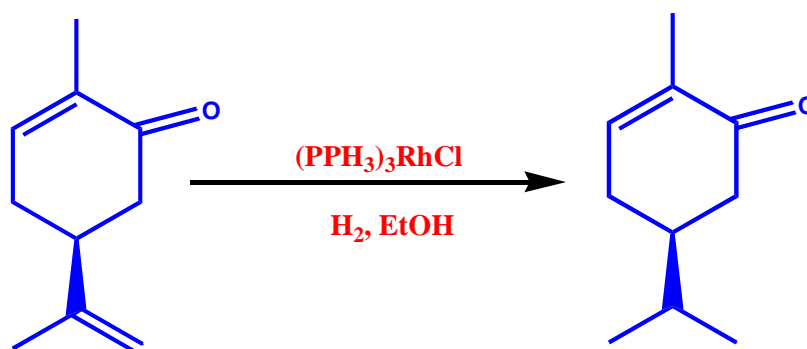
6. How can you classify the following reactions?



- a) Regioselective reactions
- b) Stereoselective reactions
- c) Chemoselective reactions
- d) None of the above

Ans: \_\_\_\_\_

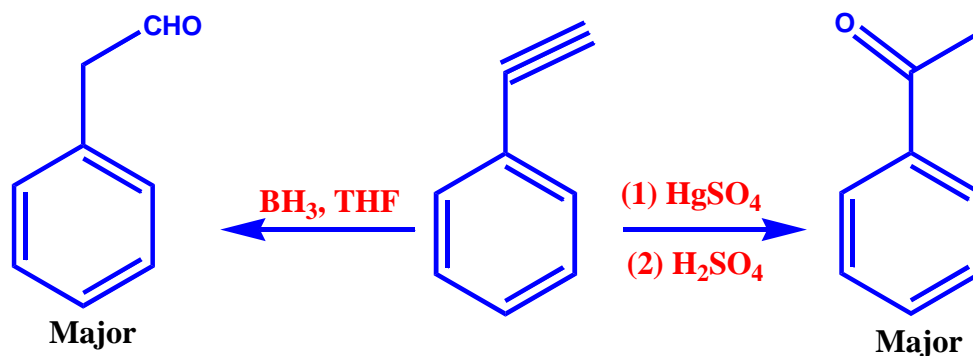
7. How can you classify the following reaction?



- a) Regioselective reaction
- b) Stereoselective reaction
- c) Chemoselective reaction
- d) None of the above

Ans: \_\_\_\_\_

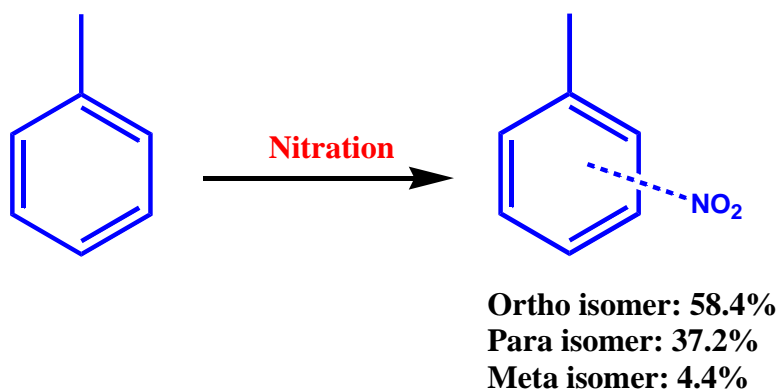
8. How can you classify the following reactions?



- a) Regioselective reaction
- b) Stereoselective reaction
- c) Chemoselective reaction
- d) None of the above

Ans: \_\_\_\_\_

9. How can you classify the following reaction?

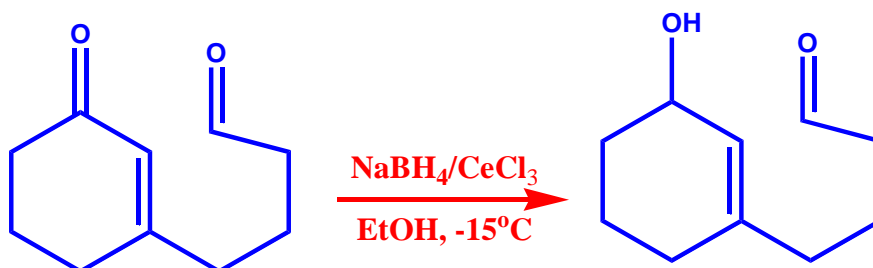


- a) Regioselective reaction
- b) Stereoselective reaction
- c) Chemoselective reaction
- d) None of the above

Ans: \_\_\_\_\_



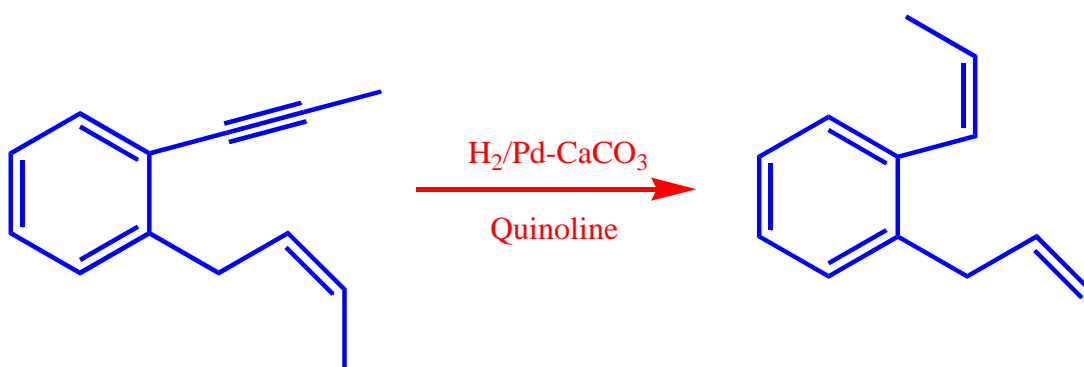
10. How can you classify the following reaction?



- a) Regioselective reaction
- b) Stereoselective reaction
- c) Chemoselective reaction
- d) None of the above

Ans: \_\_\_\_\_

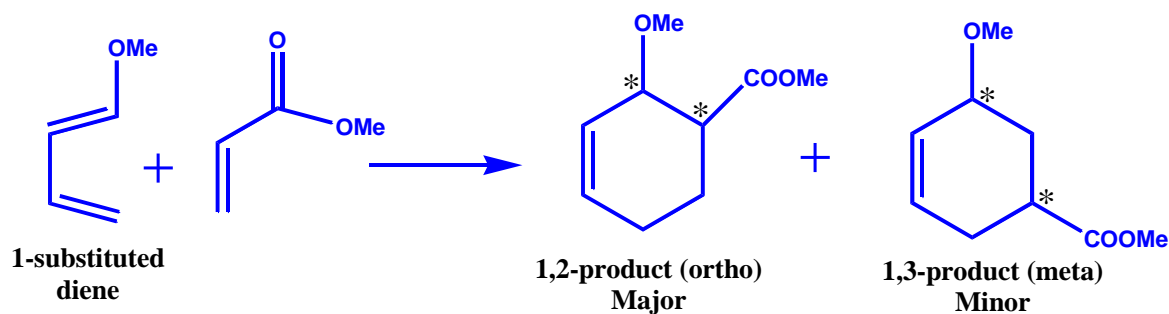
11. How can you classify the following reaction?



- a) Regioselective reaction
- b) Stereoselective reaction
- c) Chemoselective reaction
- d) None of the above

Ans: \_\_\_\_\_

12. How can you classify the following reaction?



- a) Regioselective and stereoselective reaction
- b) Stereoselective reaction
- c) Regioselective reaction
- d) None of the above

Ans: \_\_\_\_\_

13. Regioselective reactions involve

- a) Selectivity along different sites of a functional group
- b) Selectivity of the reagent for different functional groups
- c) Both (a) and (b)
- d) None of the above

Ans: \_\_\_\_\_

14. Chemoselective reactions involve

- e) Selectivity along different sites of a functional group
- f) Selectivity of the reagent for different functional groups
- g) Both (a) and (b)
- h) None of the above

Ans: \_\_\_\_\_

15. Regiospecific reactions involve

- i) 100% Selectivity along different sites of a functional group
- j) 100% Selectivity of the reagent for different functional groups
- k) Both (a) and (b)
- l) None of the above

Ans: \_\_\_\_\_

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