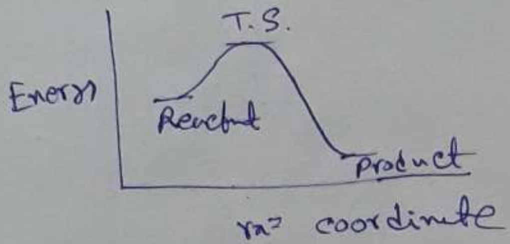
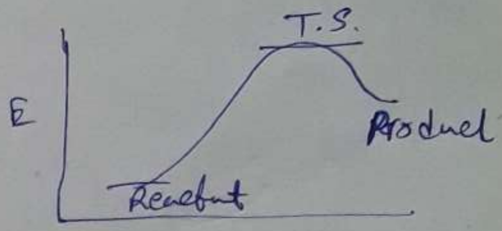
Hammond's postulate states that the structure of the T.S. must be somewhere between ~~the~~ that of the reactant or product. In an exothermic reaction the T.S. is closer in structure and energy to the reactant than product. Therefore the T.S. will be geometrically more similar to the reactant than the product. In an endothermic reaction the reverse is true, that means the T.S. is very similar to the product than reactant.

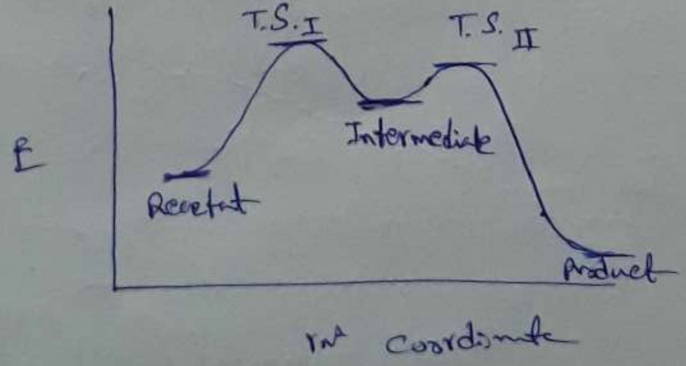


exothermic

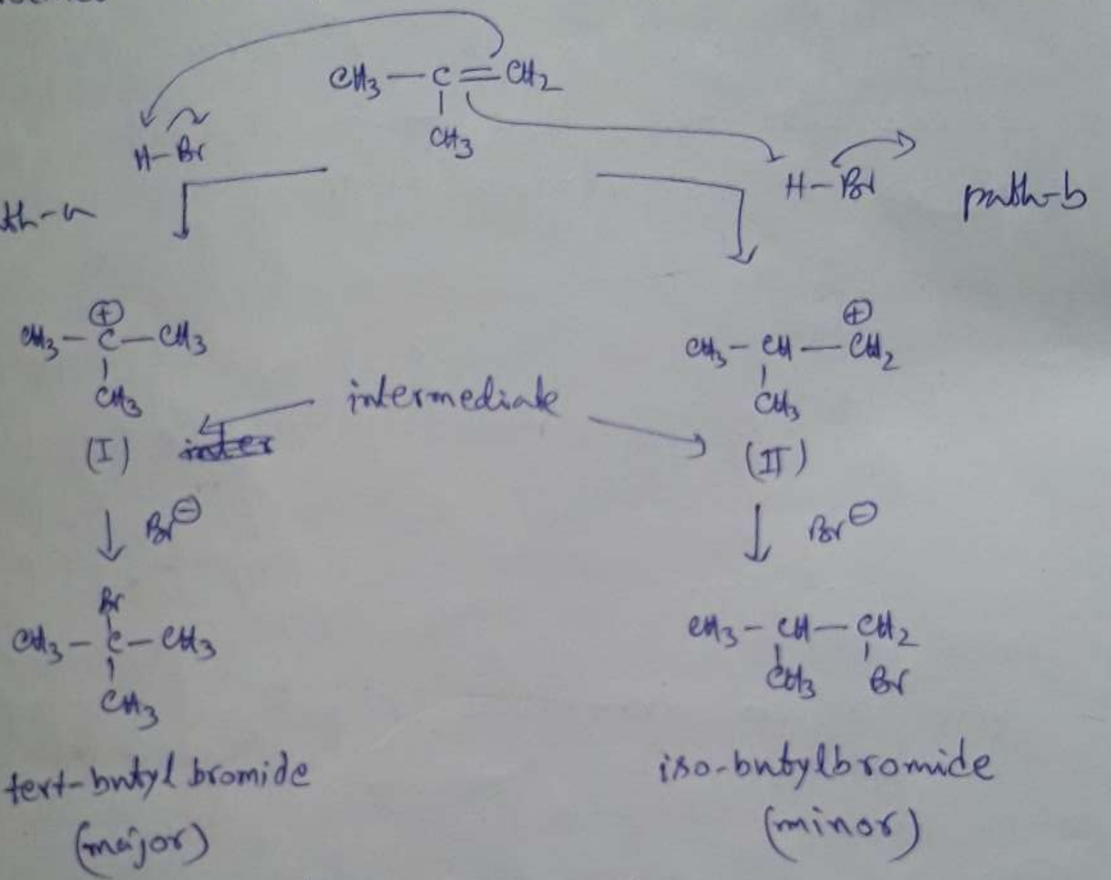


endothermic

If there is an intermediate then also Hammond's postulate is applicable. In this case the intermediate acts as product for proceding T.S. and acts as reactant for ~~second~~ following second T.S.



Now in case of HBr addition to isobutene there are two possible carbocation intermediates (I) is tertiary which is more stable and hence leads to major product tert-butylbromide and (II) is primary which is less stable and leads to minor product iso-butylbromide.



~~Now This reaction is exothe~~

In iso-butene the central 'C' atom is sp^2 hybridized and in carbocation (I) also it is sp^2 but in carbocation (II) it become sp^3. So the ~~st~~ planar structure is not much changed from reactant to (I) but it is changed significantly (tetrahedral) ~~to~~ in (II). According to Hammond's postulate the T.S. should follow that pathway where the ~~intermediate is~~ it is structurally close to reactant and/or intermediate (in exothermic rxn). ~~So (I) should be the major~~

So path-a should be favourable according to Hammond's postulate and tert-butylbromide should be major product.

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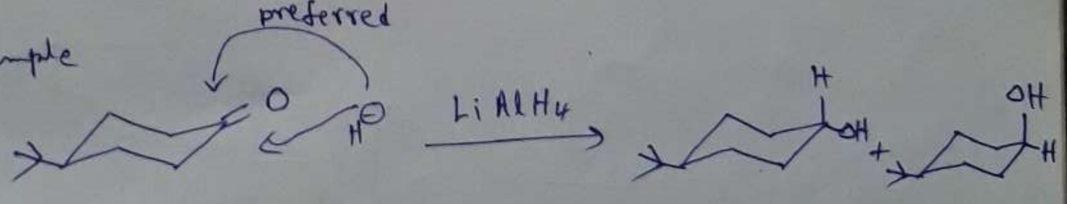
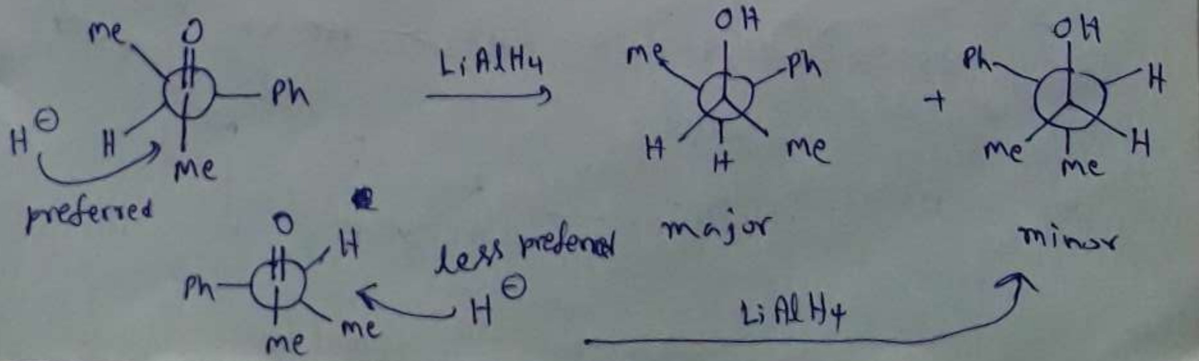
Stereoselective reactions : The reactions where one stereoisomer of product is formed predominantly (out of several other stereoisomeric products) becaus the reaction has a choice of pathways, and one pathway is more favourable than the other, then the reaction is called stereoselective reaction.

Let us say A on reaction produces X, Y etc products which are stereoisomers. And say X is major and Y is minor. Then this is called stereoselective reaction.

Example



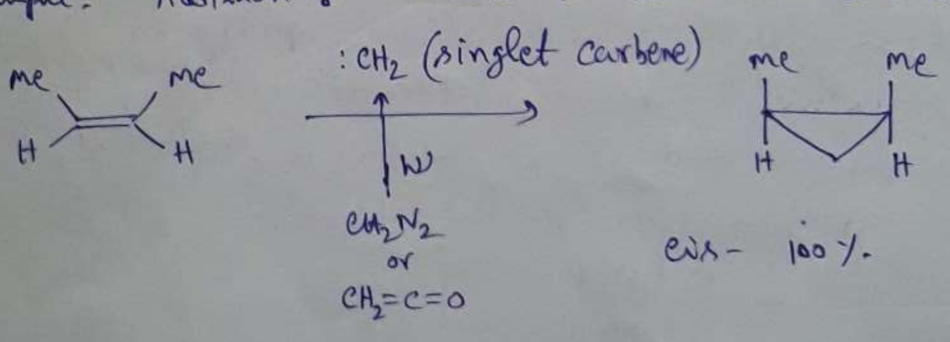
4-tert-butyl cyclohexanone major minor



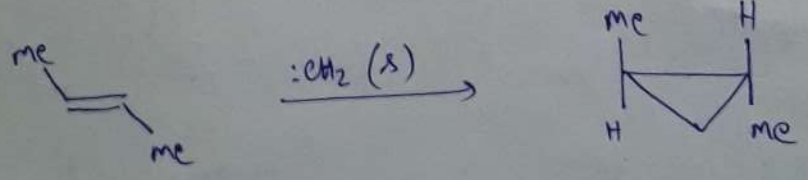
Stereospecific reaction: The reaction where the mechanism means that the stereochemistry of the starting material determines the stereochemistry of the product and there is no choice involved, is called stereospecific rn^n.

Suppose A & B are two stereoisomeric reactant molecule. Now A gives rise to C only (100%) and B gives D only (100%). And C & D are also stereoisomers. That means a stereoisomeric product is formed exclusively or specifically (100%) from a particular stereoisomeric starting material (reactant), then this type of reaction is called stereospecific reaction.

Example: Addition of carbene to cis & trans-2-butene

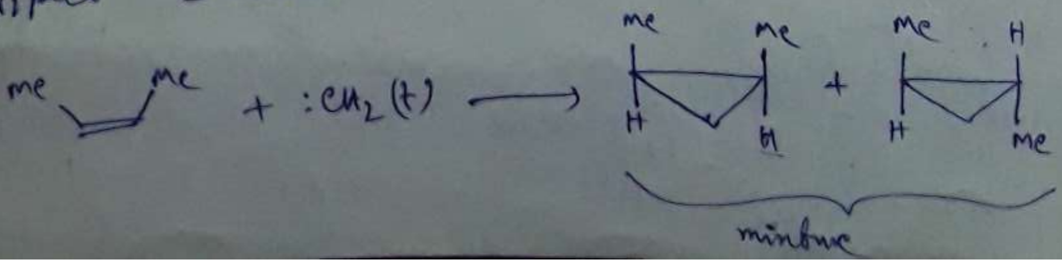


cis- 100%.



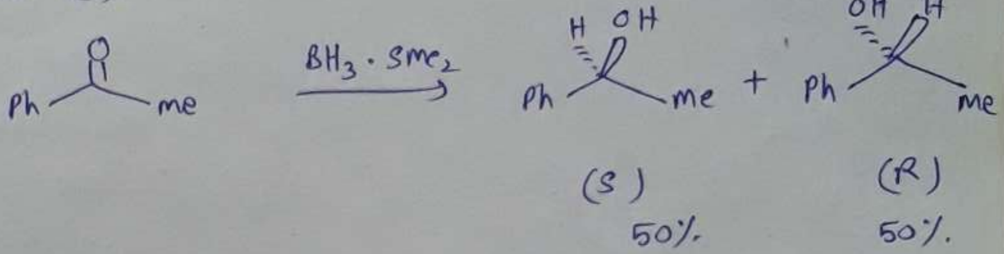
trans- 100%.

But sterespecificity is lost if ~~the~~ we use triplet carbene

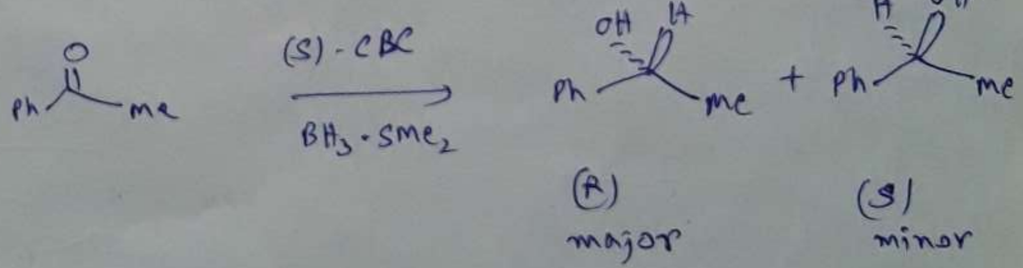


Enantioselective reaction: In a stereoselective reaction if the products are enantiomers and one enantiomer is formed predominably then it is called enantioselective reaction.

Example: When acetophenone is reduced with BH_3 only the we get a racemic mixture of (R) and (S) alcohol. There is no enantioselectivity



But when the same reaction is carried out in presence of (S)-CBS catalyst (Corey-Bakshi-Shibata catalyst a chiral catalyst) then (R)-alcohol become major. This is then called enantioselective reaction.



give the definition of stereoselective rxn first

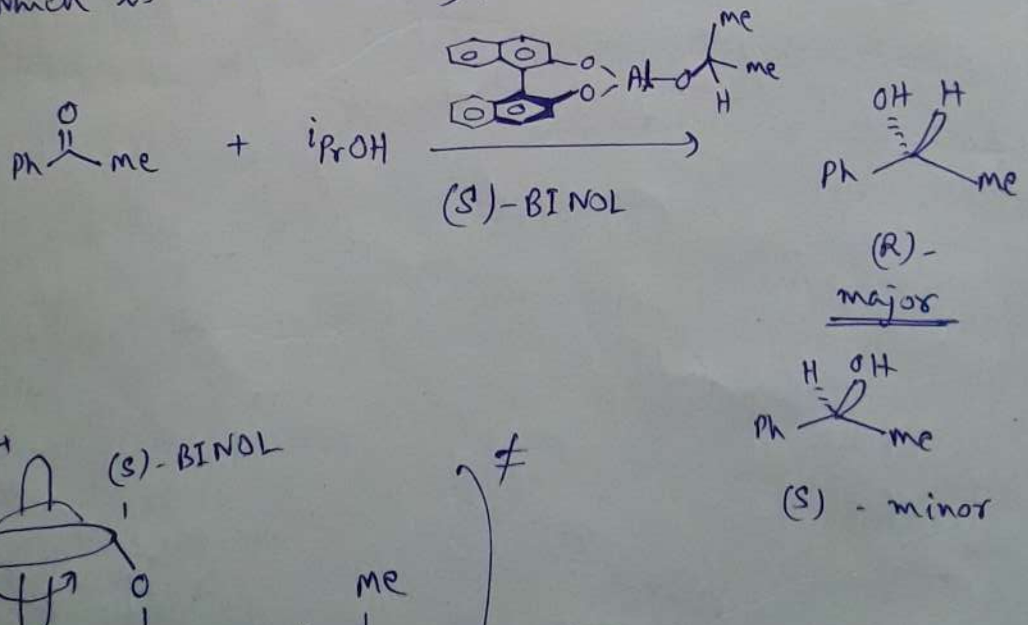
★★ Give the definition of stereoselective rxn & diast

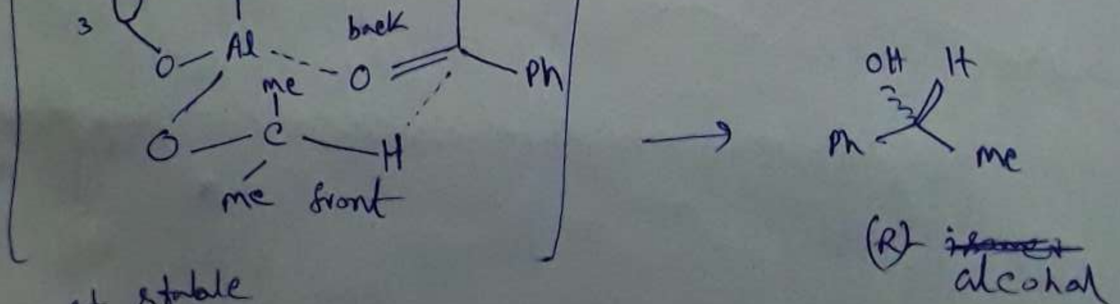
Diastereoselective reaction : In a stereoselective reaction if the products are diastereomers and if one diastereomer is formed predominantly then it is called diastereoselective rxn.

Example : See book - Felkin-Ahn model any example

Kinetically controlled MPV reduction :

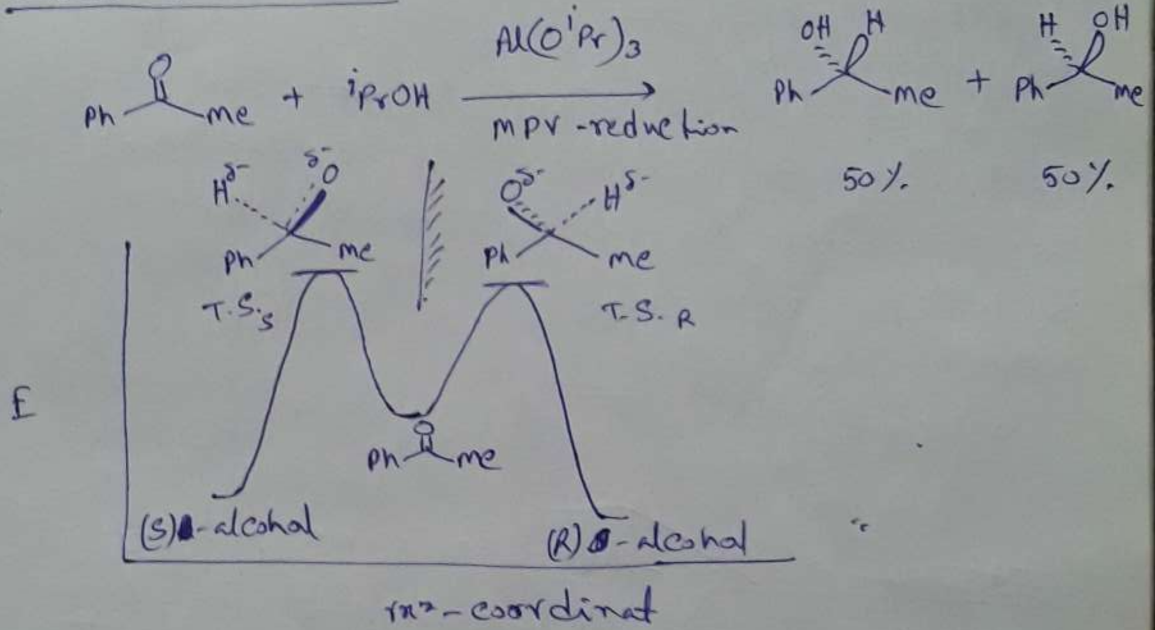
This is an enantioselective reaction, where a prochiral ketone is reduced with ~~chiral~~ ~~ligand~~ aluminium alkoxide using chiral ligands (which is chiral alcohol).



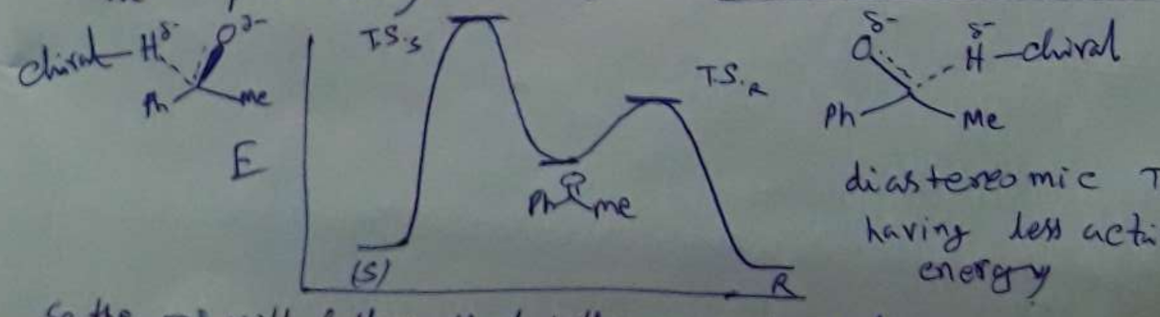


most stable T.S.

In MPV-reduction ~~both~~ the products are pair of enantiomers and thus has same energy. So under thermodynamic control we will get racemic mixture ~~(1:1)R~~ (R:S = 1:1). This happens when we use achiral aluminium alkoxide as reducing agent. Here both the T.S. are enantiomeric T.S. having same energy. So there is no enantioselectivity.



So in order to get enantioselectivity we have to use chiral aluminium alkoxide ~~ligan~~ catalyst, so that the T.S. become diastereomeric in nature and ~~hence~~ has unequal energy. In this way we can apply the kinetically control rxn pathway to get enantioselectivity



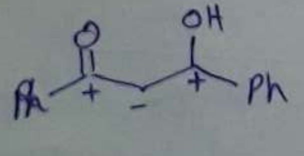
diastereomic T.S. having less activation energy

So the rxn will follow that pathway which is lower in energy and give major product

Umpolung: Umpolung means polarity inversion in organic chemistry is the chemical modification of a functional group with the aim of the reversal of polarity of that group. This modification allows secondary reactions of this functional group that ~~was~~ would otherwise not possible. It is mainly applicable in carbonyl chemistry. ~~Give example~~ Generally the carbonyl carbon is electrophilic in nature. Now if ~~so~~ by some means we ~~chan~~ can change this character that means if we can make this carbonyl carbon nucleophilic then it is called umpolung.

Give example —

Latent polarity: Latent or hidden polarity concept is the imaginary pattern of alternating +ve and −ve charges in target skeleton (bonds). This helps in the identification of the disconnection and hence the syntons of a T.M..



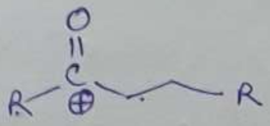
~~Consonant~~

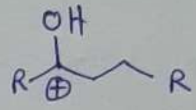
Consonant & dissonant polarity:

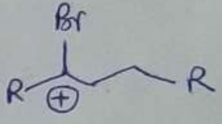
In retrosynthetic analysis functional groups are classified in main three types —

E-class: The groups which confer (generate) electrophilic character to the attached carbon (i.e., +ve charge)

Ex: $-NH_2$, $-OH$, $-OR$, $=O$, X (halogen)







G-class: The groups which confer nucleophilic character to the attached carbon (-ve)

Ex: $-Li$, $-MgX$, $-AlR_2$

$\overset{\ominus}{CH_3}-MgBr$, $\overset{\ominus}{CH_3}-Li$

A-class: Functional groups that confer ambivalent character (+ve or -ve)

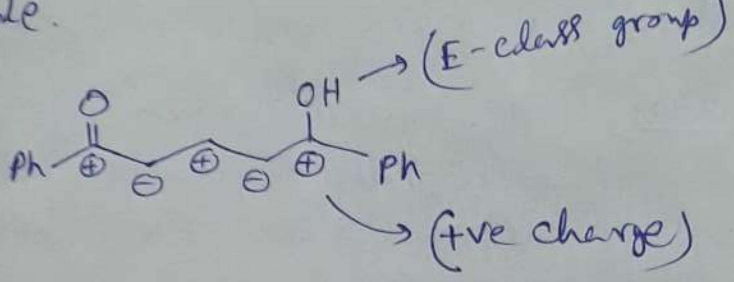
Ex: $-BR_2$, $-NO_2$, $\equiv N$

CH_3-NO_2

~~When~~ In finding latent polarity when (+ve) charge is placed at the carbon attached to an E-class functional group (groups which confer electrophilic character (+ve) to the attached carbon) or (-ve) charge is placed at carbon attached to a G-class functional group, then that is called consonant polarity.

If consonant pattern is present then we can get logical synthons and synthesis of T.M become simple.

Ex:



On the other hand if reverse polarity arises, means if (+ve) charge is placed at the carbon atom attached to G-class gr. or (−ve) charge is placed at the carbon atom attached to E-class gr., then it is called dissonant polarity/pattern. Here we get illogical synthons and synthesis become difficult

Ex: