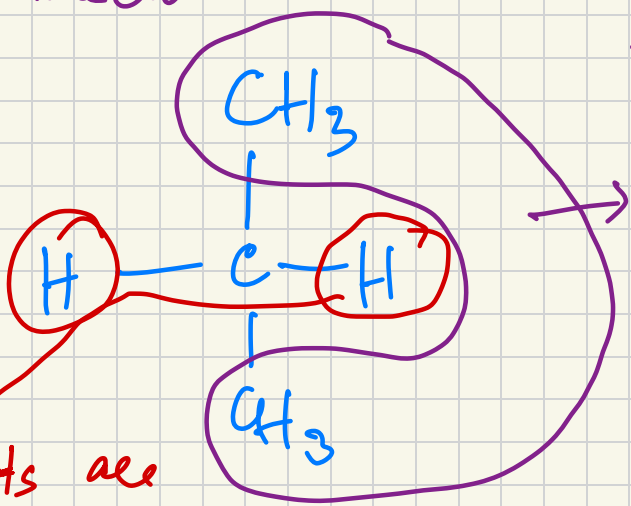
Stereochemistry

Dr. Irshad Ahmad Bhat
Assistant professor
Department of Chemistry
Amar Singh College, Srinagar

Topicity & Prostereoisomerism

Topicity refers to the relationship between various groups/atoms/faces (called ligands) in a molecule.



Two $-CH_3$ groups are same in look & constitution

Two Hs are exactly same

Such atoms/groups which are indistinguishable from one another when considered in isolation are called as homomorphic groups

Topicity is relationship between the homomorphic groups/atoms in a molecule.

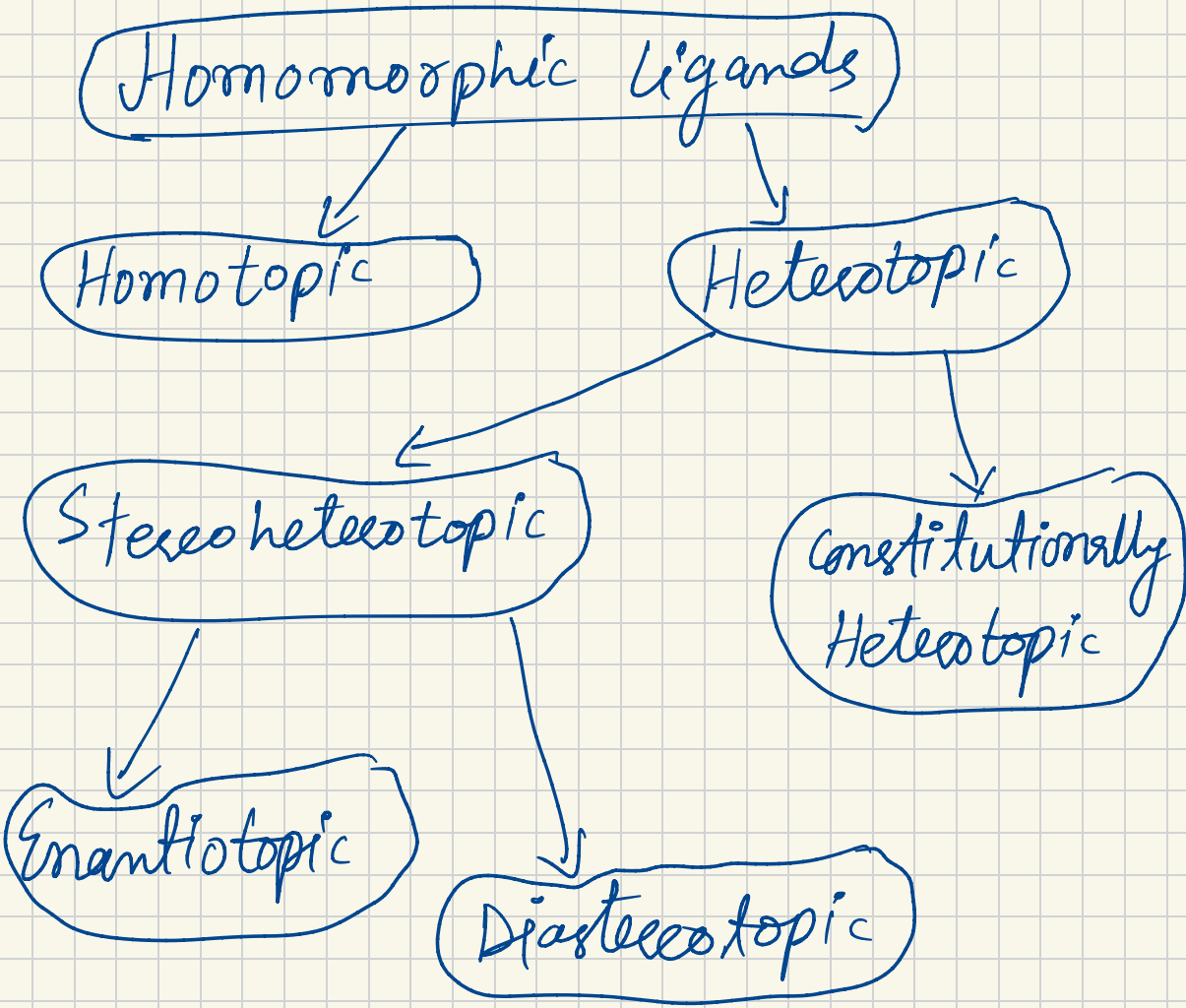
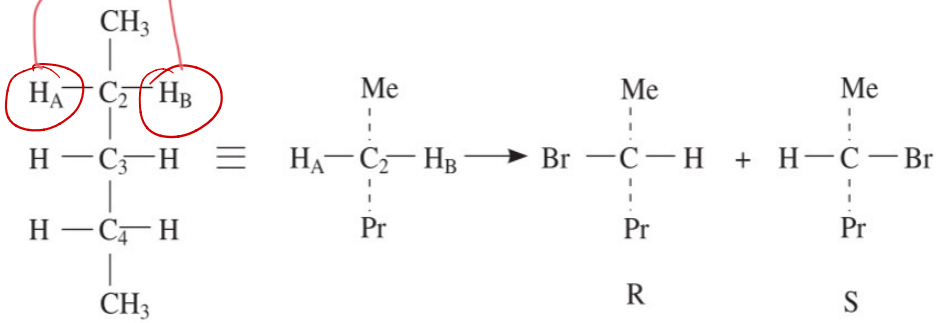


Chart showing the classification of homomorphic ligands (atoms/groups/faces)

H_A and H_B are homomorphic because they are indistinguishable when looked at in isolation



Homotopic and heterotopic ligands

H_A and H_B are homomorphich and they are stereoheterotopic

H_A and C_3H will be **Constitutionally heterotopic.**

The Hs at C_3 are homotopic as replacing them by any group will produce the same molecule.

→ Molecules that have stereoheterotopic ligands exhibit Prostereoisomerism.

→ Stereoheterotopicity and prostereoisomerism are inter-related.

Just like we need stereogenic centers for stereoisomerism, we need prostereogenic centers for prostereoisomerism.

Stereocenter → prostereocenter

Stereoaxis → prostereoaxis

so on & so forth

Chiral → pro-chiral

Homotopic / Heterotopic terms are used while comparing different groups / ligands / faces in a molecule with one another and hence cannot be used in isolation.

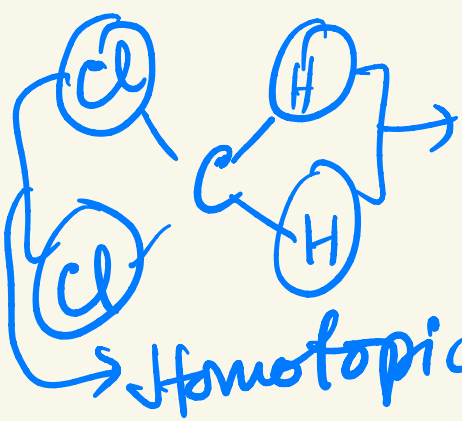
There are two ways/criteria that can be applied to predict relationship b/w two homomorphic groups.

(i) Substitution (addition) criteria

(ii) Symmetry criteria

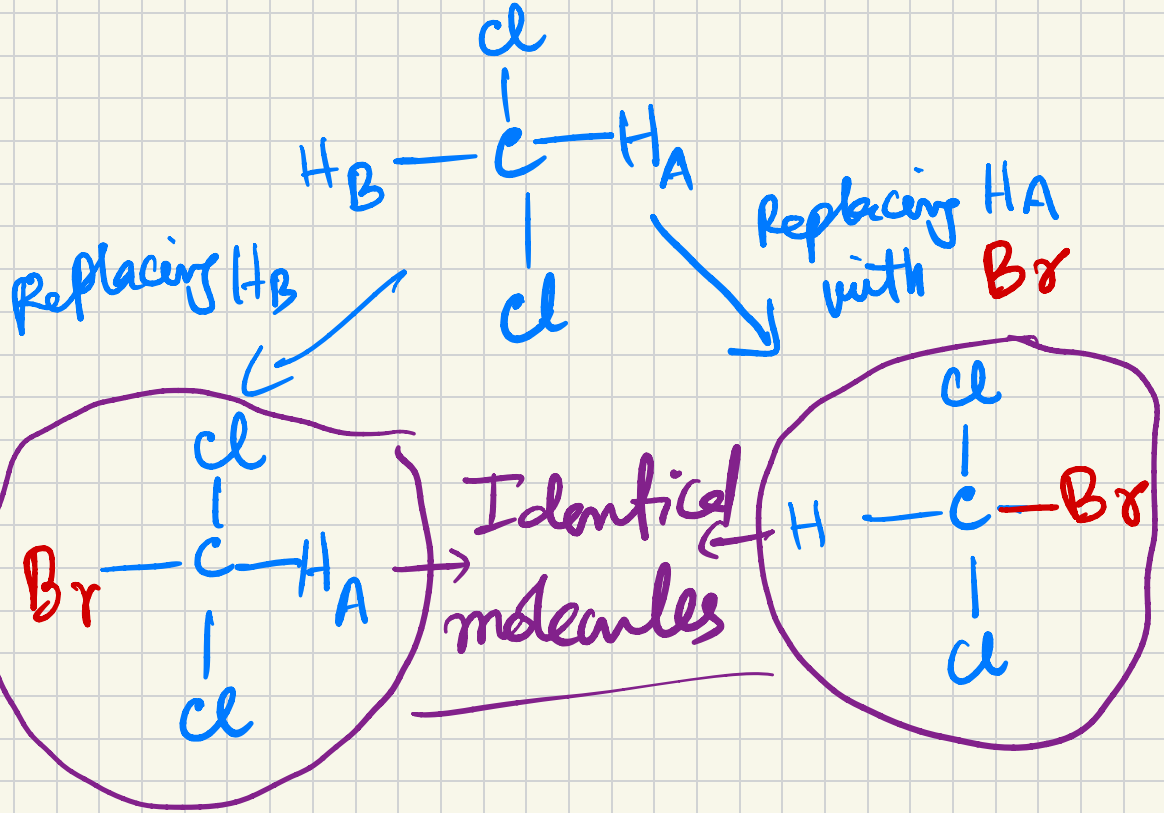
Homotopic atoms/groups/faces

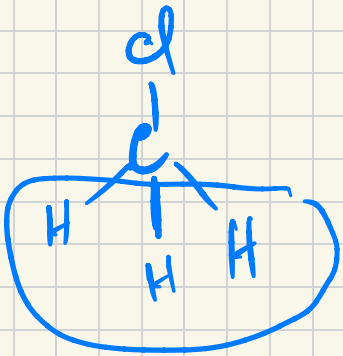
Two groups are homotopic if replacing them with successively with another group (not already present in molecule) produces same (identical) molecules



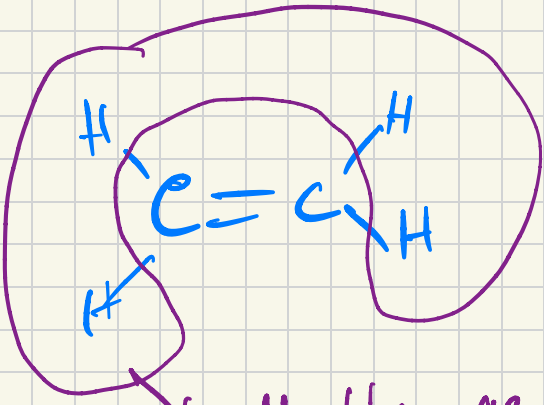
homotopic Hs

Homotopic Cls

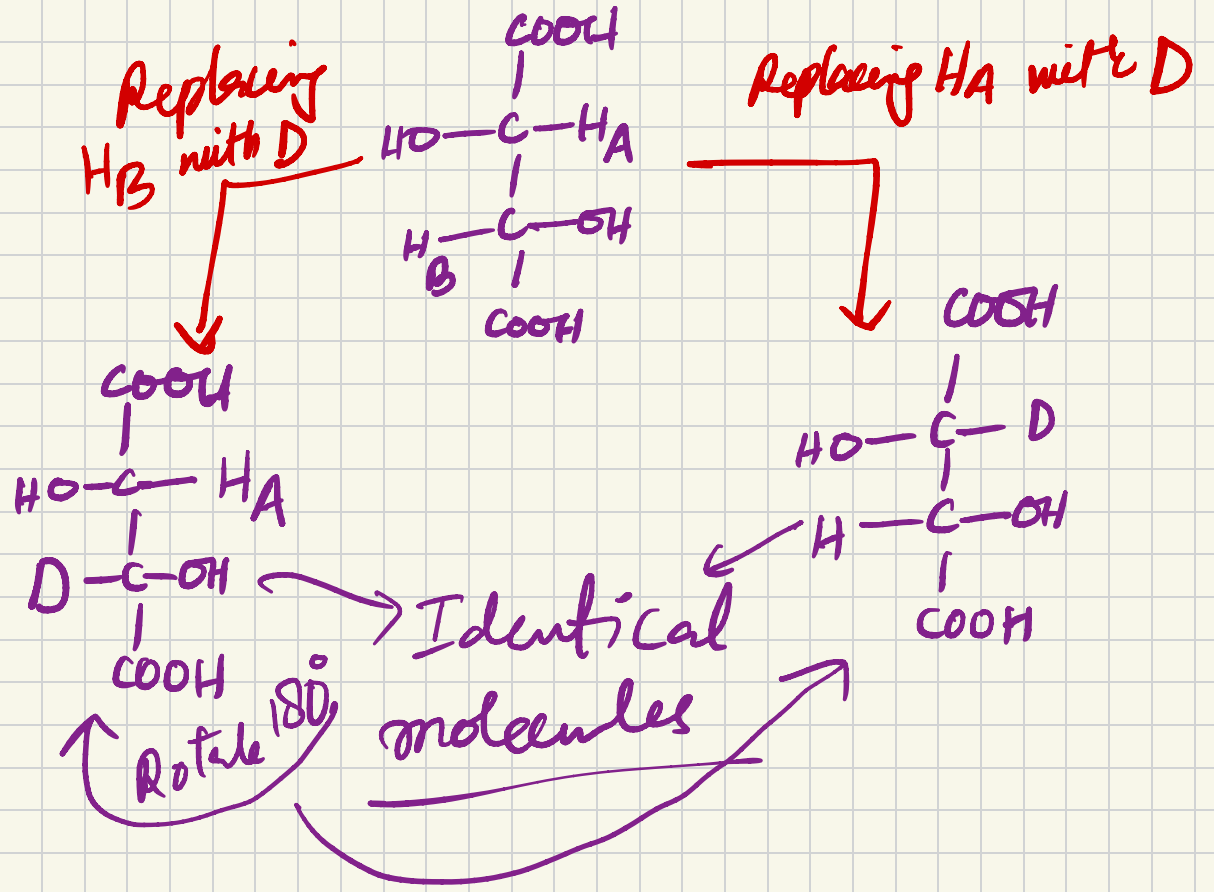




all three are homotopic



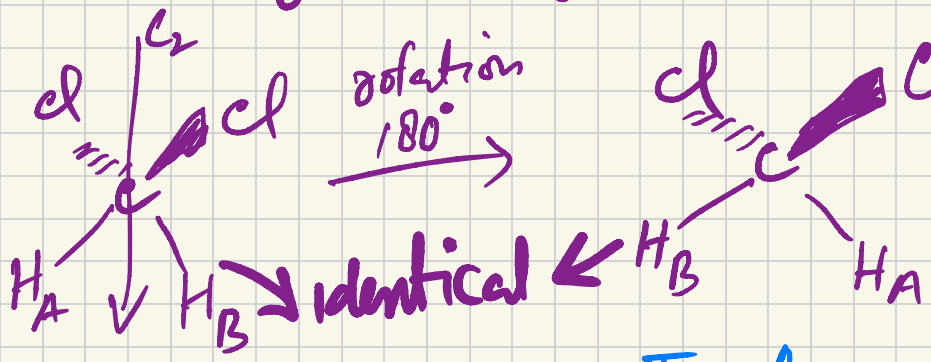
all Hs are homotopic



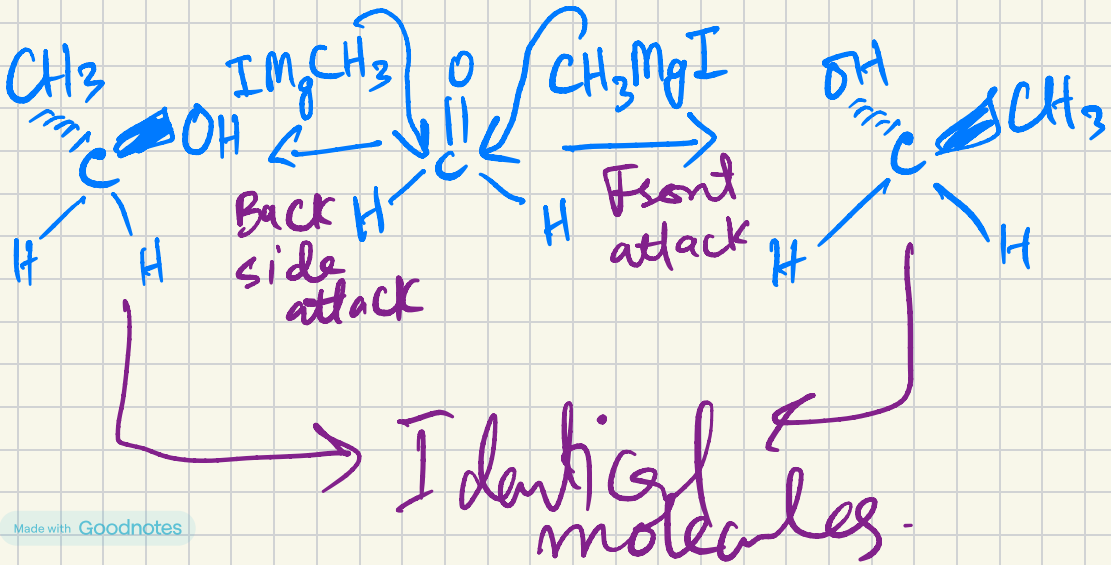
H_A and H_B are homotopic as replacing them by D produced the same/identical molecules.

Symmetry Criteria

The two Hs of CH_2Cl_2 can interchange positions by rotating the molecule



Homotopic Faces: Two faces of a double bond are homotopic if addition from either side gives the same product



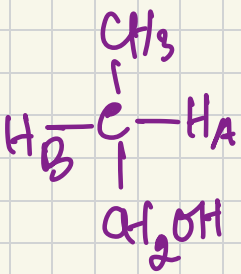
Stereoheterotopic (or simply Heterotopic)

Enantiotopic
when two groups in a molecule are related in a mirror-image fashion

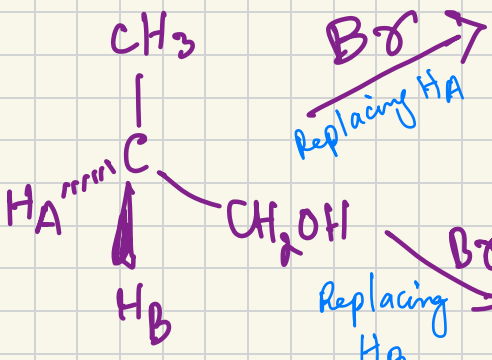
Diastereotopic
when two groups in a molecule are not related in a mirror-image fashion.

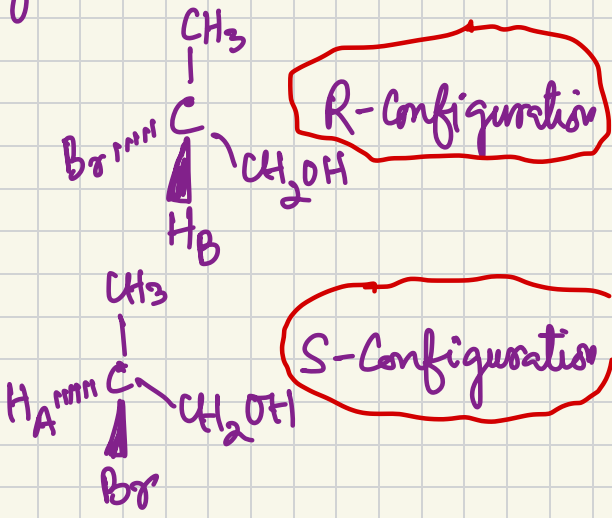
Exactly same criteria applies to atoms & faces

→ Tetrahedral Carbon of the the type $Caabc$ the two a's are always enantiotopic

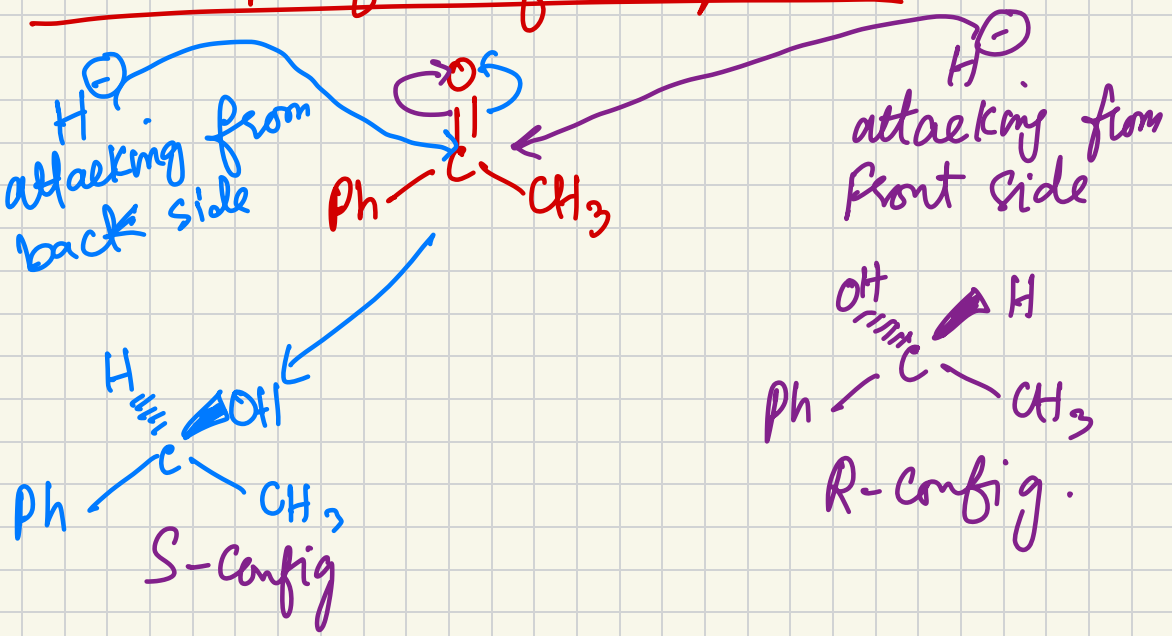


→ Substituting H_A and H_B successively with a group that is not already present in a molecule is always producing two enantiomers.



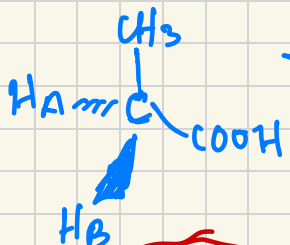


Enantiotopic faces of acetophenone

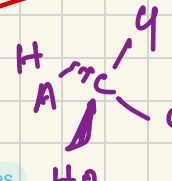


Symmetry criteria for enantiotopic groups

Enantiotopic groups/atoms in a molecule exchange their places with one another when symmetry operation (σ or S_n) are applied



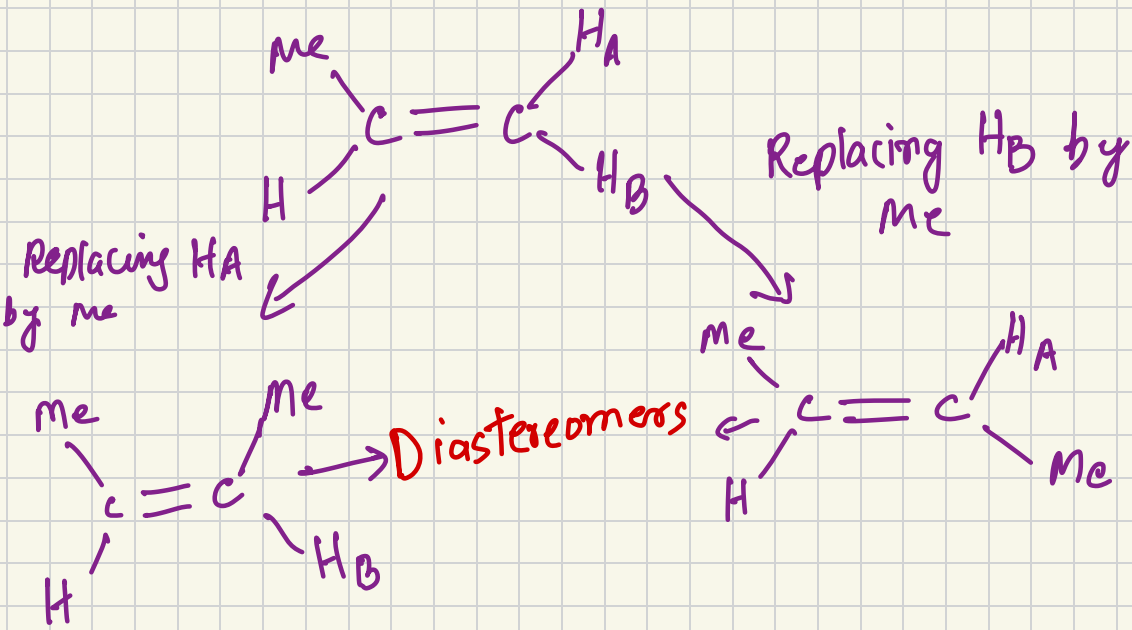
→ σ plane crossing through $-CH_3$, $-C-$ & $-COOH$ exchange H_A & H_B.



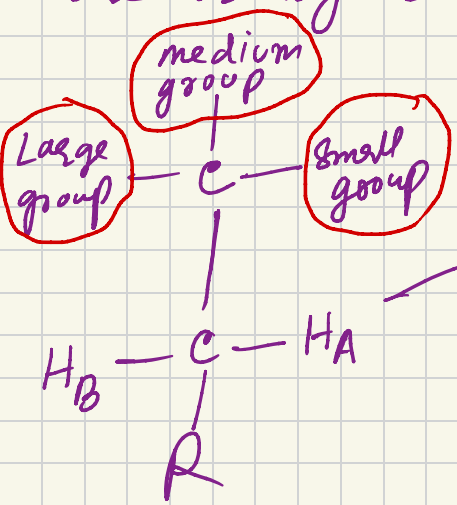
→ C_2 axis exchanges positions of H_A & H_B → hence homotopic

Diastereotopic groups / faces / atoms

When two groups / atoms in a molecule are related in such a manner that replacing them alternatively with another group produces stereoisomers that are not mirror images of one another (diastereomers), then those atoms / groups can be said to be diastereotopic.



The Geminal protons (or any other homomorphic) groups that are adjacent to a chiral Center are usually diastereotopic in nature



H_A and H_B are geminal and are attached to a C atom that is adjacent to a chiral Center.

↓

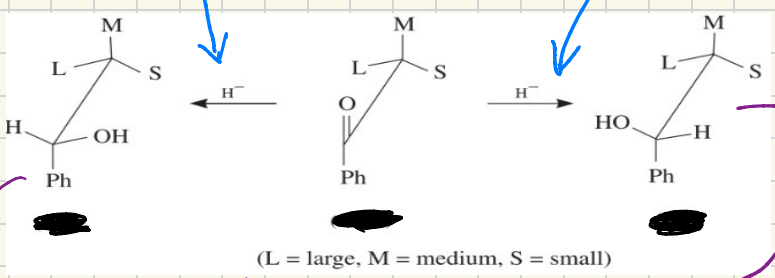
Hence Diastereotopic

Diasterotopic Faces

The two faces of the Carbonyl group that is adjacent to a chiral Center are diastereotopic in nature

Addition of $H^{\ominus}$ on the left side of C=O

Addition of $H^{\ominus}$ on the right side of C=O



→ Diastereomers

Topicity Summary based on Symmetry Criteria