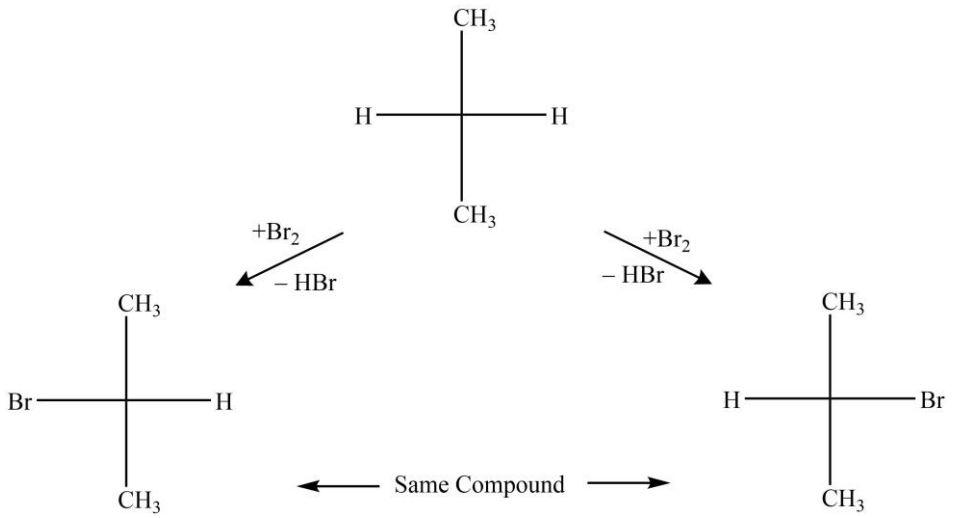
❖ Enantiotopic and Diastereotopic Atoms, Groups and Faces

The topicity in stereochemistry may simply be defined as the stereochemical relationship between substituents and the structure with which they are bonded. Based on such relationships, groups can be classified as homotopic, enantiotopic, or diastereotopic. A general discussion on these three types is given below.

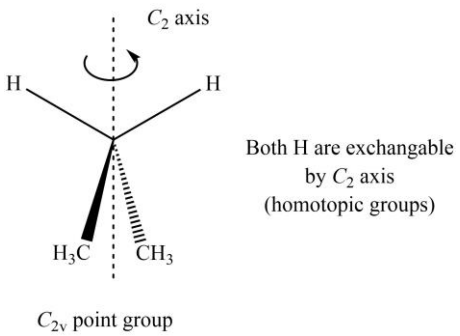
➢ *Homotopic Groups and Faces*

Homotopic groups and faces in an organic molecule can be found either based on chemical replacement or by using the symmetry criteria.

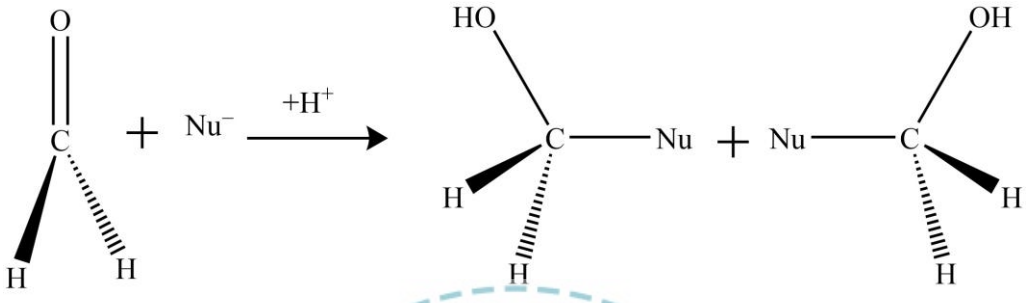
1. Homotopic groups: Homotopic groups in an organic molecule are equivalent groups. Two groups A and B are said to be homotopic if the resulting molecule remains the same (counting stereochemical notation also) when the groups are replaced with some other atom or group (such as bromine) whilst the remaining portion of the molecule is kept intact. Homotopic atoms or groups are always identical whether the environment is chiral or not. Also, NMR-active homotopic groups have the same chemical shift in NMR spectra. For instance, the four H of CH_4methane are homotopic, like two H or the two Cl groups in CH_2Cl_2).



On the basis of molecular symmetry, two groups are said to be homotopic in nature if they are exchangeable by a primary symmetry element i.e. proper axis of rotation (C_n).

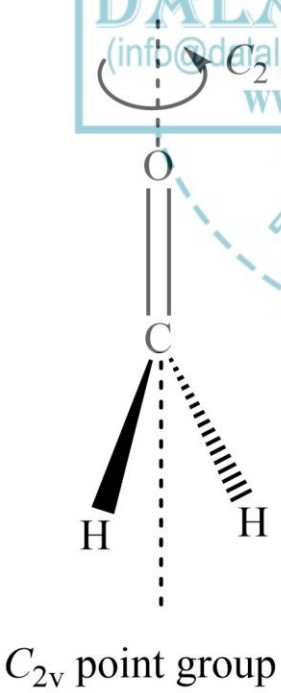


2. Homotopic faces: Homotopic faces in an organic molecule are equivalent faces, i.e., two faces A and B are homotopic if the molecule remains the same (including stereochemically) when the faces are attacked with some reagent (such as Cl^-) while the remaining parts of the molecule stay fixed. Homotopic faces are always identical, in any environment. For instance, two faces of methyl carbocation are homotopic, as the attack on two faces by an incoming nucleophile generates the same products.



Same compound

On the basis of molecular symmetry, two faces are said to be homotopic in nature if they are exchangeable by a two-fold axis symmetry (C_2).



C_{2v} point group

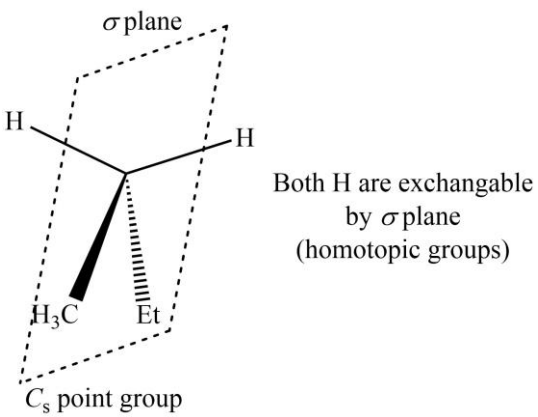
Both faces are exchangable by C_2 axis (homotopic groups)

➢ ***Enantiotopic Groups and Faces***

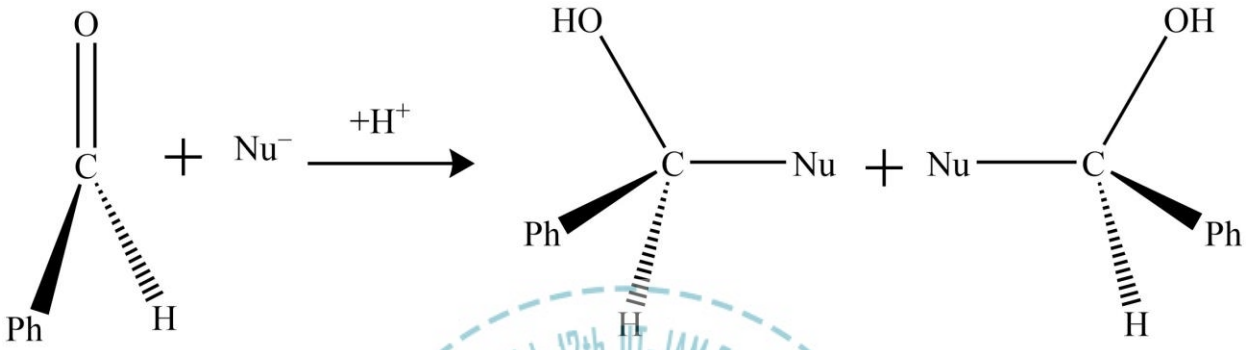
Homotopic groups and faces in an organic molecule can be found either on the basis of chemical replacement or by using the symmetry criteria.

1. Enantiotopic groups: Enantiotopic groups in a chemical compound are non-equivalent groups. Two groups A and B are enantiotopic if the enantiomers are obtained when the groups are interchanged with some other atom (such as bromine) while the remaining parts of the molecule stay fixed. Enantiotopic atoms are always identical in any achiral media while different in chiral media. Enantiotopic NMR-active nuclei have the same chemical shift in an NMR spectrum in achiral media and different chemical shifts in achiral media. For example, the two hydrogen atoms in CH_2ClBr are enantiotopic with one another, as the replacement by a third group gives rise to the enantiomeric pair.

On the basis of molecular symmetry, two groups are said to be enantiotopic in nature if they are exchangeable by a secondary symmetry element i.e. plane of symmetry (σ), the center of symmetry (*i*), or alternating axis of symmetry (S_n).

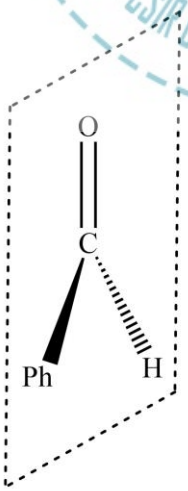


2. Enantiotopic faces: Enantiotopic faces in a chemical compound are non-equivalent faces, i.e., two faces A and B are enantiotopic if the molecule gives rise to enantiomeric pair when the faces are attacked with some reagent (such as Cl^-) while the remaining parts of the molecule stay fixed. Enantiotopic faces are always identical in the achiral environment and different in chiral media. For instance, two faces of primary carbocation are homotopic, as the attack on two faces by an incoming nucleophile generates enantiomeric pair.



Enantiomeric pair

On the basis of molecular symmetry, two faces are said to be enantiomeric in nature if they are exchangeable by a secondary symmetry element i.e. plane of symmetry (σ), the center of symmetry (i), or alternating axis of symmetry (S_n).



C_s point group

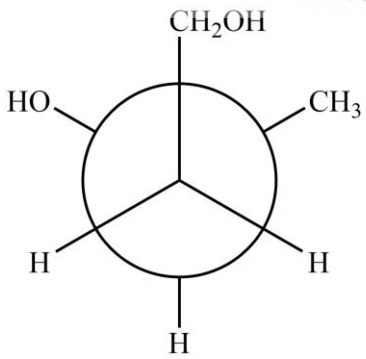
Both faces are exchangable by C_2 axis (homotopic groups)

➢ ***Diastereotopic Groups and Faces***

Diastereotopic groups and faces in an organic molecule can be found either on the basis of chemical replacement or by using the symmetry criteria.

1. Diastereotopic groups: Diastereotopic groups in a chemical compound are non-equivalent groups. Two groups A and B are diastereotopic if the diastereomers are obtained when the groups are interchanged with some other atom (such as bromine) while the remaining parts of the molecule stay fixed. Diastereotopic atoms are always different in any type of media whether it is chiral or achiral. Diastereotopic NMR-active nuclei have different chemical shifts in an NMR spectrum in any medium and different chemical shifts in achiral media. For example, the two hydrogen atoms in (Et)(OH)(Me)C–CH_2ClBr are CH2ClBr with one another, as the replacement by a third group gives rise to the diastereomeric pair.

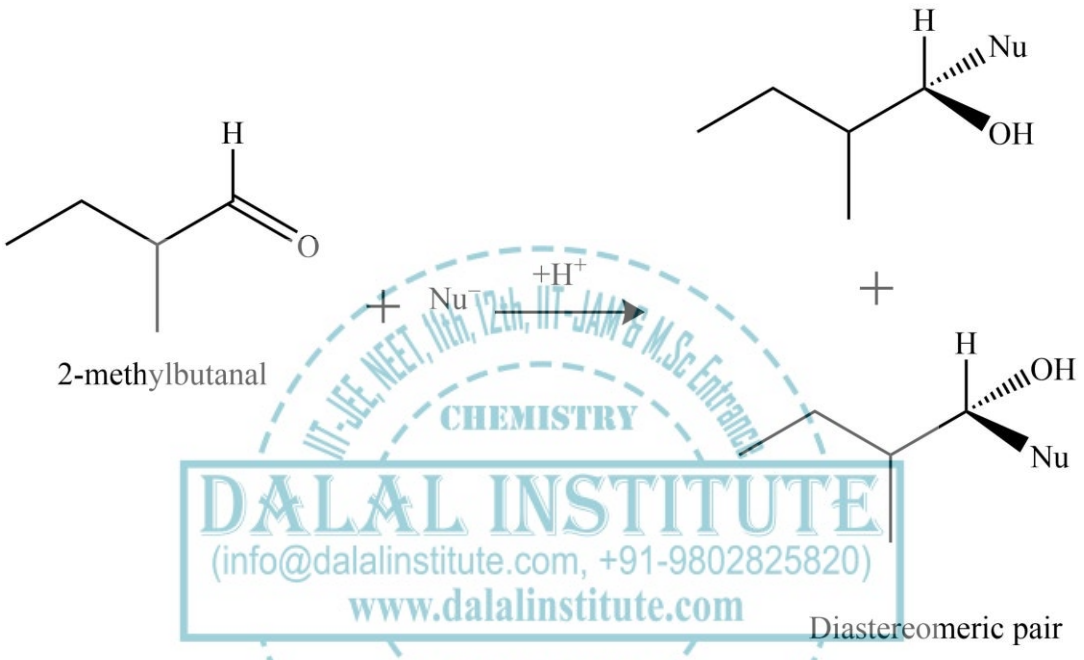
Based on molecular symmetry, two groups are said to be diastereotopic if they are not exchangeable by any symmetry element whether it is primary or secondary.



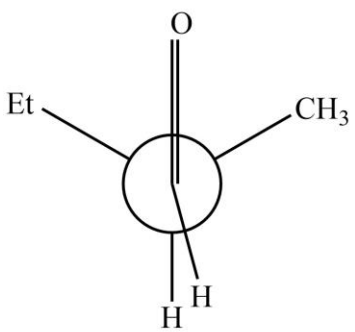
Both H are not exchangable by any symmetry element (diastereotopic groups)

C_1 point group

2. Diastereotopic faces: Diastereotopic faces in a chemical compound are non-equivalent faces, i.e., two faces A and B are diastereotopic if the molecule gives rise to diastereotopic pair when the faces are attacked with some reagent (such as Cl^-) while the remaining parts of the molecule stay fixed. Diastereotopic faces are always non-identical in any type of environment whether it is chiral or achiral. For instance, two faces of 2-methylbutanal are diastereotopic, as the attack on two faces by an incoming nucleophile generates diastereomeric pair.



On the basis of molecular symmetry, two faces are said to be diastereotopic in nature if they are not exchangeable by any symmetry element, i.e. neither by primary nor by secondary symmetry element.



Both faces are not exchangable by any symmetry element (diastereotopic faces

C_1 point group

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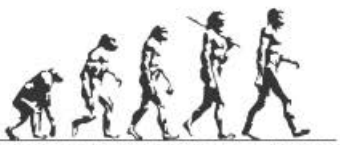

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