It has been found that - interference for free rotation can be minimised by

(i) Bending ortho H & other substituents
(ii) Compressing C–H (ortho bonds)
(iii) Stretching intramolecular bonds
(iv) Deforming the angle between benzene and interannular bonds.
(v) Deforming benzene rings themselves.

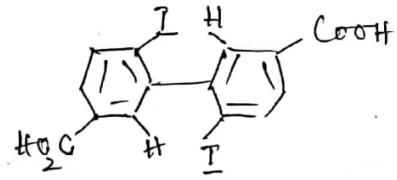
Order of - activation energy for racemisation

$I > Br > CH_3 > Cl > NO_2 > COOH > OMe > F > H$.

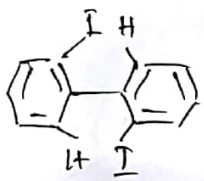
Buttressing Effect -

found that - the activation energy of racemisation for active biphenyls is increased when a substituent is present in meta position to C bond joining the rings. This is called buttressing effect.

Reason: Prevention of outward bending of - ortho substituents.

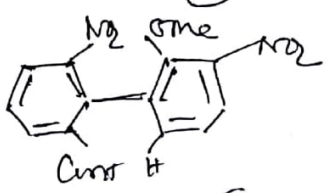


(X)

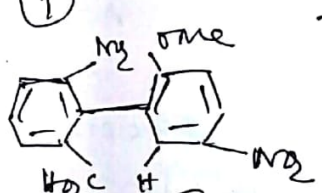


(Y)

$E_{act}(X) - E_{act}(Y) \simeq 21$ K-Cal/mole



(A)

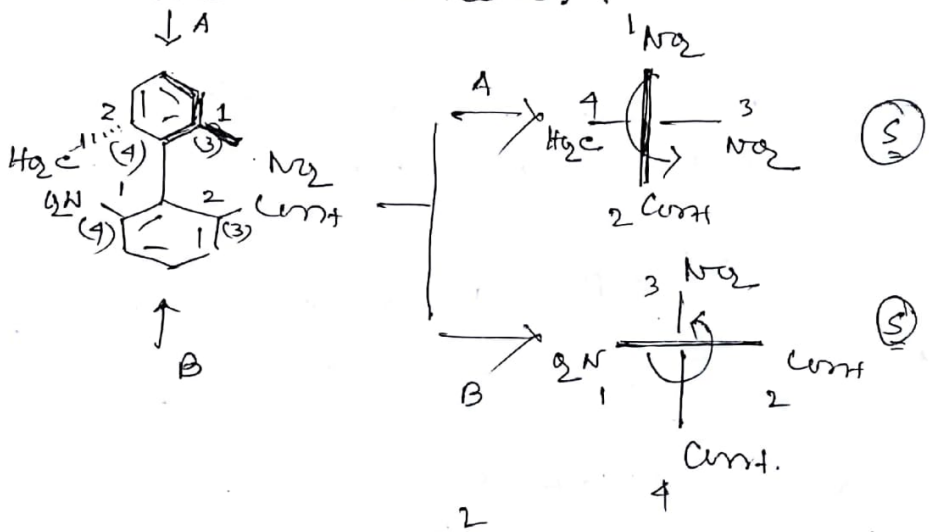


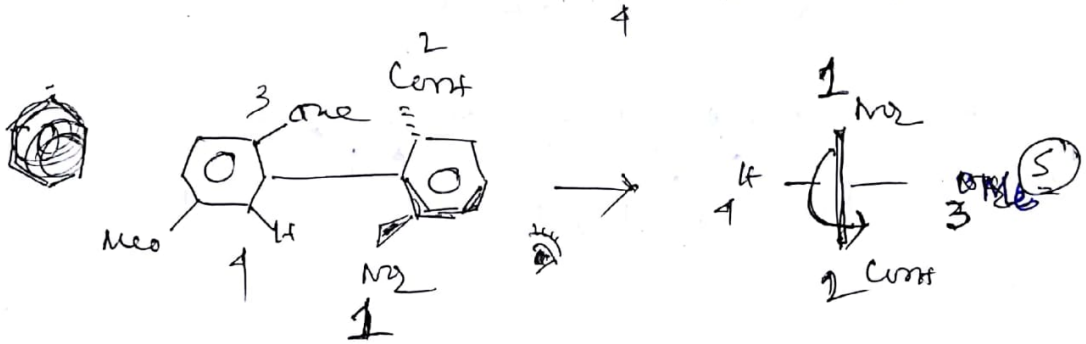
(B)

(B) racemises faster than (A)

Nomenclature

Same as allenes.

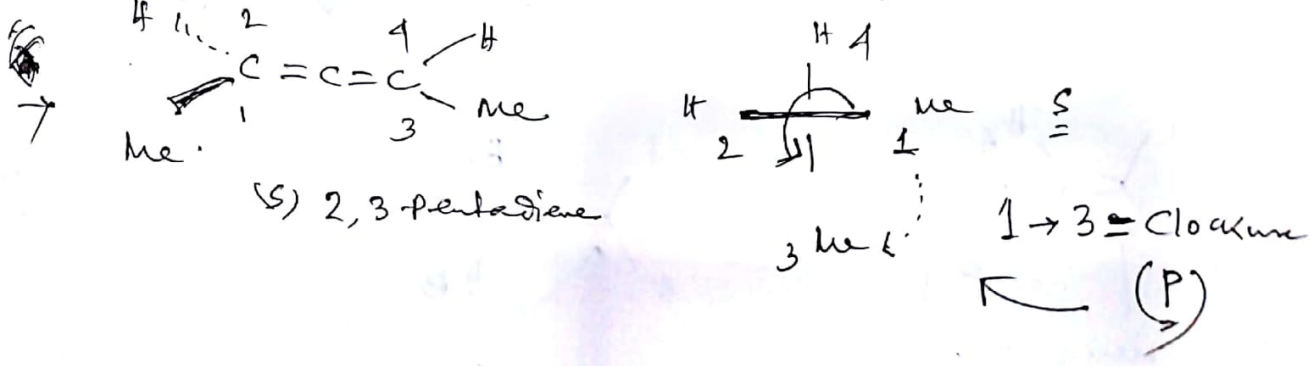




P, M descriptors for molecules with Chiral axis

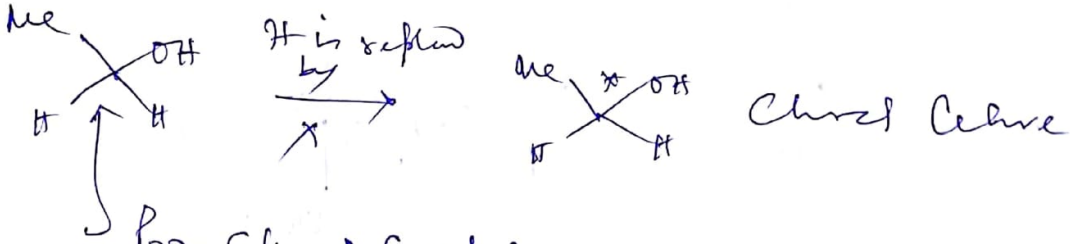
For assigning helical descriptors, only the groups of highest priority nearest to the viewer direction and the far are considered (1 → 3).

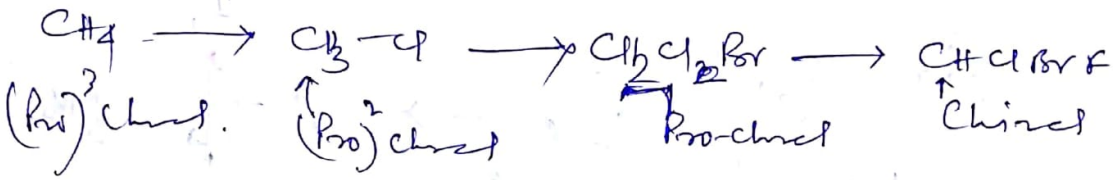
If 1 → 3 clockwise it is P (plus) if anti clockwise it is M (minus).



Pro-chirality

Replacement of one ligand leading to chiral centre, known as prochiral centre.

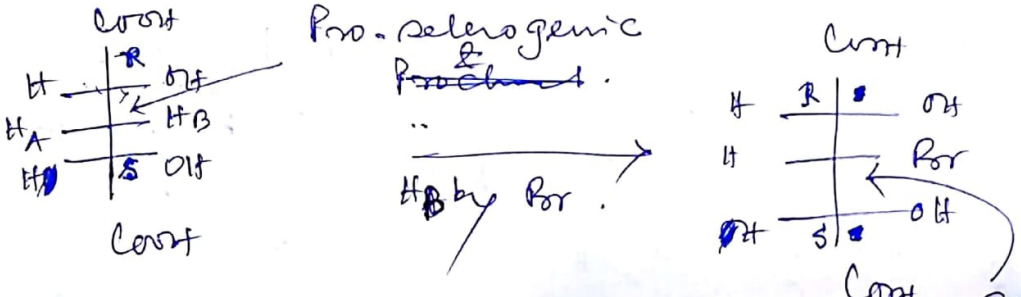


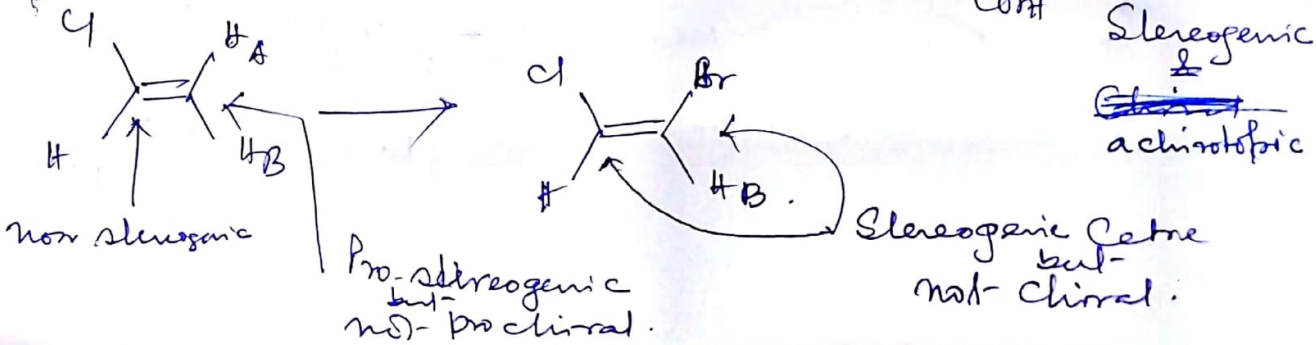


Pro-stereogenic centre.

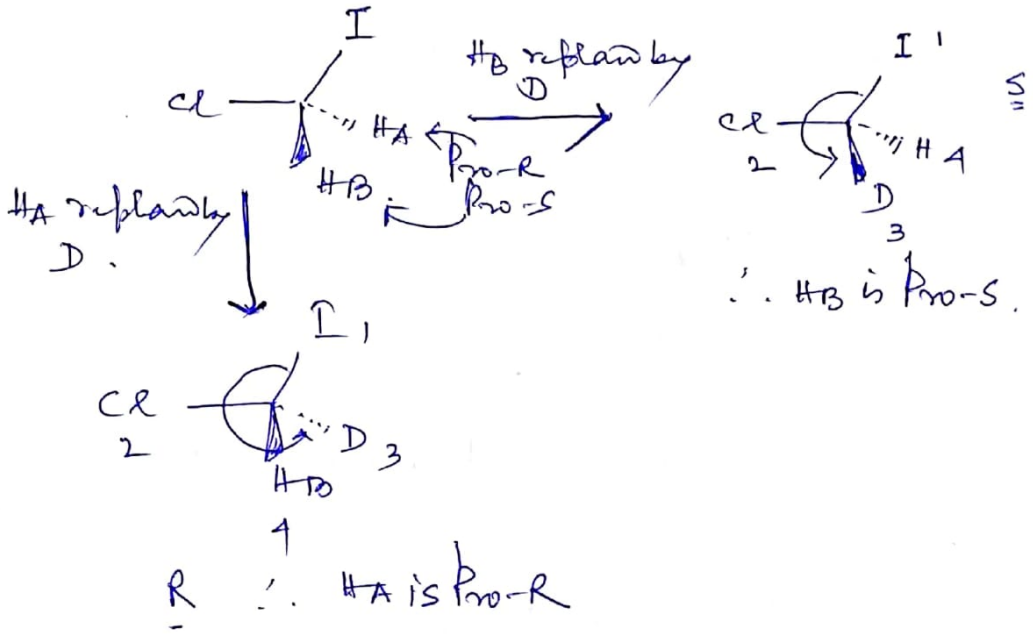
~~Replacement of~~

Centre bearing homomorphic ligands or groups which can be converted into a stereogenic centre by replacing one of them by different substituents.

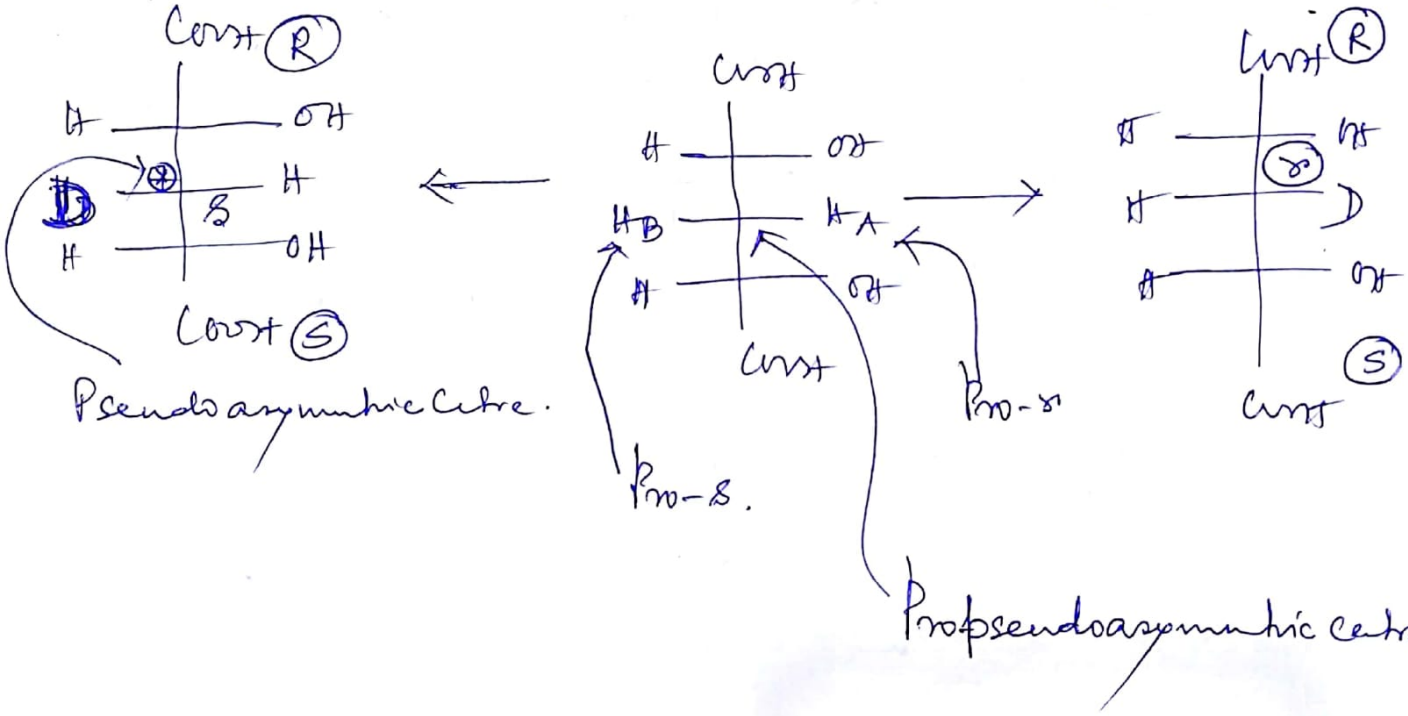




Pro-R & Pro-S.

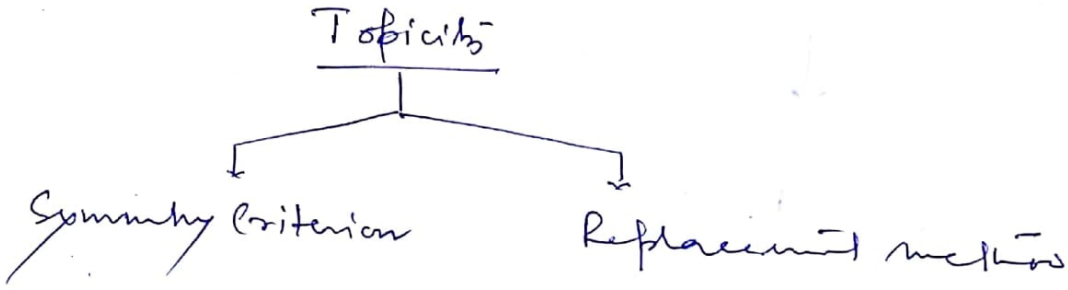


In case of pro-pseudoasymmetric centre the ligands are named Pro-r and Pro-s.



Topicity of ligands.

Nature of two homomorphic ligands (atoms or groups).

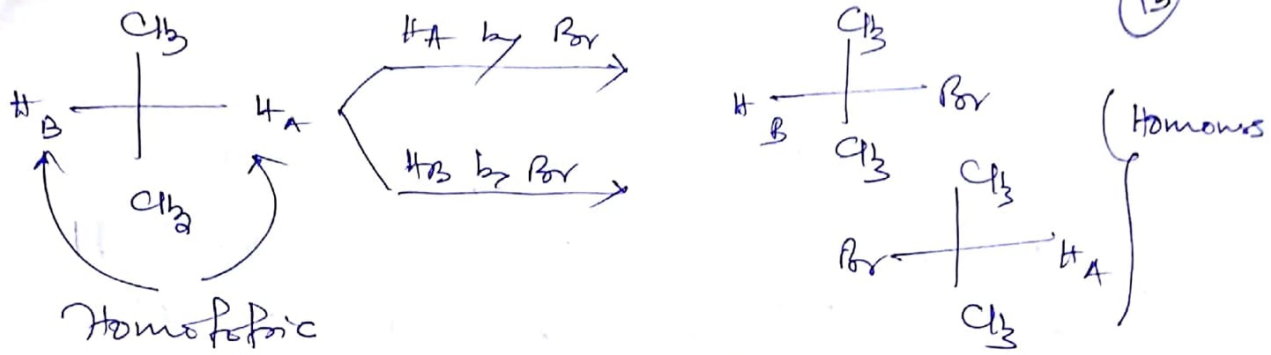


* Symmetry method (Criterion)

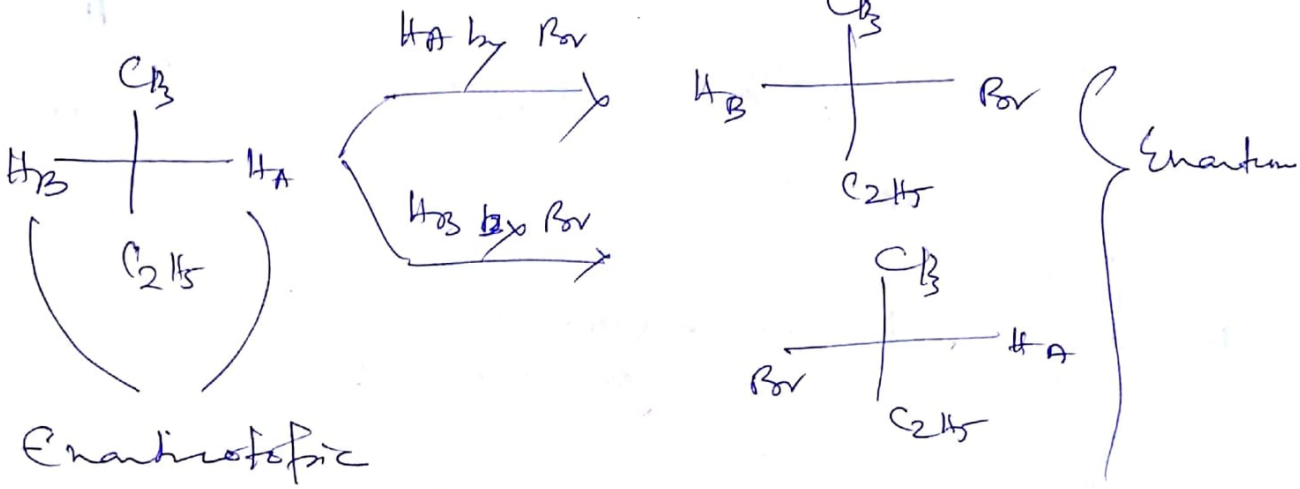
1. Replaced by C_2 or exchangable by C_2 - Homotopic
2. Exchanged by σ - Enantiotopic
3. Non-exchangable w.r.t C_2 or σ → Diastereotopic
4. Chemical environment are different
   ↓
   Constitutionally heterotopic.

* Replacement method

Replacement leading to homomers → Homotopic
" " " Enantiomers → Enantiotopic
" " " Diastereomers → Diastereotopic

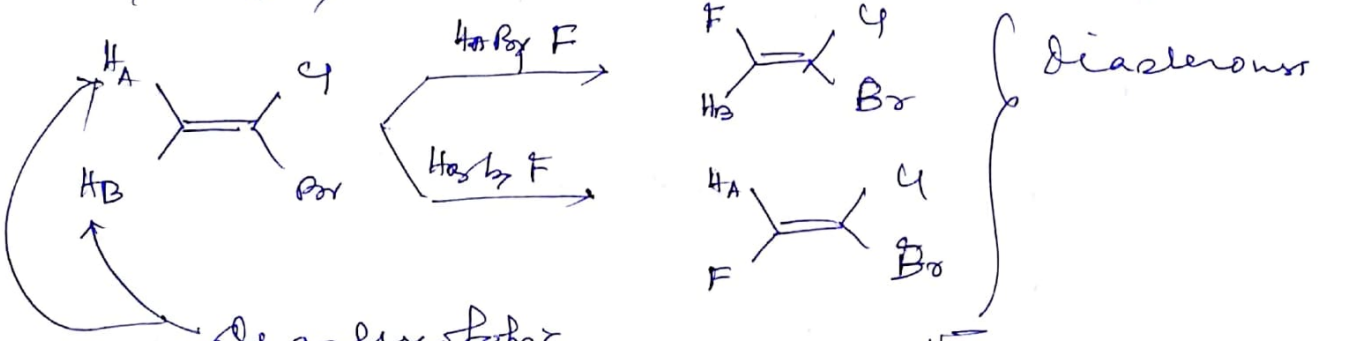


Exchangable with C_2.



Enantiotopic

Exchagaby with O



Diastereotopic

now exchangeable with C_2 or O.