LEC (10) CHEM 30A Oct 22nd

(1) R/S DESIGNATION
(2) FISCHER PROJECTIONS
(3) CIS/TRANS DIASTEREOISOMERS
(4) CONSEQUENCES OF CHIRALITY

Problems: HANDOUTS 3.6-3.9, 3.24-3.36
Reading: REVIEW Ch 3

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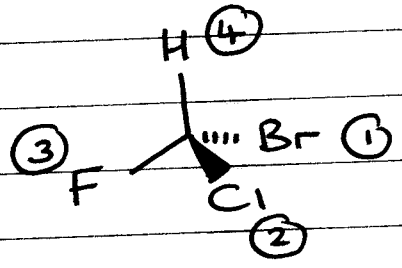
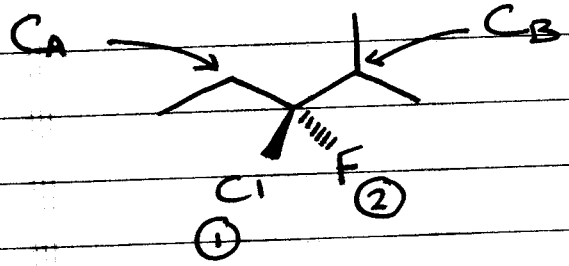
(1) R/S DESIGNATION

- assigning priority

(i) ATOMIC WEIGHT

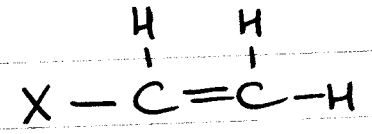
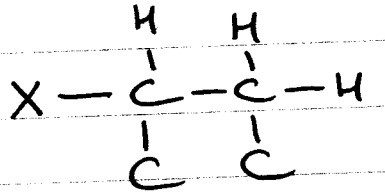


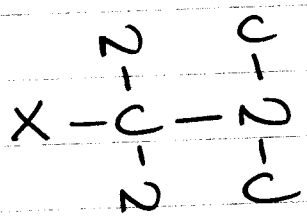
(ii) First POINT of DIFFERENCE

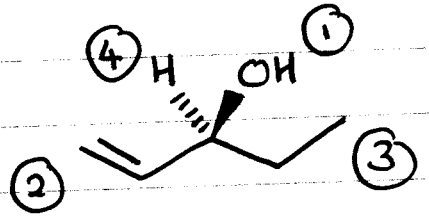


C_A C, H, H (4)
C_B C, C, H (3)

(iii) MULTIPLE BONDS = EQUIVALENT # of SINGLE BONDS

So,  is 

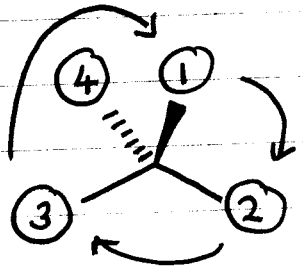
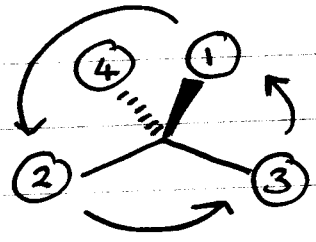
 is 

so 

- determining R/S

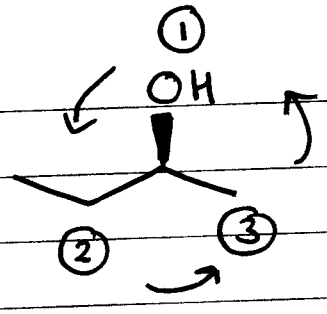
Rotate molecule to put lowest priority group in the background →

TWO POSSIBLE ORIENTATIONS

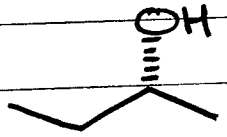
 or 

CLOCKWISE (R) COUNTERCLOCKWISE (S)

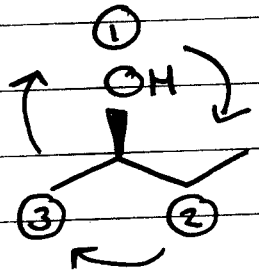
So



S-2-BUTANOL



rotate 180°



small group is not in the back

R-2-BUTANOL

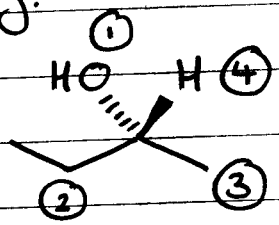
or if you have trouble rotating molecules...

TRICK

SWITCH LOWEST PRIORITY GROUP (4) WITH THE GROUP THAT IS IN THE BACK

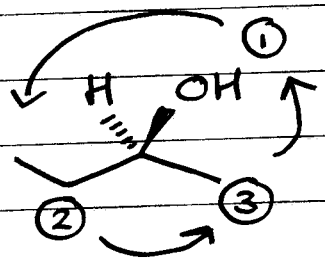
ASSIGN R/S, REALISING THAT THE STEREOCHEMISTRY OF THE ORIGINAL MOLECULE IS THE OPPOSITE...

e.g.



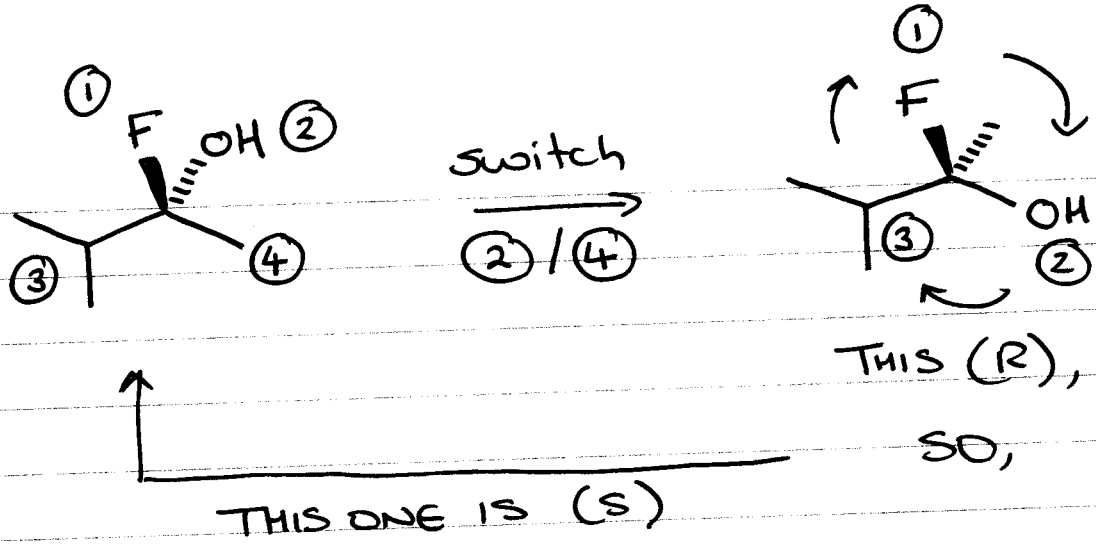
switch

1 / 4



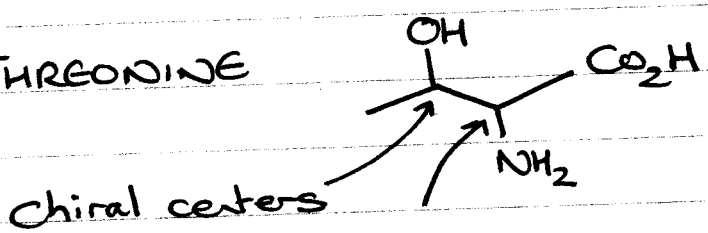
(S)

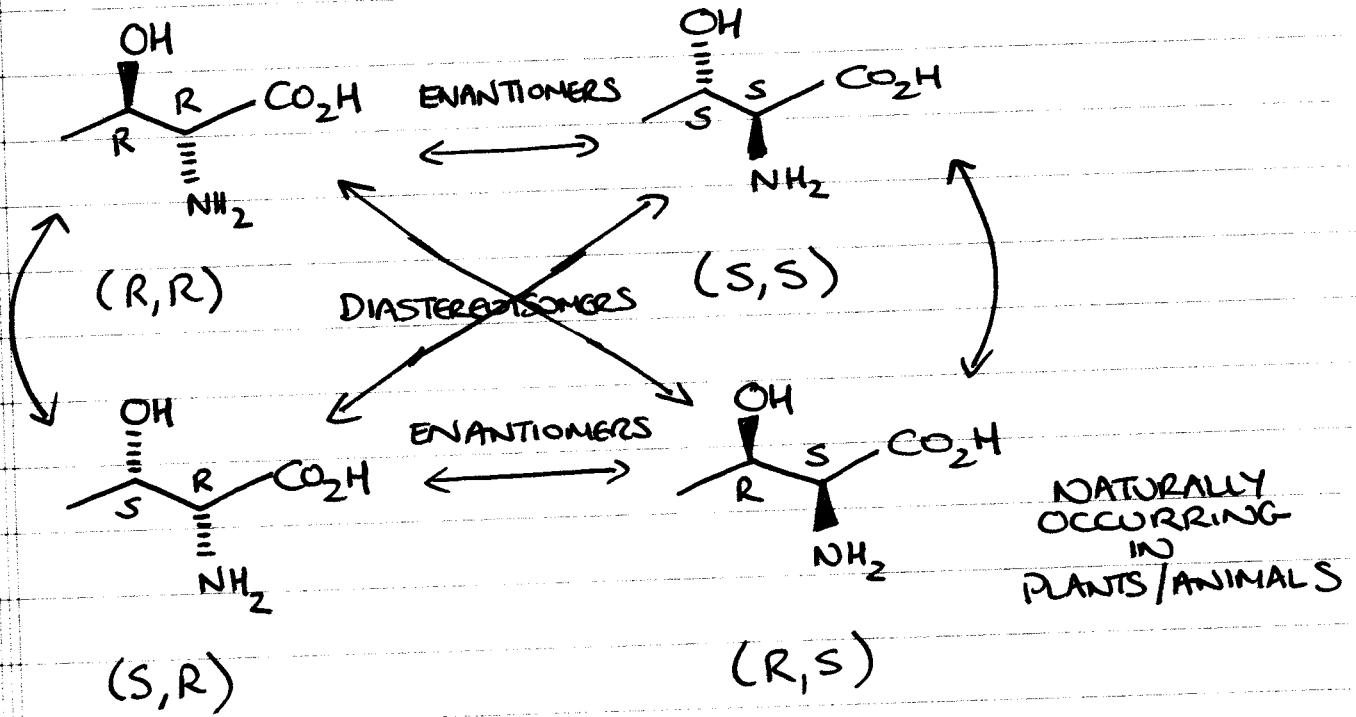
SO THIS MUST BE (R)



- COMPOUNDS W/ MORE THAN ONE STEREOCENTER

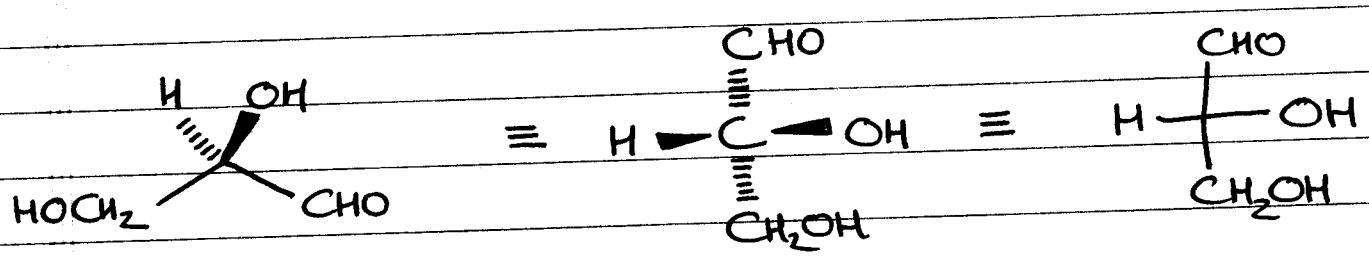
amino acid THREONINE





DIASTEREOISOMERS – NON MIRROR IMAGE STEREOISOMERS

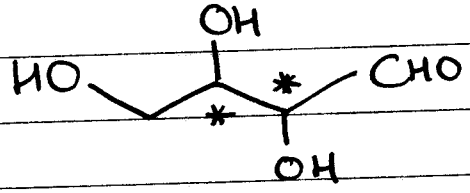
- FISCHER PROJECTIONS

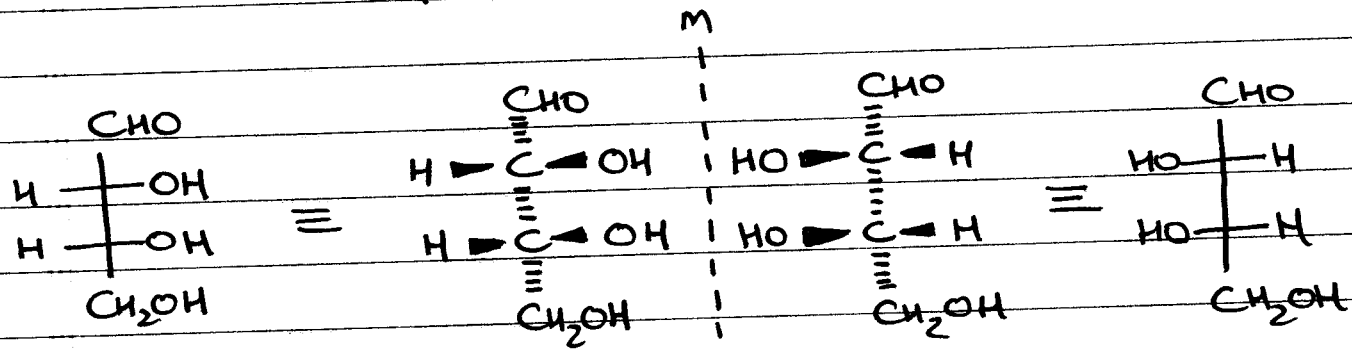


Glyceraldehyde

Useful for compounds with many continuous stereocenters

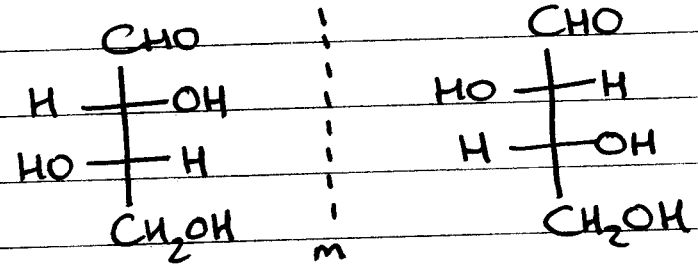
2,3,4-trihydroxybutanal



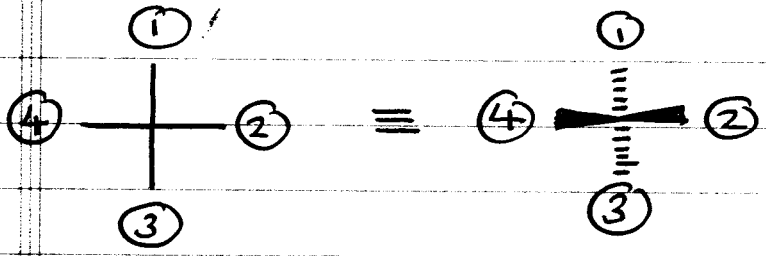


ENANTIOMERS

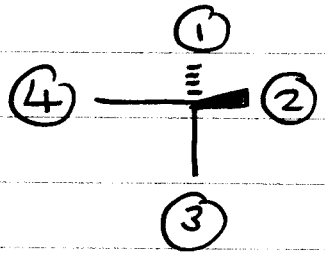
ANOTHER PAIR OF ENANTIOMERS



Determing Stereocenter Configuration in FISCHER projections



SWITCH one wedge and one dash for straight lines



⇐ assign R/S

THIS ONE IS (S)

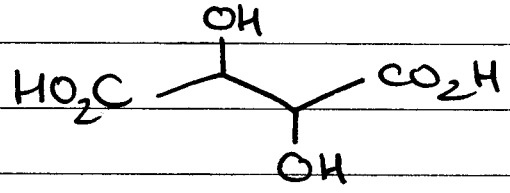
GO BACK and determine R/S for 2,3,4 trihydroxybutanal

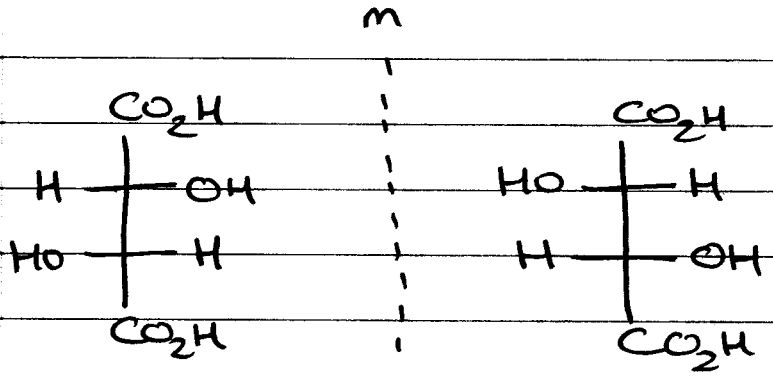
- A molecule with n chiral centers can have a maximum number of stereoisomers = 2^n

i.e., 2,3,4 trihydroxybutanal has 2 stereocenters and

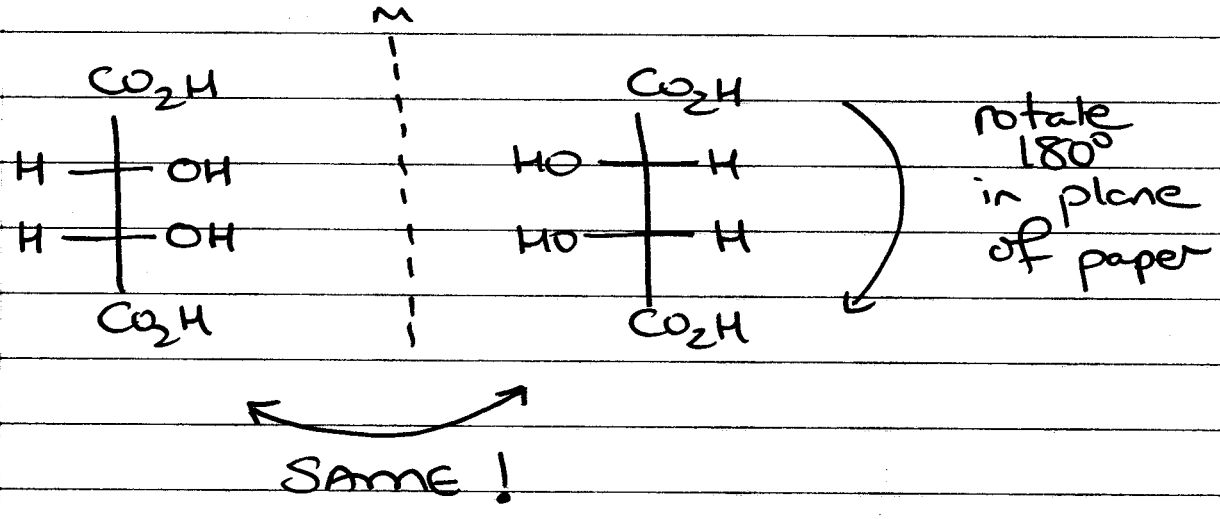
$2^2 = 4$ stereoisomers

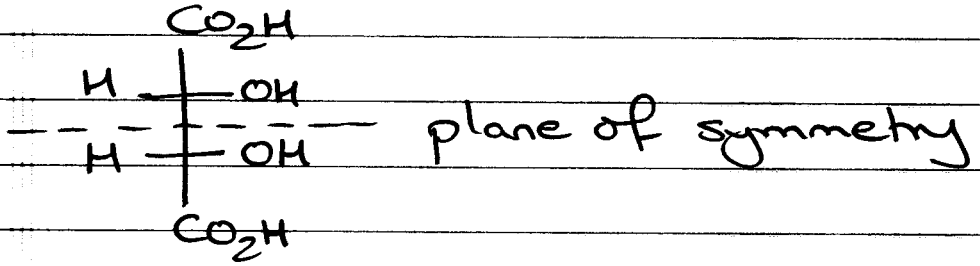
Consider TARTARIC ACID





ENANTIOMERS





Cmpd with stereocenters, but is achiral
=> MESO

ENANTIOMERS ✓

DIASTEREOISOMERS → CONFIGURATIONAL ✓

DIASTEREOISOMERS → CIS/TRANS → RINGS, ALKENES

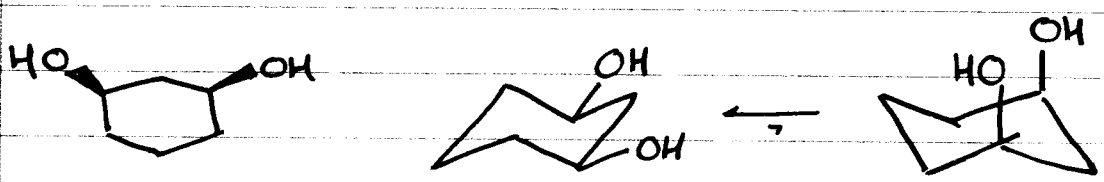
RINGS

cis (meso) | trans | trans

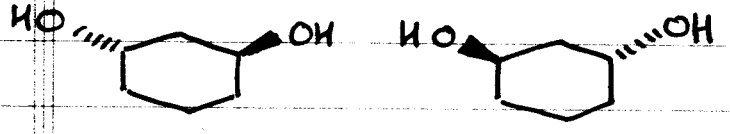
trans, trans: ENANTIOMERS

CONSIDER CYCLOHEXANES

1,3



cis (meso)

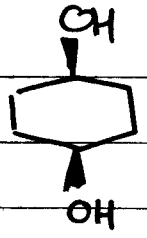


ENANTIOMERS

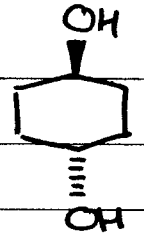
DRAW CHAIR FOR EACH AND DO RING FLIP

FOR EACH ENANTIOMER CHAIRS ARE IDENTICAL

1,4



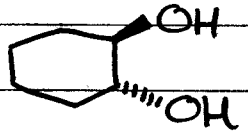
cis



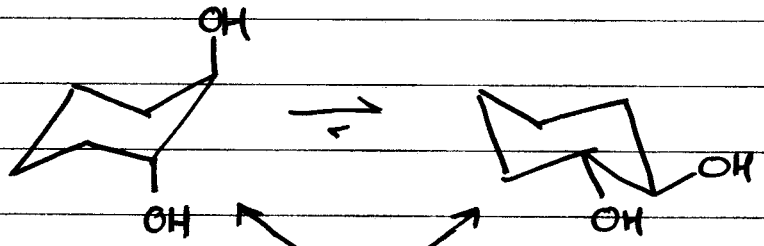
trans

BOTH ACHIRAL

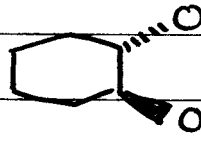
1,2

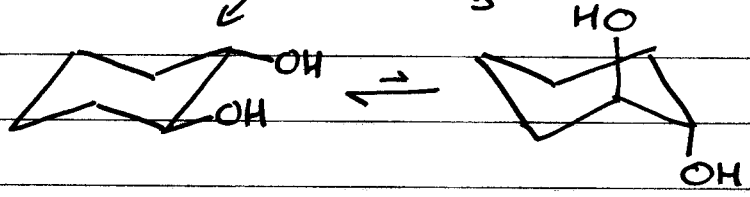


trans

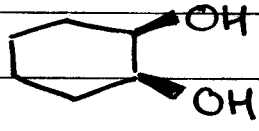


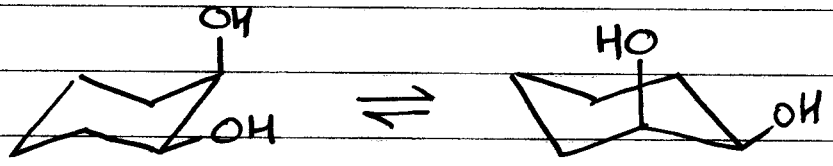
MIRROR IMAGES





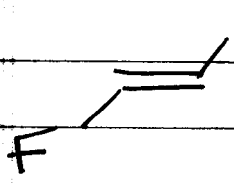
cis



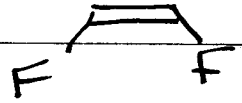


MIRROR IMAGES

ALKENES

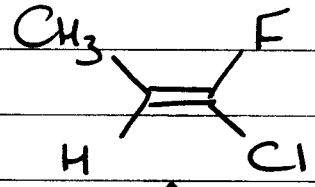


trans



cis

DIASTEREOISOMERS

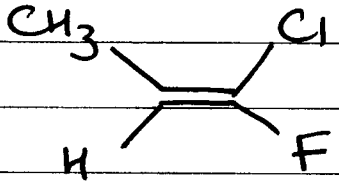


cis/trans ? (E)

↑

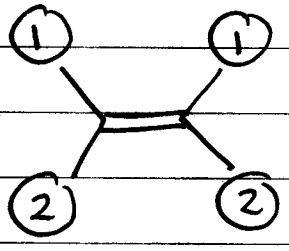
DIASTEREOISOMERS

↓

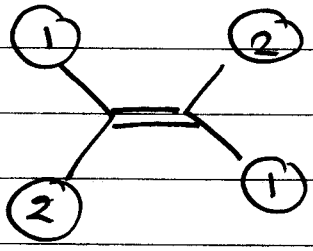


? (Z)

Use same priorities as for R/S on each C of double bond

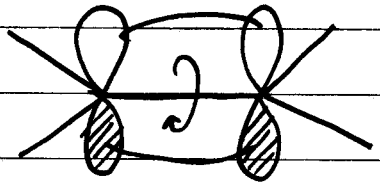


Z



E

WHY NO ROTATION ABOUT DOUBLE BONDS ?



ROTATION WOULD REMOVE OVERLAP (BREAK π BOND) AND THIS DOESN'T HAPPEN UNDER NORMAL CONDITIONS

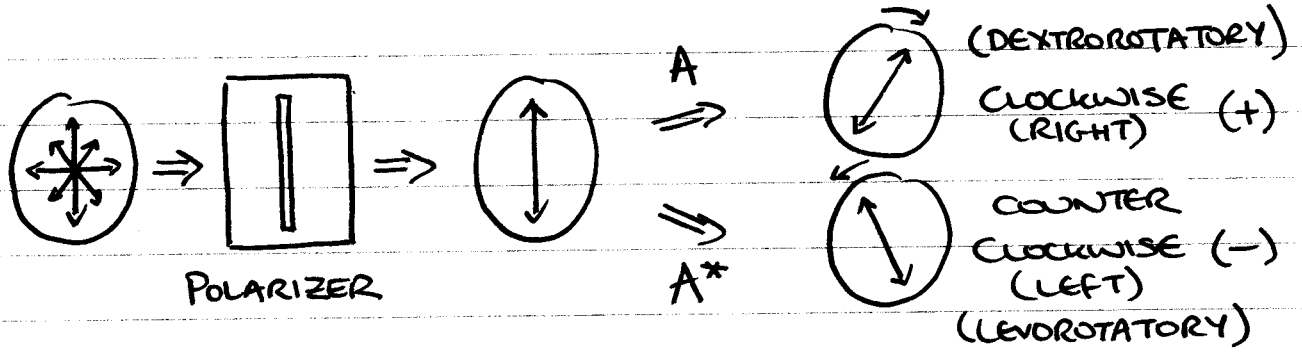
(3) PROPERTIES OF STEREOISOMERS

ENANTIOMERS – Identical PHYSICAL & CHEMICAL PROPERTIES (in an achiral environment)

e.g. mp, bp, solubility in water etc

DIASTEREOISOMERS – DIFFERENT....

OPTICAL ACTIVITY
– ROTATION OF PLANE POLARIZED LIGHT



$$\text{Specific rotation } [\alpha]_{\lambda}^{T} = \frac{\text{Obs rotation (°)}}{\text{Length (dm)} \times \text{Conc (g/mL)}}$$

T = temperature (°C)
λ = wavelength of light

Racemic mixture → specific rotation = ϕ ($\pm$)

NO RELATIONSHIP B/WEEN R/S +/–

ENANTIOMERIC EXCESS (ee)

$$ee = \frac{[R]-[S]}{[R]+[S]} \times 100$$

$$= \%R - \%S$$

e.g. if a sample is 90% R and 10% S,

the ee = 90 − 10 = 80%

READ SECTIONS 3.8 / 3.9

CHIRALITY IN THE NATURAL WORLD
(DNA, PROTEINS, ENZYMES, DRUGS)