Stereochemistry
4-Exceptions and Resolution

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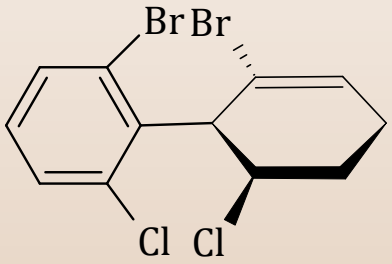
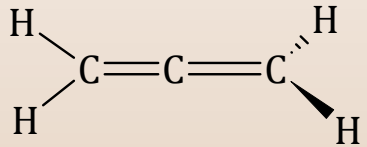
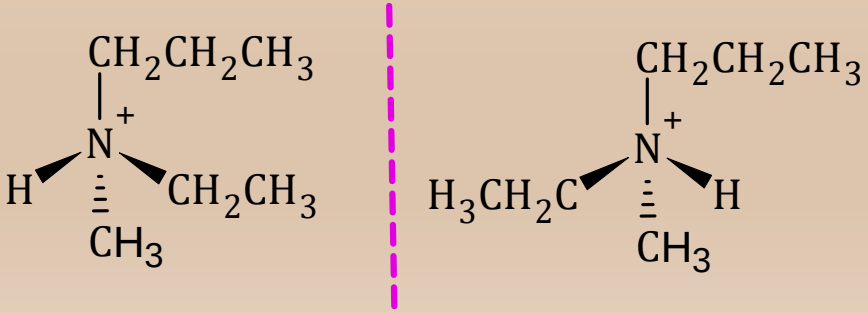
Stereoisomers - Exceptions

Some compounds may not have a chiral center but are still chiral because of steric hinderance. Examples given below of the sterically hindered rings and allenes.





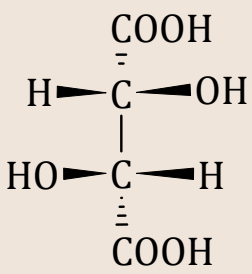
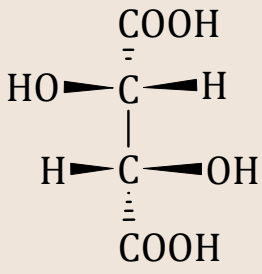
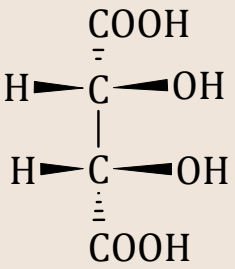
There are also heteroatoms that have chirality, specifically an atom that has sp^3 hybridization. Common example are amines. The lone pair of electrons on the N is considered as the fourth group. However, this can cause flipping of the molecule and not maintain chirality. To avoid that and maintain a stereoisomer's chirality, the amine is converted into a salt with four bonds.



Properties of Stereoisomers

Enantiomers have identical physical and chemical properties.

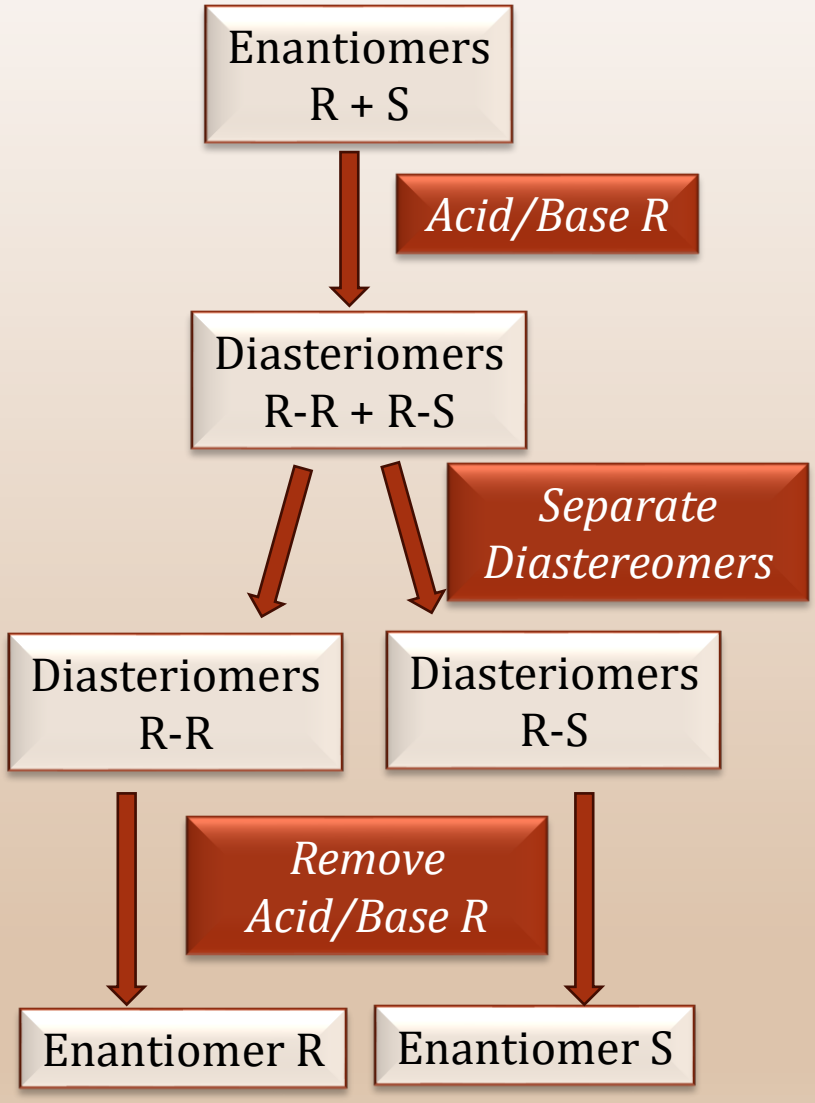
- Diastereomers are different compounds and have different physical and chemical properties. Meso tartaric acid, for example, has different physical and chemical properties from the R,R and S,S enantiomers. See the properties of the stereoisomers below.

	RR	**SS**	**Meso**
			
Specific rotation	+12.7	-12.7	0
Melting point (°C)	171-173	171-173	146-148
Density (20°C, g/cm^3)	1.76	1.76	1.66
Solubility in water (20°C, g/100 mL)	139	139	125
pK_1	2.98	2.98	3.23
pK_2	4.34	4.34	4.82

Resolution

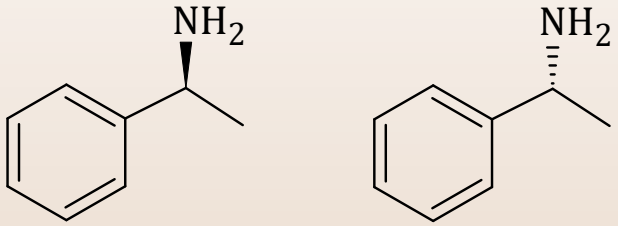
- Racemic mixture is an equimolar mixture of two enantiomers causing the rotation to be zero as it is an equal mixture of (+) and (-) isomers.
- Resolution is the separation of a racemic mixture into enantiomers. This is done by converting the pair of enantiomers into two diastereomers which have different physical properties. Using these physical properties, the enantiomers are separated and then converted back to enantiomers.
- A common reaction for chemical resolution is salt formation.

$$RCOOH + :B \rightleftharpoons RCOO^{-}B^{+}$$



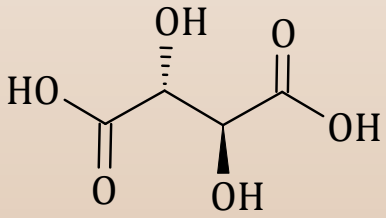
Resolving Agents

- Racemic acids can be resolved using commercially available chiral bases such as 1-phenylethanamine.



(S)-1-phenylethanamine

- Racemic bases can be resolved using chiral acids such as tartaric acid.



(2S,3S)-(+)-tartaric acid

Key Words/Concepts

- Stereoisomers
- Chiral Center
- Chirality
- Enantiomer
- Plane polarized light
- Dextrorotatory (d)
- Laevorotatory (l)
- Diastereomers
- Meso compounds
- Cahn Ingold and Prelog nomenclature
- Configurations (R and S)
- Racemic mixtures
- Fisher projections
- Enantiomeric excess
- Absolute configuration
- Resolution