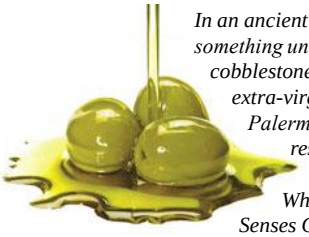
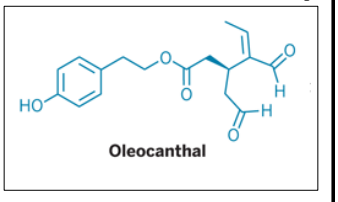
BEHIND OLIVE OIL'S BITE



In an ancient village perched on a Sicilian mountaintop, Gary K. Beauchamp tasted something unexpected. He'd come to the hamlet of Erice, with its medieval castles and cobblestone lanes, for a 1999 meeting on molecular gastronomy. But after sampling extra-virgin olive oil fresh-pressed by a colleague from Italy's University of Palermo, he returned home with a hunch that's fueled a decade's worth of research.

When Beauchamp, a biopsychologist at Philadelphia's Monell Chemical Senses Center, tasted the olive oil—his first taste of it alone, outside the context of food—he noticed an irritating sensation in a very specific spot: the back of his throat. And it just so happened he'd felt that sensation before, tasting a liquid form of the over-the-counter painkiller ibuprofen. "I was dumbfounded that the burn was exactly the same," he says. "It struck me that maybe the similarity of the throat irritation signaled pharmacological similarity."

It's a decades-old idea in the taste field that a compound's taste properties might predict its drug potency in the body, Beauchamp explains. On a team with Monell colleague Paul A. S. Breslin, who already was studying ibuprofen's sensory properties, and Monell and University of Pennsylvania chemist Amos B. Smith III, Beauchamp found a possible connection. They confirmed that a specific compound in extra-virgin olive oil, which they dubbed ***oleocanthal****, is responsible for the oil's sting, and they found that like ibuprofen, oleocanthal blocks cyclooxygenase enzymes, which are players in inflammation and pain "The idea is if oleocanthal is an anti-inflammatory compound like ibuprofen, then maybe it helps explain some of the beneficial effects of consuming olive oil over a lifetime," Beauchamp says.*



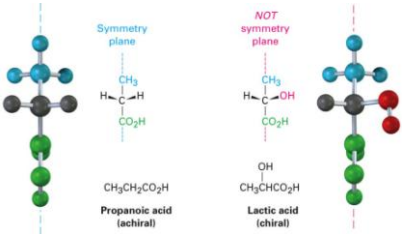
Oleocanthal

Chemical & Engineering News, March 21, 2011

CLASS PLAN – WEDNESDAY, OCTOBER 5

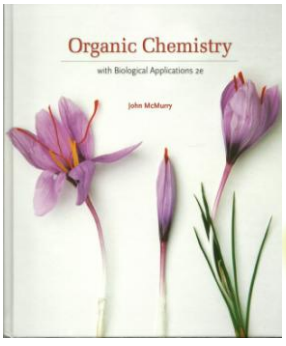
- **OWL Homework – Summary and Feedback**
- **Chapter 5 Mini-Lecture – Introduction to Chirality**
- **Chapter 5 Learning Activities**
  - → **identifying chirality centres**
  - → **applying the Cahn-Ingold-Prelog Rules**
  - → **determining relationships between compounds**
  - → **optical activity questions**
- **Today's Class – Summary**
- **What's Next?**

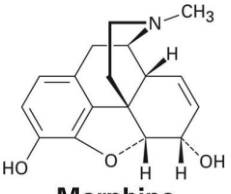
1

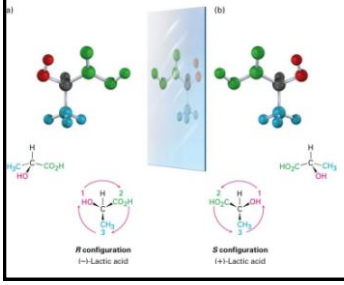


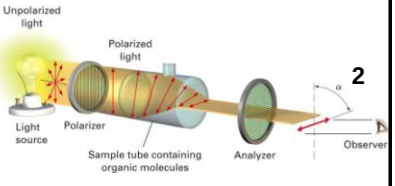
McMurry Chapter 5

STEREOCHEMISTRY









2

Chapter 5	Stereochemistry
5.9	A Review of Isomerism
5.1	Enantiomers and Tetrahedral Carbon
5.2, 5.10	Chirality
5.12	Chirality in Nature
5.5	Sequence Rules for Specifying Configuration
5.3, 5.4	Optical Activity
Supplement:	*Fischer Projection Formulas (see Section 21.2)*
5.11	Prochirality
5.6, 5.7	Diastereomers and Meso Compounds
5.8	Racemates and Resolution of Enantiomers

week 1

week 2

3

OWL HOMEWORK

4

WEEK 4 PRE-CLASS OWL HOMEWORK

5.2 MAS – Chirality Centres

→ 95% participation; mean score: 88%; mastered; 83%; 4 min

5.3 MAS – Optical Activity. Calculation of Optical Rotation

→ 94% participation; mean score: 88%; mastered; 82%; 11 min

5.5 MAS – Cahn-Ingold-Prelog Sequence Rules

→ 94% participation; mean score: 90%; mastered: 85%; 5 min

5.5-5.6a MAS – Specifying Absolute Configurations in JMOL Images

→ 93% participation; mean score: 78%; mastered: 60%; 12 min

CH5 EOC Questions

→ 93% participation; mean score: 78%

Q5.27 – Assigning R/S to JMOL Images

→ 92% participation; mastered; 74%; 5 min

Q5.34 – How Many Chirality Centres?

→ 91% participation; mastered; 76%; 7 min

Q5.40 – Rank the Following Substituents (CIP)

→ 92% participation; mastered; 64%; 5 min

Q5.44 – Draw Correct Enantiomer

→ 84% participation; mastered; 56%; 14 min

AVERAGE TIME TO COMPLETE: 63 MIN

5

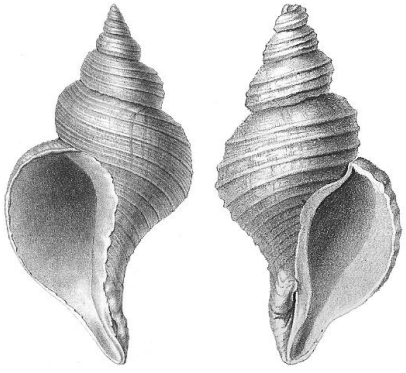
CHIRAL OBJECTS AND ENANTIOMERS

6

CHIRAL OBJECTS AND ENANTIOMERS

A chiral object is one that is not superposable on its mirror image.

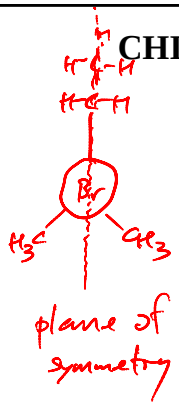
Left hand Right hand



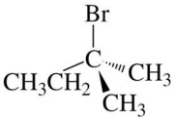
Two objects that are non-superposable mirror images are called ENANTIOMERS.

7

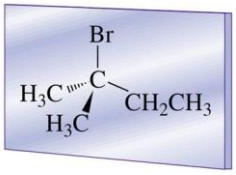
CHIRAL MOLECULES AND ENANTIOMERS



plane of symmetry

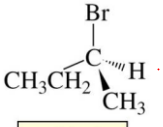


an achiral molecule

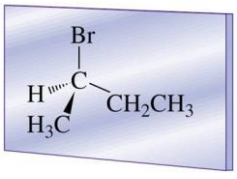


superposable mirror image

no plane of symmetry



a chiral molecule



nonsuperposable mirror image

A molecule with a <u>single</u> tetrahedral carbon bonded to four different groups will always be chiral.

Achiral molecules have planes of symmetry. Chiral molecules do not.

8

FACIAL SYMMETRY

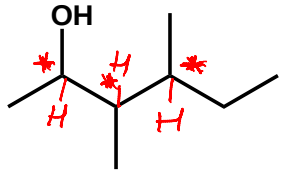
Submit your pictures

(celebrity, friend, yourself, replacement for Denzel)

IDENTIFYING CHIRALITY CENTRES

11

How many chirality centres are present in the following molecule?

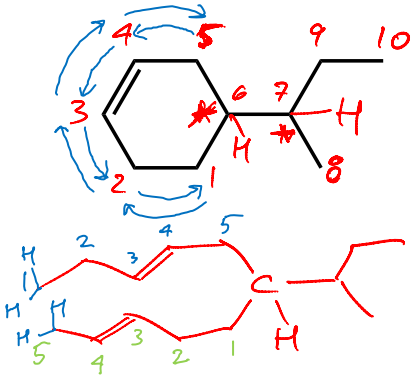


tetrahedral carbons bonded to 4 different atoms/groups

A. 0
B. 1
C. 2
D 3 ✓
E. 4

12

How many chirality centres are present in the following molecule?



2 chirality centres

6 + 7

For chirality centres that are part of a ring, "walking" around the ring clockwise is considered as one substituent; counterclockwise is another substituent.

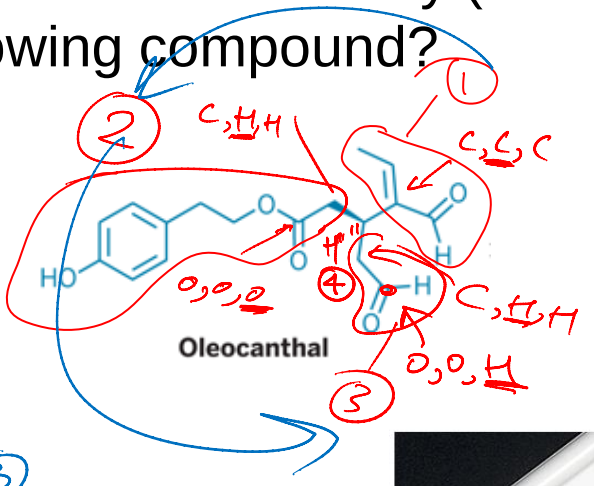
13

CAHN-INGOLD-PRELOG RULES

14

What is the stereochemistry (*R* or *S*) of the following compound?

A. R
B. S ✓

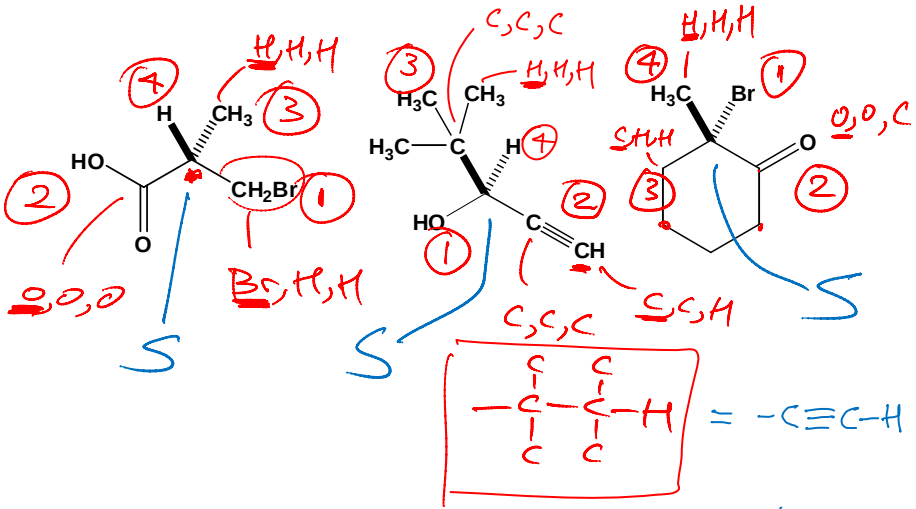


1 → 2 → 3 counterclockwise

S

15

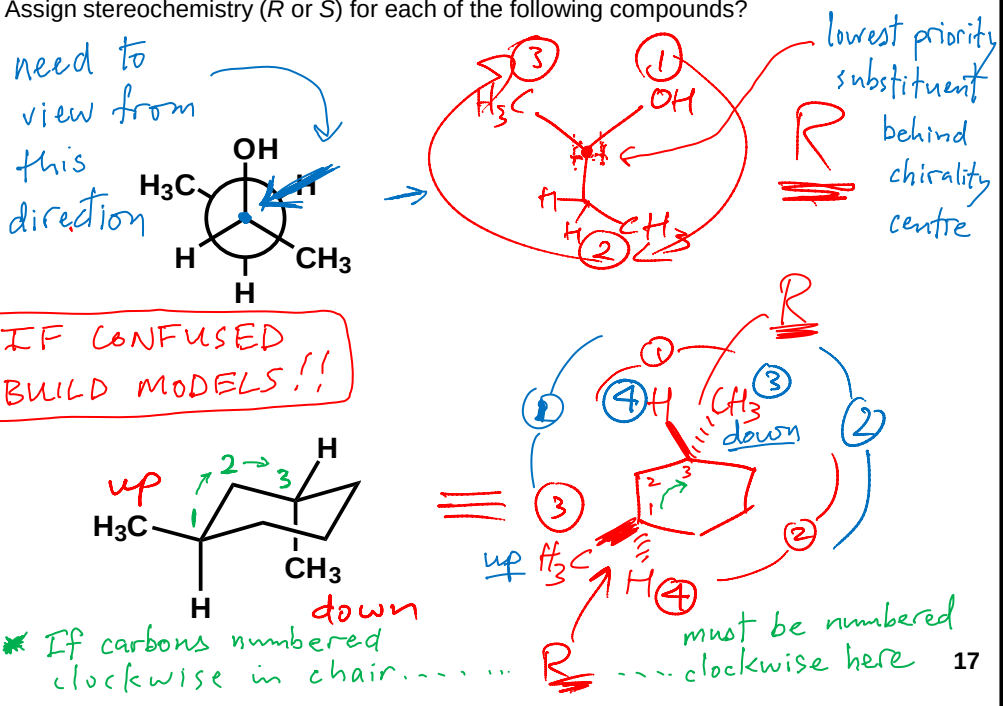
Assign stereochemistry (*R* or S) to each of the following molecules.



Compare substituents at chirality centre one atom at a time listing atoms in priority sequence

16

Assign stereochemistry (*R* or *S*) for each of the following compounds?



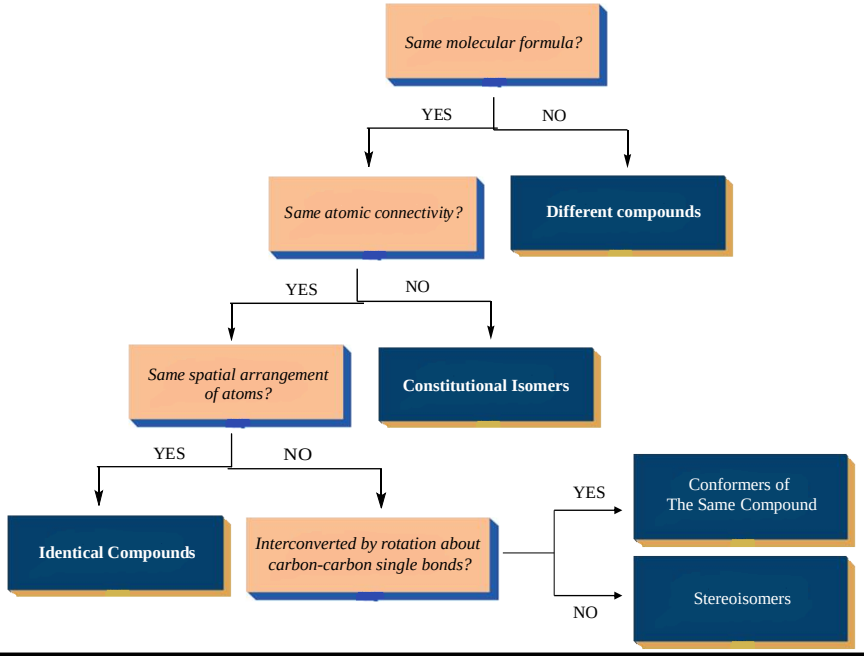
17

DETERMINING RELATIONSHIPS BETWEEN COMPOUNDS

18

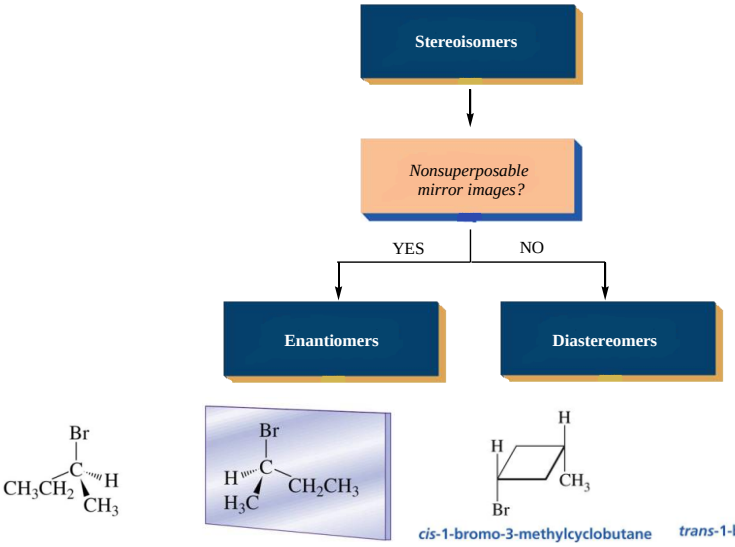
STEREOISOMERISM REVISITED

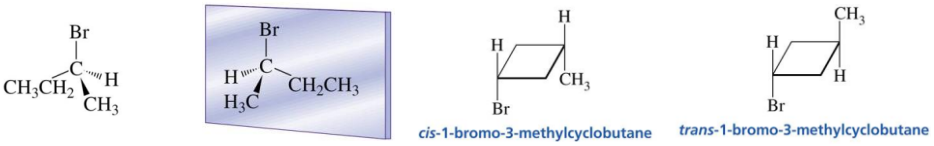
"What is the relationship between the following compounds?"



19

STEREOISOMERISM REVISITED



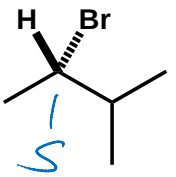


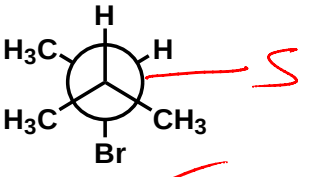
cis-1-bromo-3-methylcyclobutane

trans-1-bromo-3-methylcyclobutane

20

What is the relationship between the following compounds?



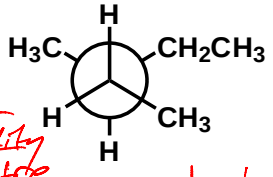


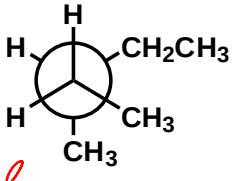
A. identical compounds
B. constitutional isomers
C. enantiomers
D. diastereomers

21

For each of the following pairs, state the relationship: identical compounds (including conformations of the same compound) or enantiomers.

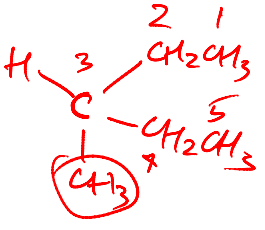
(a)





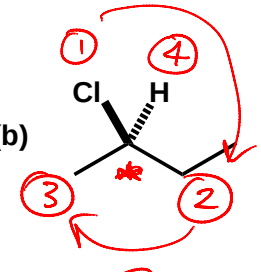
no chirality centre

identical

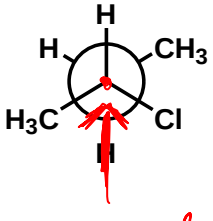


3-methylpentane

(b)

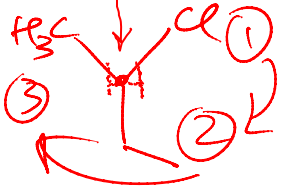


R



identical

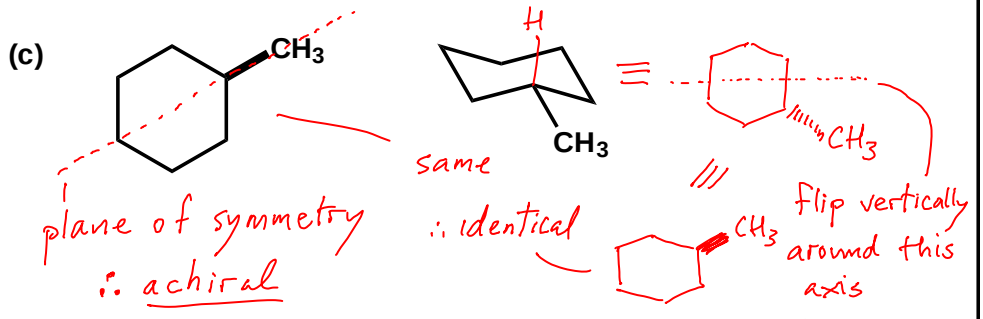
lowest priority substituent behind carbon

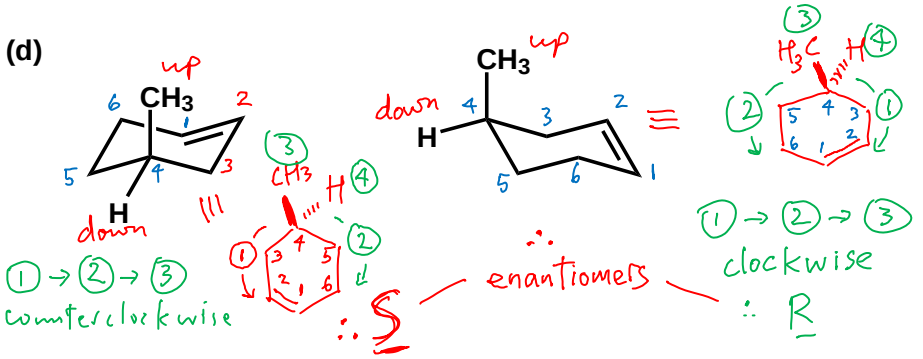


R

22

For each of the following pairs, state the relationship: identical compounds (including conformations of the same compound) or enantiomers.





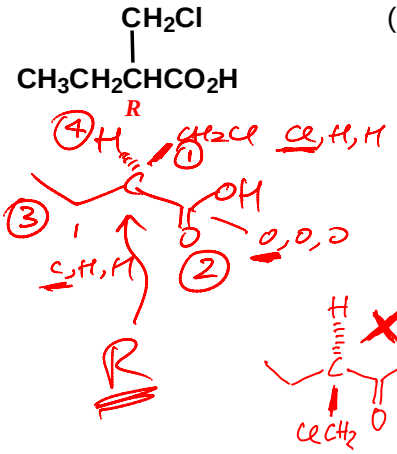
23

DRAWING CHIRAL MOLECULES

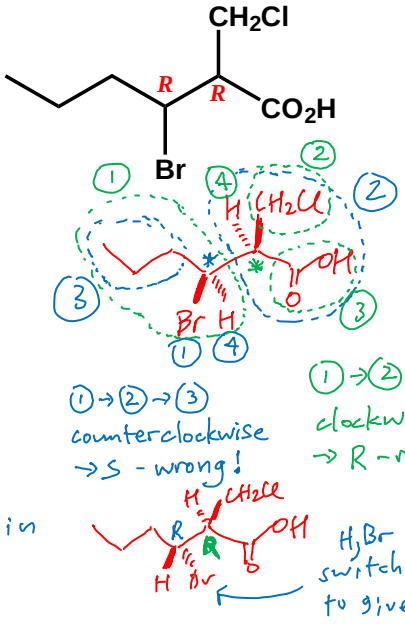
24

For each of the following, draw the indicated configuration illustrating stereochemistry about the chiral carbon using wedges and dashes.

(a)



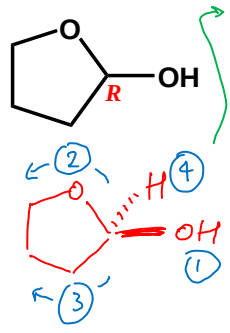
(b)



25

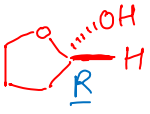
For each of the following, draw the indicated configuration illustrating stereochemistry about the chiral carbon using wedges and dashes.

(c)

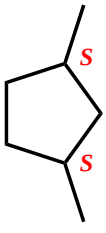


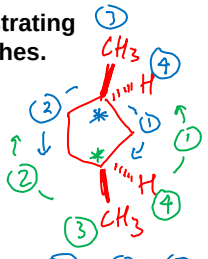
Draw with H in behind just to quickly determine stereochemistry
- if stereochem correct → done
- if stereochem wrong - switch two substituents

1 → 2 → 3 counterclockwise → S
∴ switch H, OH To get R



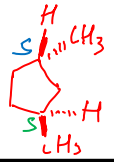
(d)





1 → 2 → 3 clockwise → R → wrong!
1 → 2 → 3 counterclockwise → S → right!

∴ switch H, CH3 at "top" chirality centre



26

OPTICAL ACTIVITY PROBLEMS

27

A reaction proceeds to give a mixture of enantiomers with an enantiomeric excess (ee) of 75%. This means that the mixture contains 75% of one enantiomer and 25% of the other enantiomer.

75% ee = 87.5 % / 12.5 %

A. True
B. False ✓

28

PRACTICE PROBLEM

The specific rotation of (+)-2-bromobutane is +23.1°.
(a) What is the observed rotation of a sample of (+)-2-bromobutane that has an ee of 75%?
(b) What percentages of (+) and (-) enantiomers are present in this sample?

(a) If pure enantiomer gives rotation of +23.1°, a mixture of enantiomers with 75% enantiomeric excess gives rotation that is 75% of 23.1°
→ (23.1°)(0.75) = 17.3°

(b) done on previous slide
87.5% (+)-2-bromobutane
12.5% (-)-2-bromobutane

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CHAPTER 5 (PART I) – SUMMARY
CHAPTER 5 (PART II) - PREVIEW

Chapter 5	Stereochemistry	
5.9	A Review of Isomerism	
5.1	Enantiomers and Tetrahedral Carbon	
5.2, 5.10	Chirality	
5.12	Chirality in Nature	
5.5	Sequence Rules for Specifying Configuration	
5.3, 5.4	Optical Activity	
Supplement:	*Fischer Projection Formulas (see Section 21.2)*	next week
5.11	Prochirality	
5.6, 5.7	Diastereomers and Meso Compounds	
5.8	Racemates and Resolution of Enantiomers	

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WHAT'S NEXT

This Week

- **Chapter 5 (Part I) required post-class OWL homework: available W 9pm; due Sat 11:59pm**
- **more Chapter 5 (Part I) practice: optional OWL homework, EOC Qs, MyLS links**

Next Week

└ nothing new released but lots of good practice in optional pre-class OWL assignments already released

Chapter 5: Stereochemistry

Supplement:	*Fischer Projection Formulas (see Section 21.2)*
5.11	Prochirality
5.6, 5.7	Diastereomers and Meso Compounds
5.8	Racemates and Resolution of Enantiomers

- **Chapters 5 (Part II) resources (learning tasks, video lectures, PP slides) – available now**

NO LEARNING TASKS INVENTORY THIS WEEK

- **required pre-class OWL Homework released 12:01am on Sunday; due Wednesday at 12:01pm**
- **optional OWL Homework – available for term**
- **extensions and applications in class next Wednesday**

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