CH203 Lecture 8

September 28, 2010

John. A. Porco, Jr.

BOSTON UNIVERSITY

Department of Chemistry

porco@bu.edu

Administrative Announcements

Exam I: Thursday October 7th 8 am – 9:20 am

- Exam locations will be as follows:

A-S STO B50

T-Z CAS 227

- Exam 1 will cover lectures 1-9 (Chapters 1- 5)

- Sample exam #1 will be posted on the course website by Friday October 1st.

- *Exam # 1 Review Session*: Monday October 4th 7-8:15 pm in SCI 115

Grab File Edit Capture Window Help Sat 2:57 PM

Assignment List

cengage.com https://owl.cengage.com/owl-c/quiz_engine/endmodule.cgi?ID=12010&SecureID=890128036&Server

Most Visited Apple News Amazon eBay Getting Started Latest Headlines Yahoo!

Oxonia-Cope Rearran... ScienceDirect - Tetra... Calcium - web calendar OWL (Online Web Lea... OWL (Online Web Lea... Assignment List

OWL

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Assignment List

Course

- My Courses
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- Clicker Registration
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Assignments

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- Assignment Calendar

Communication

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Chemistry Tables
eBook
Solutions Manual

Current Assignments | **Assignment Calendar** | **All Assignments** | **Past Assignments**

Course: Organic Chemistry - CAS CH203 - Section AA - John Porco 2:57 PM

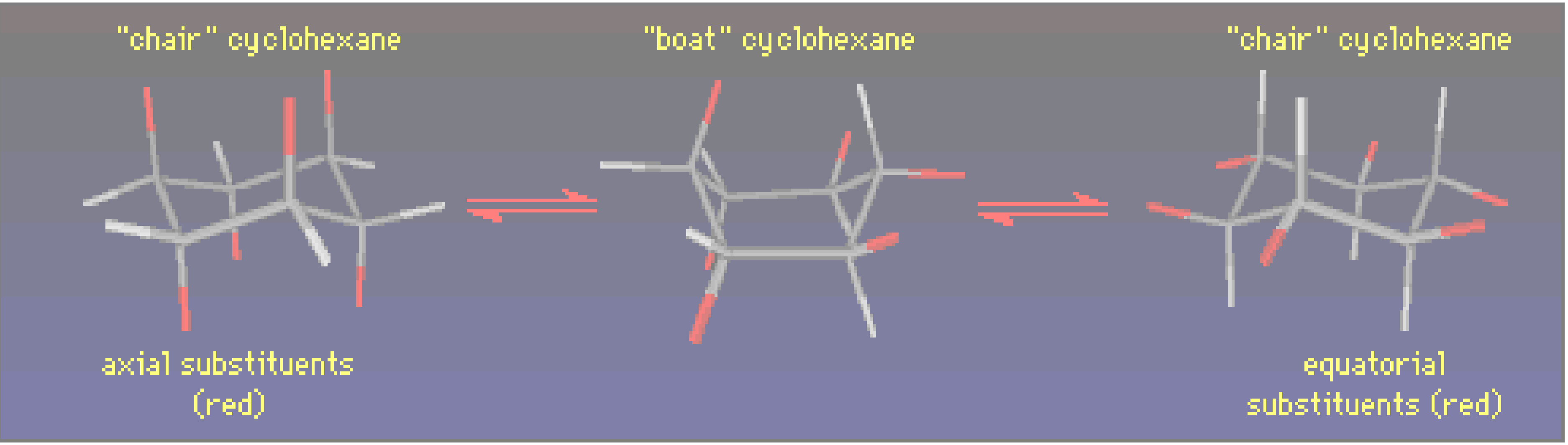
Show only required assignments.

Requirement Status	Assignment	Due Date	Your Grade
O	Intro to OWL 1: Assignment Types	12/18/2010 11:00 AM	not started
O	Intro to OWL 2: Answering Questions	12/18/2010 11:00 AM	not started
O	Intro to OWL 3: Browsers and Tests	12/18/2010 11:00 AM	not started
O	Intro to OWL 4: MarvinSketch Tutorial	12/18/2010 11:00 AM	not started
O	1.0 eBook Reading	12/18/2010 11:00 AM	NA
O	1.3 Simulation: Electron Configurations	12/18/2010 11:00 AM	not started
O	1.4a Homework: Structure and Bonding	12/18/2010 11:00 AM	not started
O	1.4b Exercise: Interpreting Lewis Structures	12/18/2010 11:00 AM	not started
O	1.4c Tutor: Drawing Lewis Structures	12/18/2010 11:00 AM	not started
O	1.4d Homework: Drawing Structural Formulas	12/18/2010 11:00 AM	not started
O	1.4e Homework: Drawing Lewis Structures	12/18/2010 11:00 AM	not started

Find: boston un Next Previous Highlight all Match case

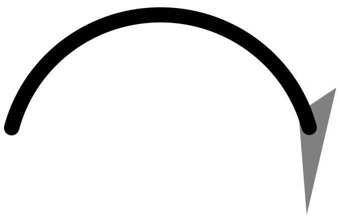
Done

Chair-Chair Interconversion

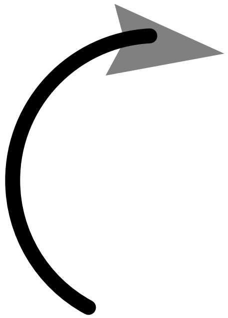


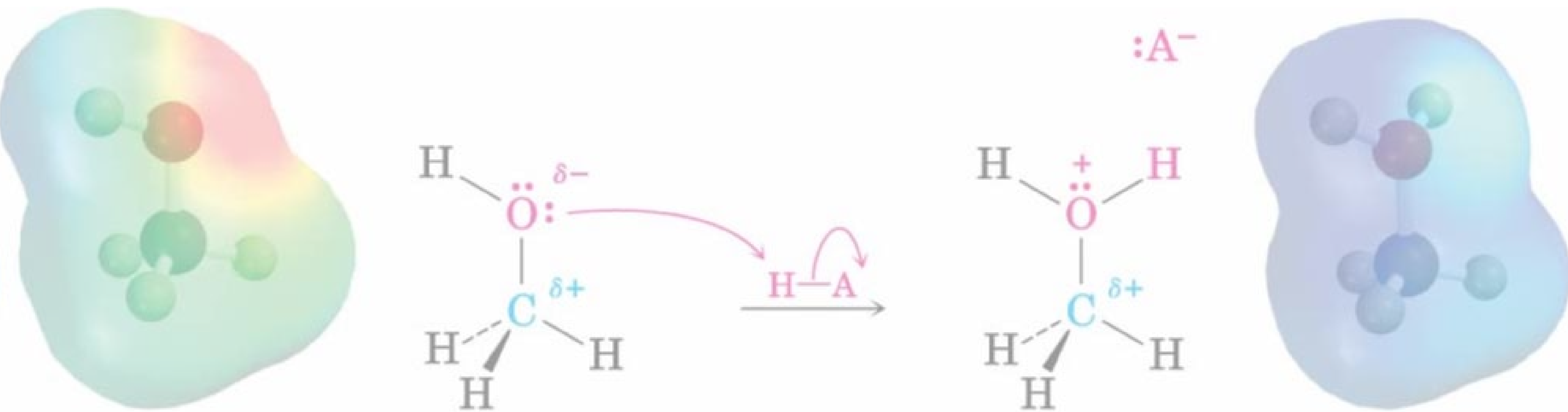
Indicating Steps in Mechanisms

- Curved arrows indicate breaking and forming of bonds
- Arrowheads with a “half” head (“fish-hook”) indicate homolytic and homogenic steps (called ‘radical processes’)



- Arrowheads with a complete head indicate heterolytic and heterogenic steps (called ‘polar processes’)



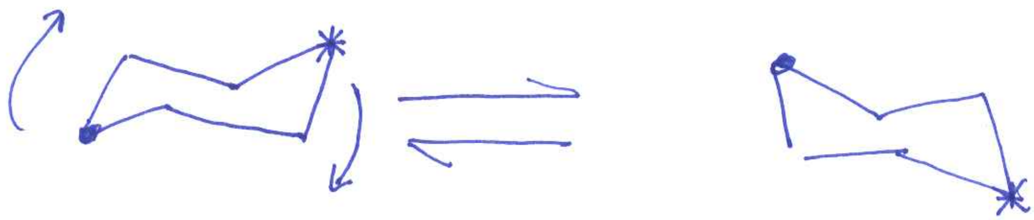


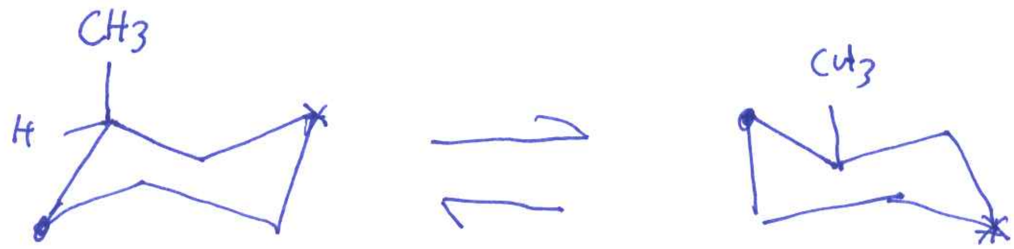
Methanol—weakly electron-poor carbon

Protonated methanol—strongly electron-poor carbon

Lecture # 8
9/28/10

Review: Chair Conformations of Cyclohexane Rings



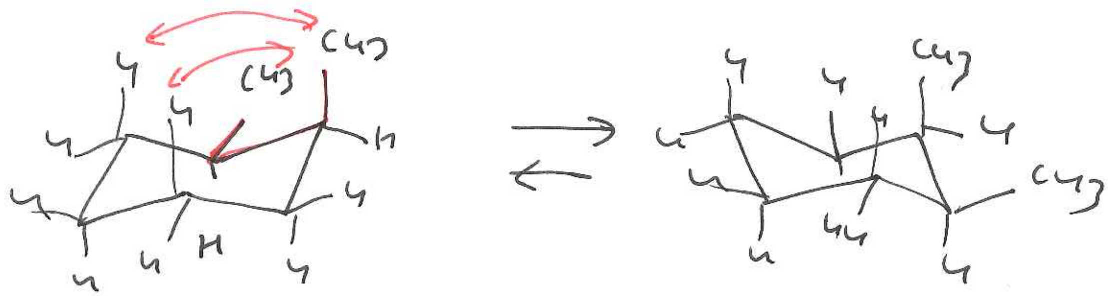


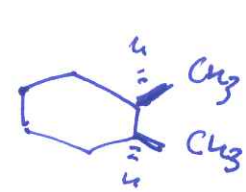
- axials become equatorials and equatorials become axials

These of course are planar representations since the cyclohexane ring is a time average of rapidly interconverting chair conformations

For example for cis 1,2 dimethylcyclohexane:

conformational analysis





one gauche 3.8 kJ/mol (0.9 kcal/mol)

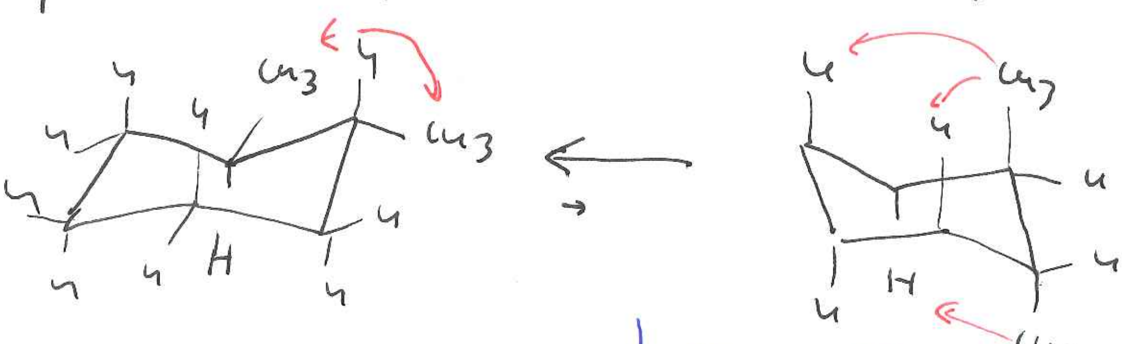
two CH_3–H diaxial 7.6 kJ/mol (2 X 0.9)

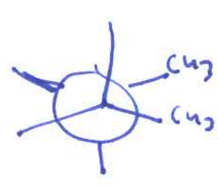
total strain = 11.4 kJ/mol (2.7 kcal/mol)

∴ Both conformations exactly equal in energy

both chair conformations have one axial + one eq. re g-o-p

For trans 1,2 dimethyl cyclohexane:





one gauche int.

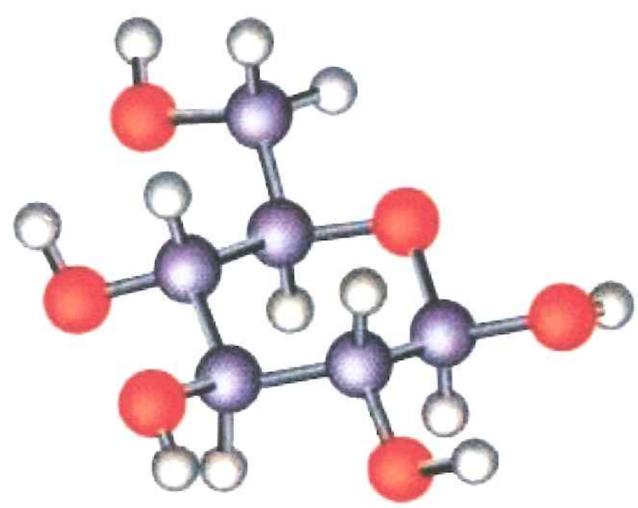
3.8 kJ/mol

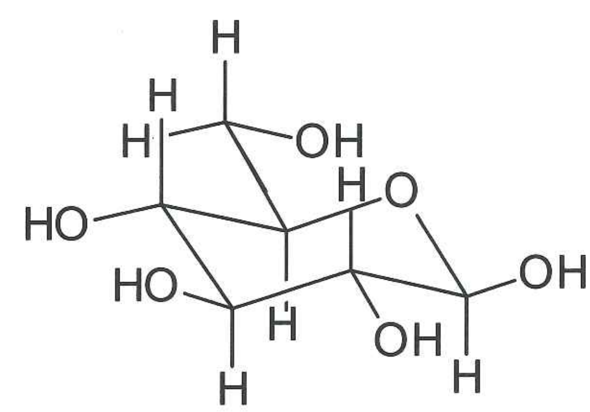
0.9 kcal/mol

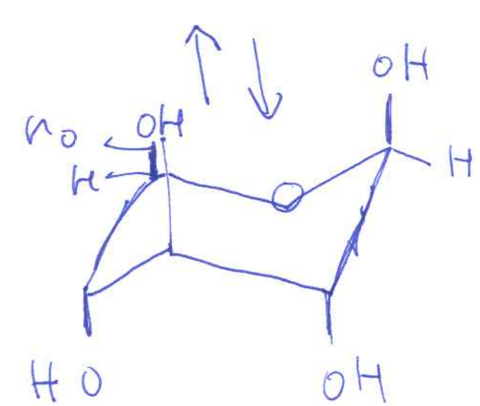
4 CH_3–H 1,3 diaxial

15.2 kJ/mol ~~0.9 kcal/mol~~ 3.6 kcal/mol

β-D-Glucose exists exclusively in the form with all substituents equatorial



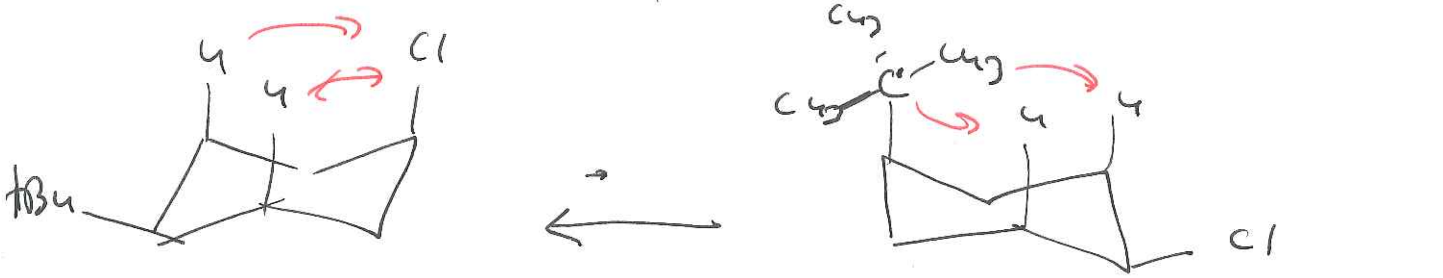




Practice problem:

Draw the most stable conf. of

cis-1-t-butyl-4-bromo cyclohexane and by how much is it favored?



2 Cl–H 1,3 diaxal
$= 2.0$ kJ/mol
(0.5 kcal/mol)

2 · tBu–H 1,3 diaxial
$= 2 \times 11.4$ kJ/mol (2.7)
$= 22.8$ kJ/mol
(5.4 kcal/mol)

Diff is 20.8 kJ/mol
(4.9 kcal/mol)

Cl axial, tBu eq.

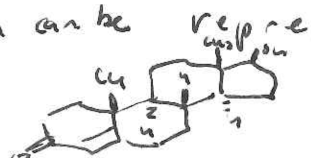
Polcyclic molecules

Decalins: 2 cyclohexane rings joined to share 2 C atoms

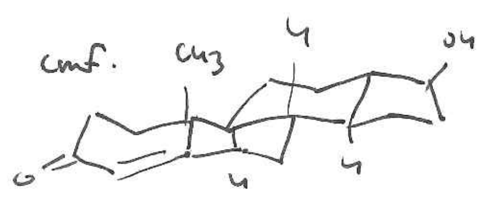
cis-dec – H's at bridgehead C are on same face of the rings

trans-dec – H's at " " are on opp face " " "

Both can be represented by chair cyclohexane conf.

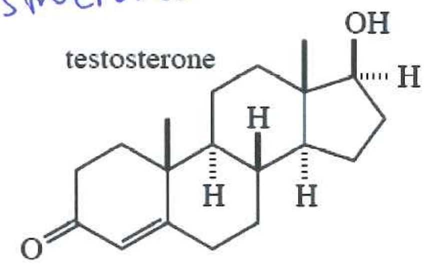


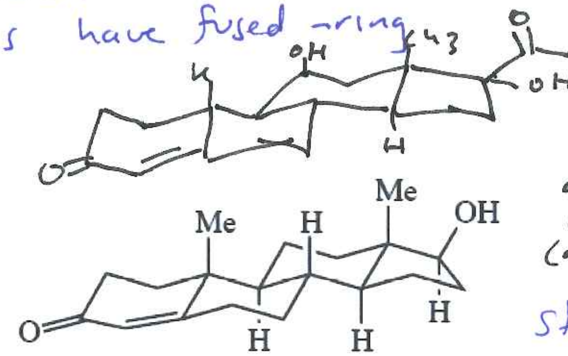
testosterone



• Polycyclic molecules are common
• many valuable substances have fused ring structures

testosterone



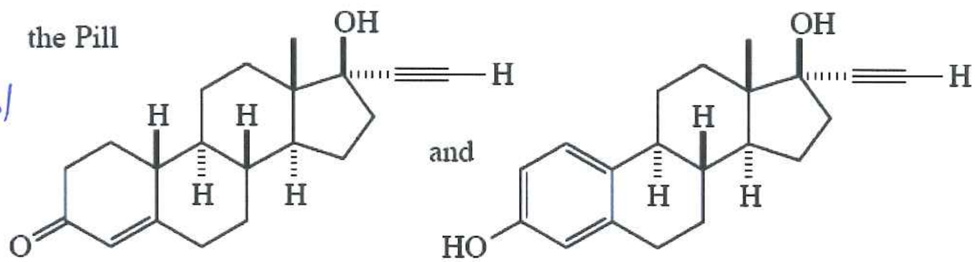


hydrocortisone
adrenal hormone (antiinflam)

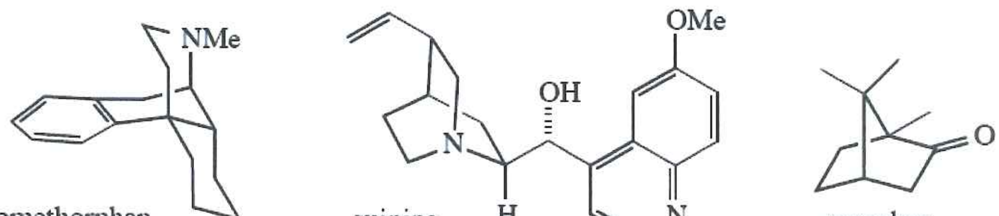
steroid

the Pill

estradiol deriv.



We can also have polycyclic compounds that are bridged. In these compounds, a chain of one or more atoms connects two noncontiguous ring atoms. These compounds can be bicyclic or tricyclic. Examples of compounds that have both bridged rings are dextromethorphan, found in your medicine cabinet as a cough suppressant, quinine, an anti-malarial medicine, and camphor, an ointment used in various remedies. Note how dextromethorphan has three cyclohexane rings (one with a N instead of C). Two of these are *cis*-fused, two are *trans*-fused, and two are bridged. There is also a benzene ring fused to one of the cyclohexane rings.

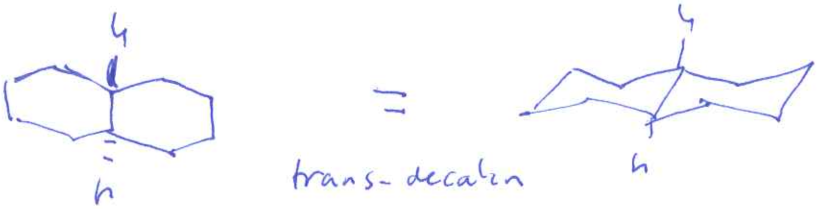


dextromethorphan (cough suppressant) | quinine (anti-malarial) | camphor (ointment)

cis-decalin

• not interconvertible by ring flips

• cis-trans stereoisomers



trans-decalin

Chapter 5 : Overview of Organic Reactions

9 17

Problems: 1, 2, 3, 4, 6, 7, ↑[redacted], 1[redacted], 19, 20

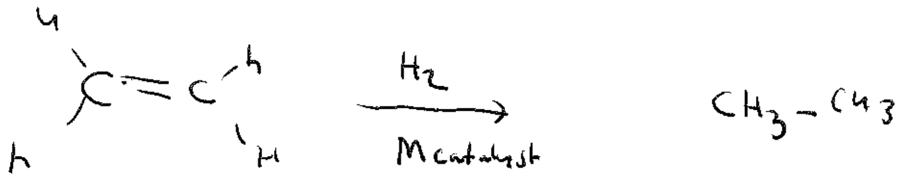
~~21, 23, 24, 31, 32, 35, 36, 37,~~

~~39, 41, 43, 47, 48, 49, 50~~

26, 28, 29, 30, 31, 32-35, 37-41

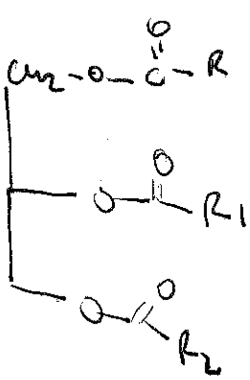
Classes of organic reactions

1) Addition reactions : two reactants add together to form a single new product with no atoms left over



ethylene (alkene)
unsaturated

ethane (alkane)
saturated



fats / oils

• greater degree of unsat. (more double bonds), more vulnerable to lipid peroxidation

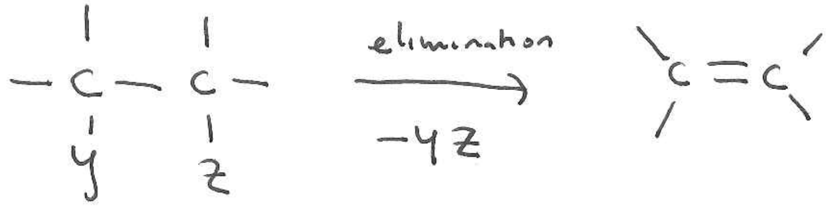
$CH_3(CH_2)_n CH=CH-(CH_2)_m CO_2H$

fatty acid

"Hydrogenation" of polyunsat. veg. oils produces semisolid fats (e.g. margarine) with improved shelf life] but incr. total cholesterol in blood

polyunsaturated	≥2 db
monounsaturated	– 1 db
saturated	– no db

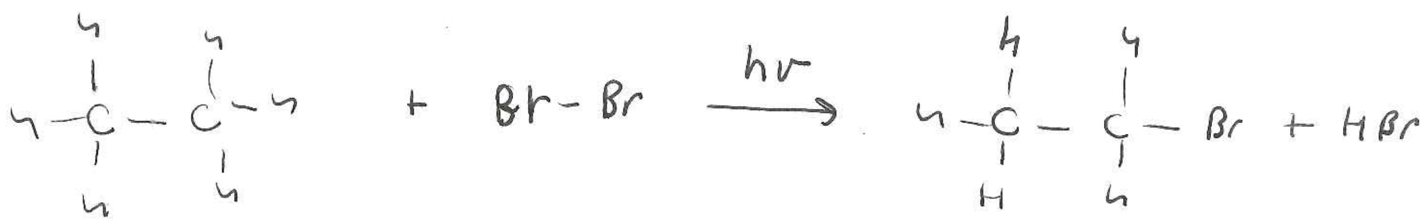
2. Elimination reactions : Single reactant → 2 products



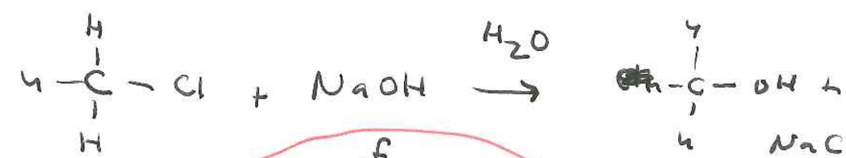
e.g. Y = H
Z = Br

elim. of HBr from adj C atoms
"dehydrohalogenation"

3. Substitution reactions : Two reactants exchange parts to give new products (one group replaces another)

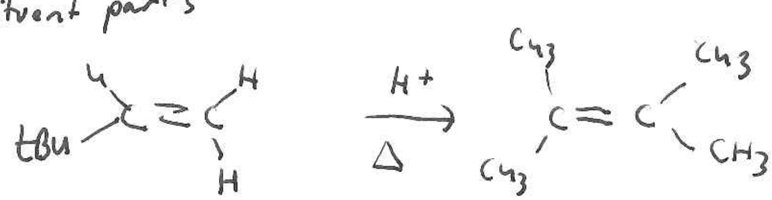


Br subst. for H



4. Rearrangements :

molecule undergoes reorganization of its constituent parts



Mechanisms of Reactions

mechanism : A description of the events that take place on a molecular level as reactants become products. Includes s.m, intermediates, + product.

Homolysis & Heterolysis of Covalent bonds

- Reactions of org. cpds. always involve making & breaking of covalent bonds
- A covalent bond may break in two fund. diff ways

• Heterolysis (polar)

$$A{:}B \longrightarrow A^+ + {:}B^-$$

ions

(2 e⁻ stay with one fragment)

• Homolysis (radical)

$$A{:}B \longrightarrow A\cdot + \cdot B$$

radicals

Radical reactions are vital in biology & med.

$\cdot\ddot{O}-\ddot{O}\cdot$ > $O_2^{\cdot-}$ superoxide

$\cdot\ddot{N}=\ddot{O}$ nitric oxide (NO) inv. in bp regulation

(free) radicals : neutral species with a single unpaired e⁻ in one of its orbitals

$:\ddot{Cl}\cdot$ $3s^2 3p^5$

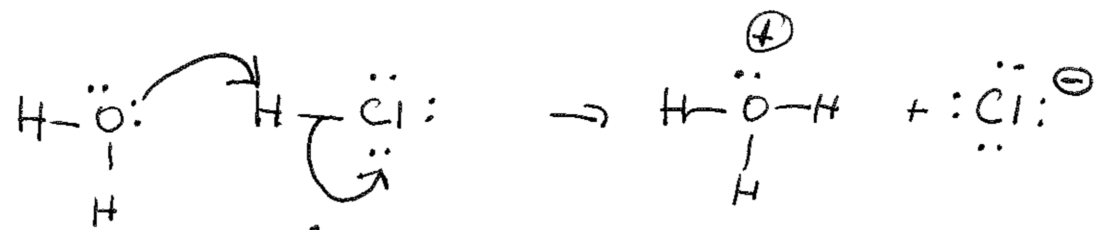
- short-lived, highly reactive

Use of Curved arrows in Illustrating reactions:

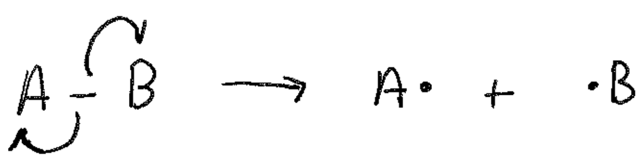
- movement of an e^- pair shown with a curved arrow which points from e^-s to the atom receiving the e^-s
- shows direction of e^- flow in a rX

e.g. $H_2O + HCl \longrightarrow H_3O^{\oplus} + Cl^{\ominus}$

reaction:



↑ bond breaks
e^- pair goes
to Cl



(homolysis)

- Movement of a single $\cdot e^-$ indicated by single-barbed arrows
- Each group A and B comes away with one of the e^-s of the covalent bond.

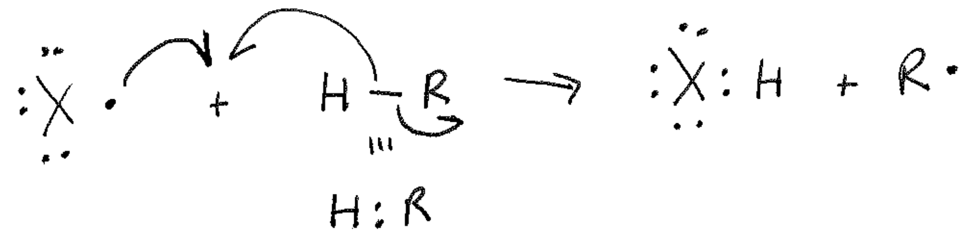
Curved arrow: indicates breaking & forming of bonds

 Fishhook - homolytic c $1e^-$

 heterolytic - $2e^-$s

Reactions of Radicals

general reaction



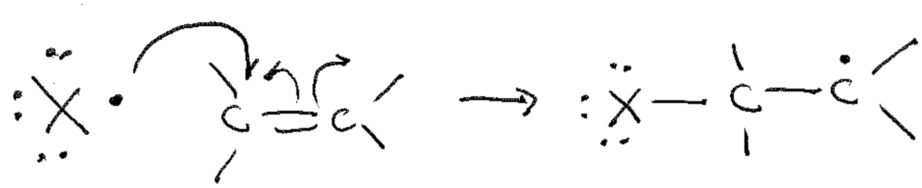
(methyl radical)

react. radical

substitution product

prod. radical

Alternatively, we can have an addition of a radical to an alkene:



react. radical

alkene

product radical