INTRODUCTORY ORGANIC CHEMISTRY II – Chem 222

Instructor **Dr. Cerrie W. Rogers**
Office hours: Tues.–Fri. 13:15-14:15 (or by appointment)
Contact info: SP-201.17, ×5838, crogers@alcor.concordia.ca

Course Format
Lectures: 2.5 h / week, Tues. & Thurs. 10:15-11:30 in SP-S110
Labs: 4 h / week, starting Sept.10-14th in Lab room SP-112

Materials required
1) P.J. Bruice, *Organic Chemistry*, 5th Edition (orange & white)
2) Bruice's Study Guide & Solutions Manual
3) Lab text: J. W. Lehman, Operational Organic Chemistry, 3rd Ed.
4) Lab manual: *Organic Chemistry II,* Dept. of Chem. & Biochem.
5) any molecular model kit, PLUS lab coat & safety glasses

Useful resources
1) Course website (moodle): lecture slides, handouts, problem sets
2) Bruice website http://www.prenhall.com/bruice/details.html
3) Other texts (Vanier library reserve): alternate explanations, *etc.*
4) Strategic learning sessions

INTRODUCTORY ORGANIC CHEMISTRY II – Chem 222

GRADING SCHEME, DEADLINES & ABSENCES

To pass: ≥ 50% theory AND ≥ 60% laboratory work

Weighting:

Problem Sets:	10%	(due 2 weeks after handout out)
Midterm Exam:	15%	(during class Oct.23)
Lab Marks:	25%	(reports 15%; lab exam 10% Nov.22)
Final Exam:	50%	(3h, December, cumulative)

Details: Problem Sets due at beginning of class on the due date.
Late submissions will not be accepted.
Papers slid under an office door will not be graded.
Solutions to the problems will be posted after the due date.

If absent from an exam / lab: official, signed note (doctor / employer)
No later than one week after exam / lab.
No valid excuse produced: **zero** grade.

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LABORATORY INFORMATION -- 4h every week, SP-112

Coordinator: **Rita Umbrasas** SP-330.01 ×3354 (All questions to her.)

Lab sections: you must attend your **registered** section only
Problems, notes, exemption requests: see Rita ASAP

Lab absence: max. 1; bring medical / employer note, or receive zero
Lab grades: based on quality of the experimental work AND report
Lab TA: 1-2 per lab section; get their contact information
Preparation: prelab, lab coat & glasses required, or entrance denied

Date:	Experiment No.	Title:
Mon. Sept. 10 - Fri. Sept. 14	Check In Exp. 4	All Sections Synthesis of Salicylic Acid from Wintergreen
Mon. Sept. 17 - Fri. Sept. 21	Exp. 9	Isolation and Isomerization of Lycopene from Tomato Paste
Mon. Sept. 24- Fri. Sept. 28	Exp.11	Identification of Unknown Ketones
Mon. Oct. 1 - Fri. Oct. 5	Exp. 7	Preparation of Camphor
Mon. Oct. 8 - Fri. Oct.12	**(No Labs – Thanksgiving Holiday)**	

and so on…

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LECTURE INFORMATION: SCHEDULE, READINGS, PROBLEMS

- Use lecture schedule to plan readings & study schedule.
- Print slides (if any) before class, & take DETAILED NOTES in class!
- Read textbook Preface, "To the student" – suggestions on how to use textbook & excellent advice on how to study organic chemistry.
- Organic chem. requires daily attention & practice – don't just cram!

Class	Date	Topics	Readings	Suggested problems from Bruice
1	Sept.04	Introduction *(Review Chem 221)*	*(4.12, 6.12, 9.11)*	*(see Chem 221 past exams on website)*
2	Sept.06	Reactions of alcohols, ethers, epoxides & sulphur-containing compounds	4.9 ,10.1-10.12, 19.2-19.3	Ch.10 #1,5,7,9,11,13,14,15,17,23,31,33,34, 43a-h,44,46,49 (not h),51,52,57,61,64,70,71; Ch.19 #8,10.
3	Sept.11			
4	Sept.13	Mass spectrometry (MS)	12.1-12.5	Ch.12 #2,3,5,10,12,13,14,15.
5	Sept.18			
6	Sept.20	Infrared spectroscopy (IR)	12.6-12.15	Ch.12#19,20,21,22,23,24,29,33,43,45,49,54, 56,58,60,61,65,66,69.
7	Sept.25	UV/Vis spectroscopy (UV/Vis)	12.16-12.20	Ch.12 #37,46.
8	Sept.27	Nuclear magnetic resonance spectroscopy (NMR)	13.1-13.7,13.9-13.14, 13.16-13.17, 13.18	Ch.13 #3,4,5,10,11,12,13,15,17,18,19,21, 27,28,30,32,38,40,41,43,45,46,48,50,54, 56,57,71,72.
9	Oct.02			
10	Oct.04			
11	Oct.09			
12	Oct.11	Reactions of dienes/delocalized e⁻s	7.4-7.12	Ch.7 #17,18,21,25,28,33,36,42,45,55, 68,70,7
13	Oct.16		7.1,7.3, 14.1,14.16	

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STRATEGIC LEARNING (SL) *http://learning.concordia.ca/SL_basics.shtml*

Research shows: students who attend SL earn higher grades
& withdraw less often

SL leaders: recently taken course themselves, & done well.

Role: facilitate collaborative learning among students
help develop learning & study strategies that match course
integrate how to learn with what to learn
use text & lecture notes as tools (they attend class too!)

SL sessions: outside class time, one hour / week, sometimes more

Who can go: anyone registered in Chem 222
attendance is voluntary, but highly recommended

Take advantage of this free programme!

CHEM 222 section 01

LECTURE #01 Tues., Sept.04, 2007

INTRODUCTORY ORGANIC CHEMISTRY II

ASAP: Review Chem 221…

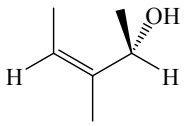
- drawing organic structures
- acidity/basicity, nucleophilicity
- reactions: electrophilic additions
  substitutions, eliminations
- mechanisms: step-by-step e^--pushing
- designing a multistep synthesis

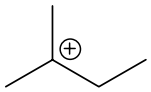
http://artsandscience.concordia.ca/facstaff/P-R/rogers

Remembering how to draw organic structures

- **Remember the rules:**
  - 2nd row elements cannot exceed octet rule !
  - Trends: C (4 bonds), N (3 bonds, 1 LP), O (2 bonds, 2 LP), X (1 bond,3 LP)
  - Against trend: atom will have formal charge +/- open valence
  - Most stable structure: minimized formal charges, atoms with full valence
- **Resonance structures:**
  - Only lone pairs & π-electrons move (nuclei & σ-bonds stay unchanged)
  - Most stable structure contributes most to the resonance hybrid (reality)
  - Less stable structures still contribute to reactivity patterns…
- **Representing structures:** formal charges always shown, but…
  - Kekule structures: Lewis structures without LPs - except if involved in rxn
  - Skeletal (line) structures: bonds as lines, C's & H's not shown
  - 3-D drawings: dashes/wedges/lines to visualize geometry & stereochem.
  - Condensed formulae: summarize connectivity without pictures

CH_3COCH_3





Remembering functional groups: 1) hydrocarbons

Substituent (hydrocarbon-based group) (symbol, abbreviation & name)			Class of compounds		Comments
$-(CH_2)_nCH_3$ or branched…	—R	alkyl	C_nH_{n+2}	Alkanes	See Table 2.2
$-CH_3$			Must know these!		
	—Et	ethyl			
$-(CH_2)_2CH_3$	—Pr	propyl			
$-CH(CH_3)_2$					
$-(CH_2)_3CH_3$	—Bu	butyl			
	—*t*-Bu	*tert*-butyl			
$-CH=CH_2$		vinyl	$R_2C=CR_2$	Alkenes	Discussed in Chem221
$-C\equiv CH$		acetylide	$RC\equiv CR$		
$-C_6H_5$	—Ph 	" "  A benzene ring as a substituent…	C_6H_5R	Aromatic hydrocarbons	Discussed in Chem222

Remembering functional groups: 2) with heteroatoms

Functional group (symbol & name)		Class of compounds (based on functional gp)		Descriptors	
—X	Halide	R—X		1° 2° 3°	RCH_2-X R_2CH-X R_3C-X
—OH		R—OH	Alcohols	1° 2° 3°	RCH_2-OH R_2CH-OH R_3C-OH
—NH_2		R—NH_2	Amines	1° 2° 3°	R-NH_2 R_2NH R_3N
—O—	Oxy	R—O—R		Symmetric Asymmetric	R-O-R R-O-R'
O ‖ —C—	Carbonyl	O ‖ R—C—R	Ketones; OR if ≥1 R=H: Aldehydes	O ‖ R—C—X Acyl halides *OR* Acid halides	
O ‖ —C—OH	Carboxyl	O ‖ R—C—OH	Carboxylic acids	O ‖ R—C—OR Esters	O ‖ R—C—NR_2 Amides
—C≡N	Cyano	R—C≡N	Nitriles		
—NO_2	Nitro	R—NO_2	Alkyl nitrates		

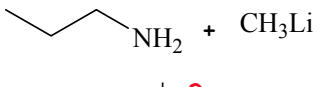
Chemistry discussed later in Chem222

Remember the general principle of reactivity:
δ^- δ^+ Nucleophiles attack electrophiles

Nucleophiles: "Nu"	Electrophiles: "E+"
▪ electron-rich atom or functional group • lone pair of e^- (a base of some sort) ? • polarizable π-electrons (alkenes, etc) ? ▪ functionally δ^-, even if no true polarity ▪ Nu's ATTACK δ^+ REGIONS	▪ electron-deficient • empty orbital ? • positive charge ? ▪ functionally δ^+ ▪ E+'s GET ATTACKED

To guess at reactivity:
Draw polarity on molecule!
- If non-polar: identify polarizable e^-s
- Can be activated by more reactive rgt

Weak Nu / E+'s are still reactive:
- if presented with <u>stronger</u> E+ / Nu's
- *OR* at high concentrations
- *OR* at elevated temperatures



↓ ?

Remembering trends in nucleophility

Bruice 8.3

(nucleophile strength in protic solvents: water, ROH)

STRONG	MODERATE	WEAK
$(CH_3CH_2)_3P$:	:Br:⁻	:F:⁻
:S-H⁻	CH_3-S-CH_3	
:C≡N:⁻	NH_3	
$(CH_3CH_2)_2NH$	:Cl:⁻	
:O-H⁻		H-O-H
:O-CH_3⁻	$CH_3C(=O)$-O:⁻	CH_3-O-H

A stronger base = a better Nu

Provided:

- low steric demand (backside attack…)
- not overly screened by the solvent

TRENDS in basicity & nucleophilicity (except #3: Nu's only, in protic solvent)

- A – charged Nu is stronger than a similar neutral species (…more δ^-).
- More electronegative atoms are less nucleophilic (…hold e^-s tightly).
- Larger, more polarizable atoms are more nucleophilic (…shielded less).

Remembering relative acidities: pK_as (see Appendix II)

protonated carbonyl groups	$RC(=O^+H)OH$	< 0
protonated alcohols	ROH_2^+	
protonated water	H_3O^+	
carboxylic acids	$RC(=O)OH$	~5
protonated aniline	$ArNH_3^+$	
protonated amines	RNH_3^+	~10
phenol	ArOH	
alcohols	ROH	~15
water	H_2O	

α-carbon (aldehyde)	$RCH(H)C(=O)H$	~20
α-carbon (ketone)	$RCH(H)C(=O)R$	
α-carbon (ester)	$RCH(H)C(=O)OR$	~25
α-carbon (amide)	$RCH(H)C(=O)N(CH_3)_2$	~30
hydrogen	H–H	35
amines	RNH_2	~40
alkanes	RCH_3	~50

conj.base H^- used as NaH *sodium hydride*

What could deprotonate acetone?

ASSIGNED READINGS:

BEFORE NEXT CLASS: Review Chem 221

- start next on chemistry of alcohols, ethers, etc

BEFORE FIRST LAB:

- Read Lehman Expt#4 & related Operations
- Note: labs often involve rxns we've not yet studied
  Lehman usually provides rxn mechanism
  if not, search in Bruice's index or library texts…

Remember:

- Labs start next week: **arrive prepared!**
  lab coat & glasses
  completed Expt.#4 prelab
- Chem101 seminars next week (only if you've not done it)

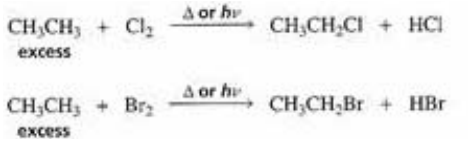
Quick rxn review at start of 2nd lecture…
Review details on your own this weekend !

Summary of basic organic rxns (see end-of-chapter summaries)

STARTING WITH AN ALKANE

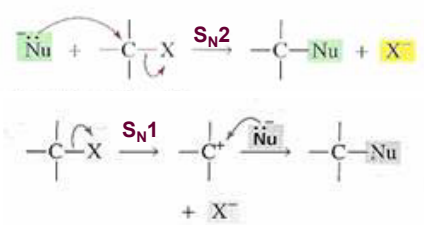
- Can add a functional group

Route to: alkyl halides

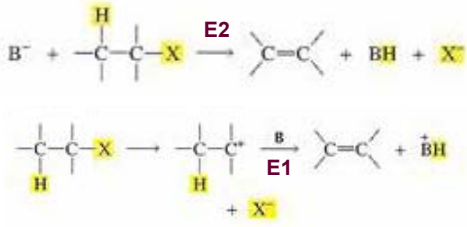


STARTING WITH AN ALKYL HALIDE

- Can replace halide (substitution) *OR* eliminate small molecule HX



Route to: different halides
alcohols, ethers,
amines, thiols,
nitriles, acetylenes,
ETC!



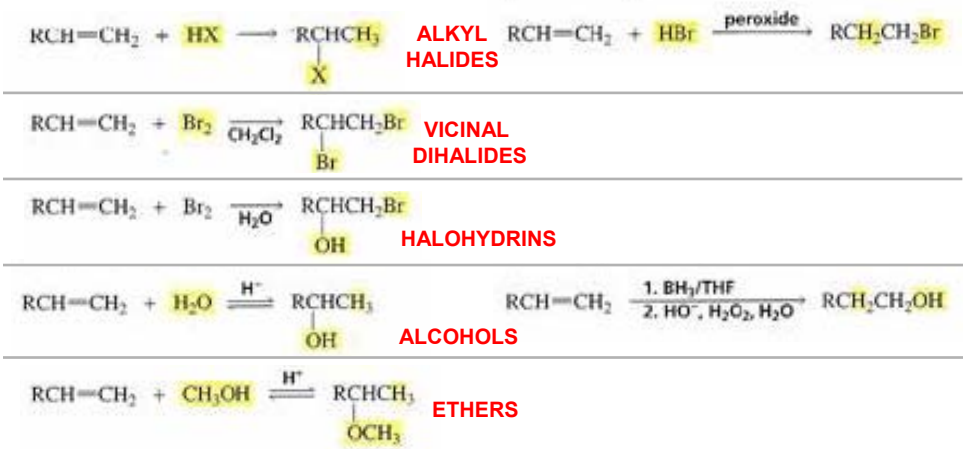
Route to: alkenes

Summary of alkene rxns: what can we make starting from here?

STARTING WITH AN ALKENE

- Can add electrophiles

MARKOVNIKOV ADDITIONS | **ANTI-MARKOVNIKOV ADDITIONS**



Your organic toolbox so far (+ acid/base chemistry)

BASIC TYPES OF ORGANIC REACTIONS

1. **Radical halogenation:**
   adds a functional group to alkanes *(unreactive!)*

2. **Substitution:**
   change to a different functional group

3. **Elimination:**
   create a π-bond

4. **Electrophilic addition:**
   use π-bond to add a new functional group
   (very helpful for switching functional group positions!)

Mixing & matching these types of rxns can provide a variety of routes to our molecules of interest ⇨ versatility!
(use trial & error to find best pathway!)

Designing a synthesis: synthetic planning & retrosynthetic analysis

(4.12, 6.11, 11.12)

OUR GOAL (ideally): **SYNTHESIZE THE TARGET MOLECULE USING…**
- fewest # steps possible
- highest yield of desired product possible (intermediate steps too)
- simplest / safest / cheapest / fastest rxns possible

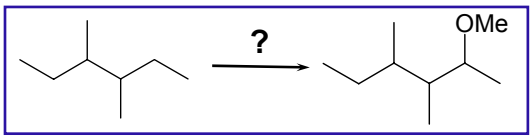
OUR GOALS FOR NOW (we are beginners…):
- use chemically reasonable sequence of rxns *(desired product = major)*
- if will get a mixture of products at any step, say so!
  ⇨ would have to purify the product before using in next step

PLANNING OUR SYNTHESIS:

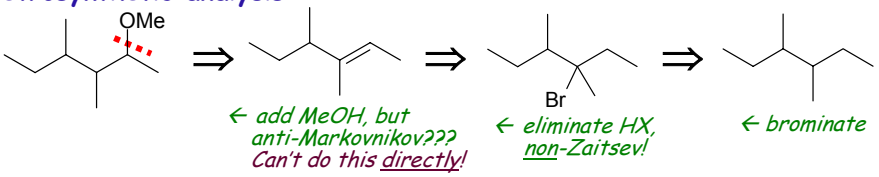
1. **Compare the SM & target molecule**
   C skeleton: How do SM & target compare? Any clear "subunits"?
   Functional groups: Any new groups? Any groups present in both?
   Choose conditions that won't react with groups that remain unchanged.
2. **Is there an obvious set of reactions to get from SM to target?**
   - Try to add very reactive functional groups near the end.
3. **If there is no obvious forward plan: try to work backwards!**
   "RETROSYNTHETIC ANALYSIS"

A multistep example

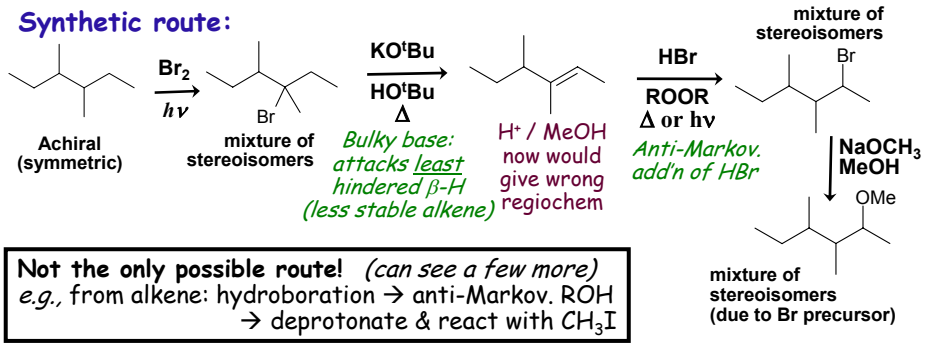
- SM = an alkane
- target = an ether
- same backbone…



Retrosynthetic analysis:



Synthetic route:

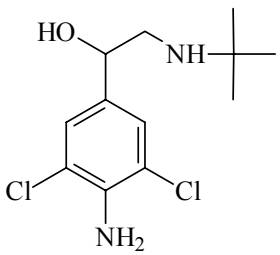


Not the only possible route! *(can see a few more)*
e.g., from alkene: hydroboration → anti-Markov. ROH
→ deprotonate & react with CH_3I

Clenbuterol

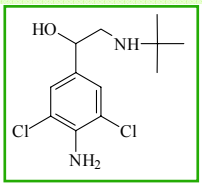
Info. from Wikipedia

- **A pharmaceutical:**
  - Recommended usage: decongestant, bronchodilator
  - Illegal uses: athletes: non-steroidal anabolic & metabolism accelerator
    public use: weight loss drug ?
    agriculture: animal feed additive, enhances leanness
  - Toxicity: causes tremors, high blood pressure, increased body temp.



- **How is it synthesized?**

Clenbuterol



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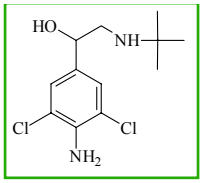
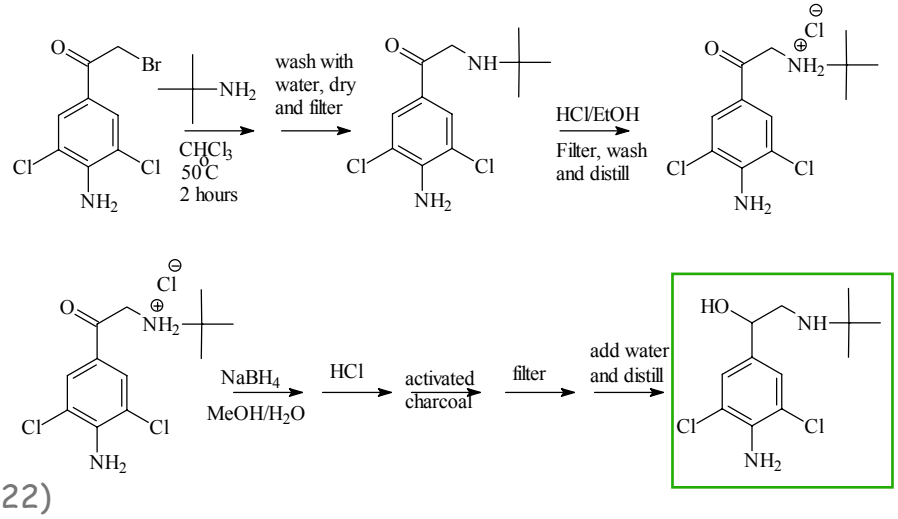
Clenbuterol





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