Problem Set #1 solutions

Problem #1 – For each reaction, provide a detailed "arrow-pushing" mechanism that explains how the product forms. For part a, you will first need to predict the major product (include stereochemistry).

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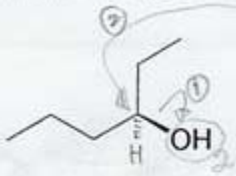
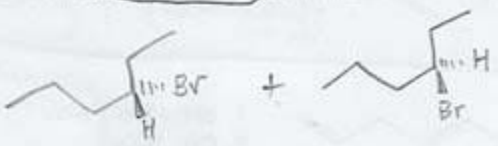
a)



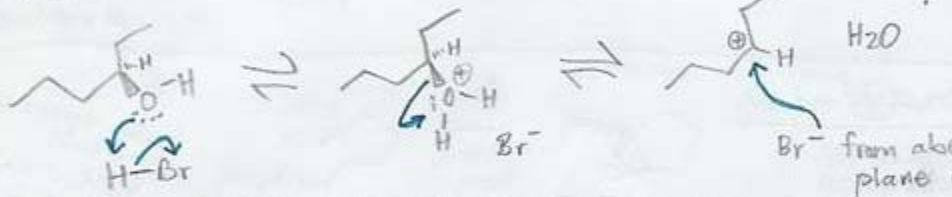
HBr

SN1 because 2° ROH.



racemic mixture = major product

Mechanism:



H_2O

Br^- from above or below plane of the sp^2 C (C⊕).

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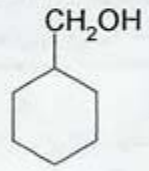
b)



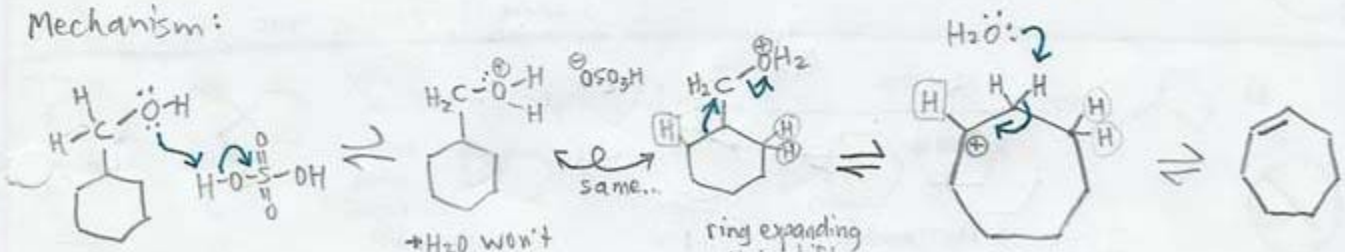
H_2SO_4(aq)

heat

(no stereo.) not likely the ONLY product!

(major = )

Mechanism:

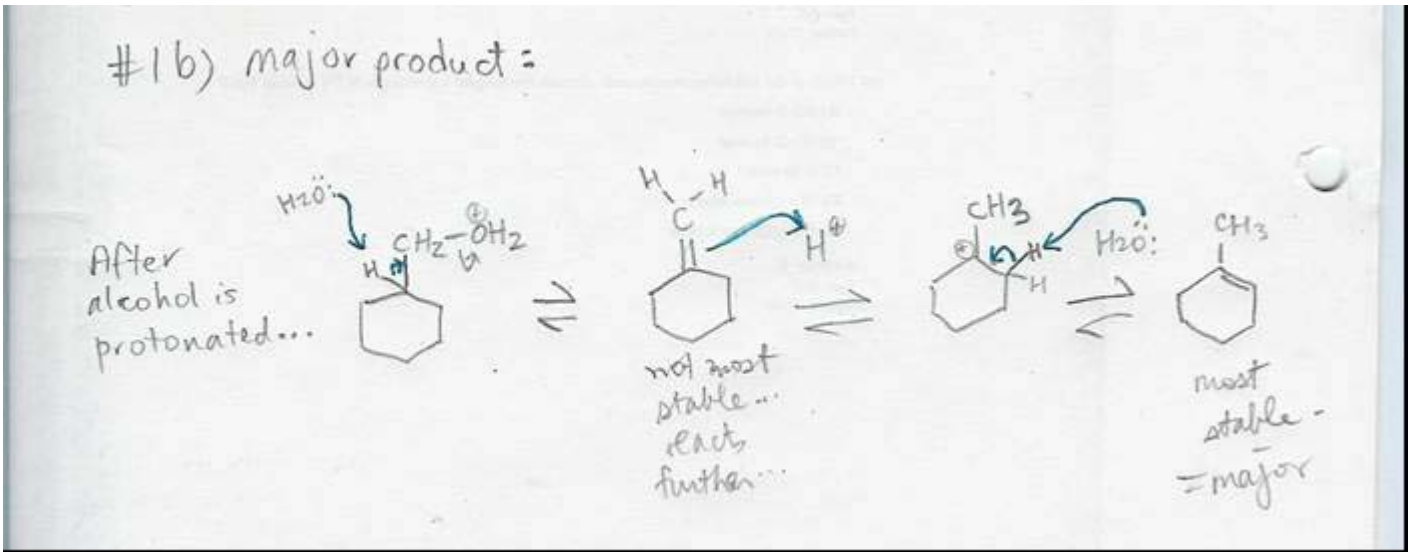


→ H_2O won't just leave now... would yield 1° C⊕.

ring expanding alkyl shift pushes H_2O off...

2° C⊕ undergoes elimination

#1b) major product =



After alcohol is protonated...

not most stable... react further...

most stable = major

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Problem #2 – Predict the major product for each reaction or reaction sequence. Also draw the structures of all stable intermediate species involved. Remember to consider stereochemistry.

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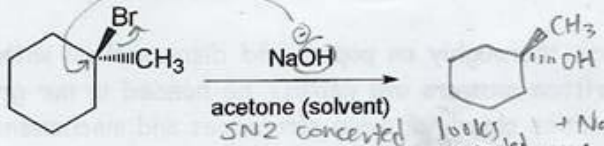
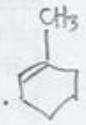
a) 

Would you expect the same products if you perform the reaction at 56°C (bp of acetone) versus at -15°C? Explain.

No → warmer T yields E2. 

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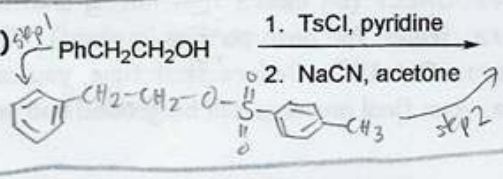
b) 

$PhCH_2CH_2C{\equiv}N:$ (achiral) $(+Na^+ {}^-OTs)$

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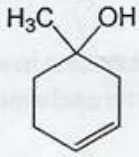
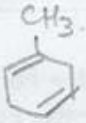
c) 

H_2SO_4(aq)

heat Δ

elimination (E1) via c⊕

conj. favoured over 

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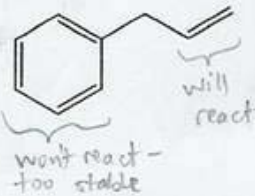
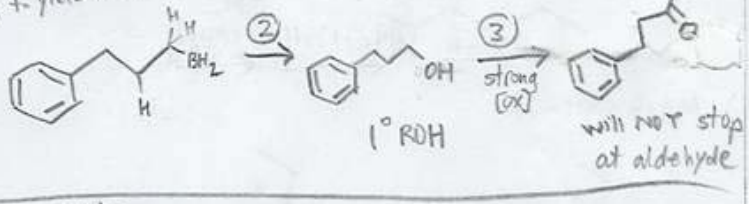
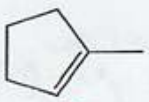
d) 

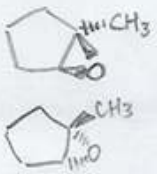
1. BH_3 / THF } Anti-Markovnikov H_2O's to yield ROH
2. OH^-, H_2O_2
3. H_2CrO_4

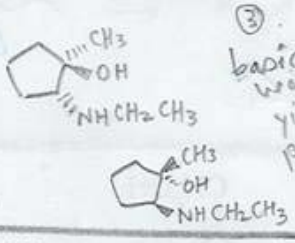


13

e) 

1. CH_3CO_3H peroxy acid ①
2. $CH_3CH_2NH_2$
3. basic workup

epoxides 

② Nu in basic conditions attacks easiest site 

③ basic aqueous workup yields amine product in neutral form.

#7 on quiz NOT COUNTED

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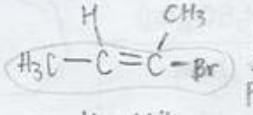
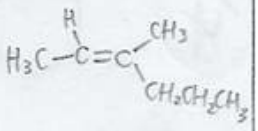
f) 

1. HBr (1 eq only) * assume...
2. $(CH_3CH_2CH_2)_2CuLi$

① HBr 

② Pr_2CuLi 

- anti addition
- name: Z....

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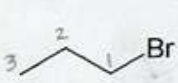
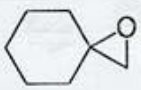
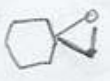
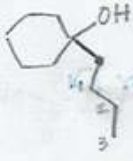
g) 

1. Mg / THF
2. add to 

3. H_3O^+ workup

① 

+ 

②+③ basic attack easiest site 

Problem #3 – Provide a three-reaction sequence (*i.e.*, synthesis) that could be used to carry out the following transformation. Use reactions we have studied in class and reactions learned in Organic I where necessary. For each step in your synthesis, please specify:

(i) reagent(s) needed
(ii) solvent, if the choice is important
(iii) temperature, if above/below room temperature
(iv) workup conditions, *e.g.*, acidic workup *vs.* basic workup

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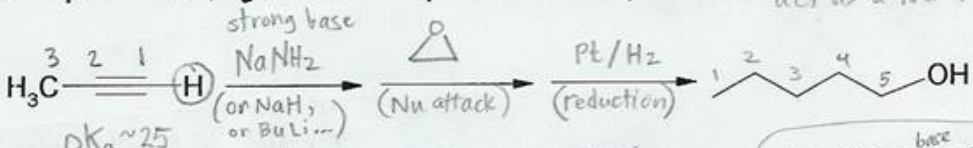
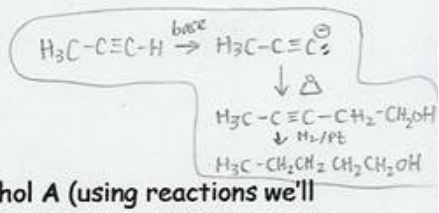
Thought process: ← #10 on quiz NOT COUNTED
① 3C SM → 5C target
② SM C#1 needs to be functionalized
too many steps ← 2a) C1 can be attacked by a 2C Nu
OR 2b) converted to base so C1 can act as a Nu to attack a 2C E⊕



- anhydrous HC solvent
- RT or lower
- NO workup

- same solvent
- same T
- acidic aq. workup

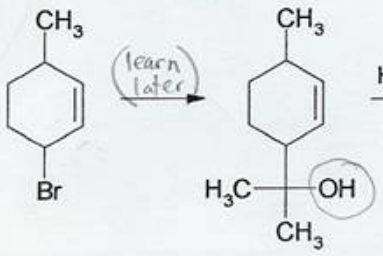
- same solvent
- same T
- no real workup



Problem #4 – A student converted 3-bromo-6-methylcyclohexene to alcohol A (using reactions we'll learn soon). She heated alcohol A with sulfuric acid and purified one of the components (compound B) from the resulting mixture.

a) The UV spectrum of compound B shows λ_{max} at 273 nm. Using elemental analysis, compound B's empirical formula was determined to be C_5H_8, and the compound's mass spectrum showed a molecular ion at *m/z* 136. Propose a structure for compound B. Explain your choice.

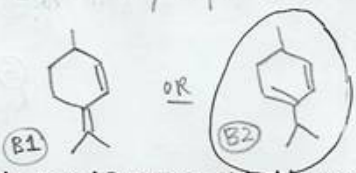
b) Propose a mechanism for the conversion of alcohol A to compound B.



alcohol A

H_2SO_4(aq), heat → compound B

✓① C_5H_8 ← FW = 68 g/mol empirical...
✓② M m/z = 136 ⇒ molecular formula = $C_{10}H_{16}$
✓③ [2(10) + 2 − 16] ÷ 2 = 3 rings/π-bonds
✓④ λ_{max} = 273 nm ⇒ conjugated π-bonds, but where? (if not conj., 1 π-bond ⇒ λmax 180 nm)
✓⑤ chemistry expected = ROH − H_2O via 3° C⊕



See mechanism

1 ring
2 π-bonds
From notes on uv... λmax suggests B2

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Problem #5 – Spectral data for isomeric compounds A and B are provided here and on the following two pages. Assign structures for both compounds, and explain your reasoning. Remember to refer to the detailed peak position summaries given in the textbook's Appendix.

#20 on quiz NOT COUNTED

	Compound A	Compound B
MS (selected peaks)	*m/z* = 148 (M, 7%), 106 (8%), 105 (100%)	not available Same molar mass as A since isomers!
IR (neat, in KBr)	See attached spectrum	See attached spectrum
^{1}H NMR (in $CDCl_3$)	See attached spectrum	See attached spectrum

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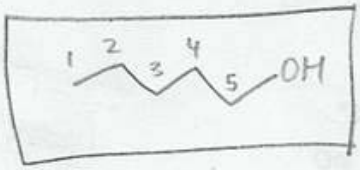
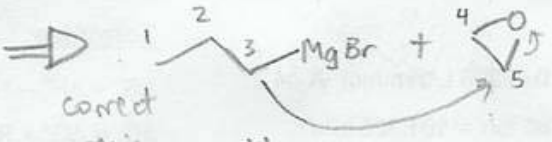
Solution - on later pages...

222 Problem Set #1

Problem #3

Try Retrosynthetic analysis





correct regio...

③ • ethylene oxide
• anhydrous ether
• RT

② • Mg / ether
• RT

OR

①

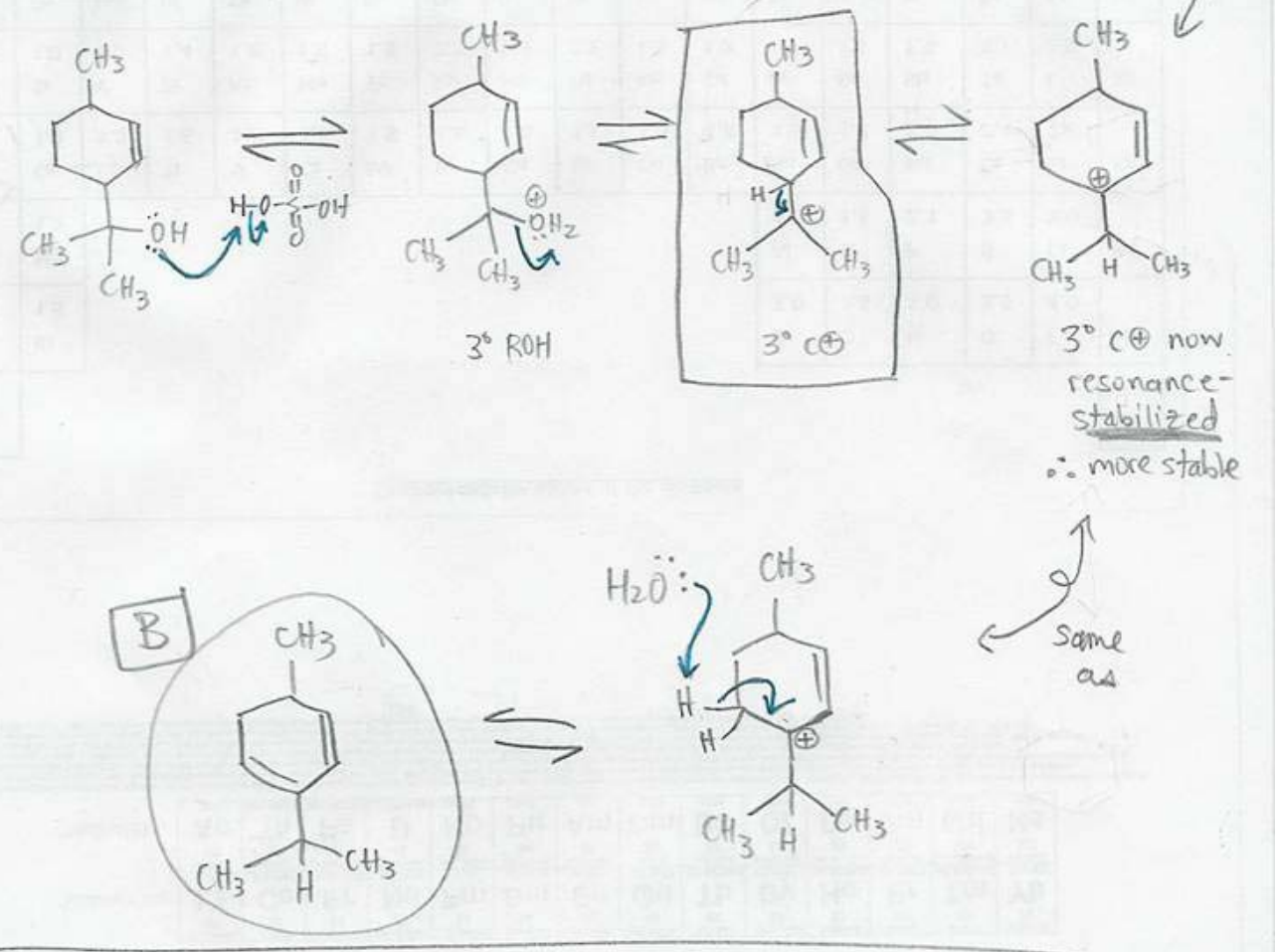
too many steps.

The paths that 1st came to mind for me (retrosynthetically) weren't suitable. Try another approach instead...

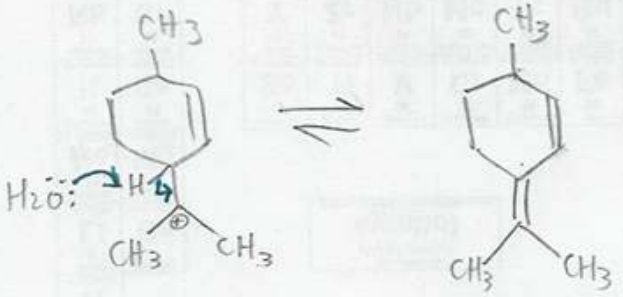
Try forward thinking: THIS WAY WORKS IN THREE STEPS...

Problem #4

b)



other possible pathway from 1st 3° c⊕:



also conjugated,
but remember class examples of λ_{max} showed different effect of conjugation to exocyclic vs endocyclic π-bonds:

232 nm
+ 2R's on chromophore +10
242 nm

256 nm
+ 10
266 nm closer!

Problem #5

1st... **(A)** | **(B)** (isomers)

(*) Solve A + then do B...

A

M 148 g/mol

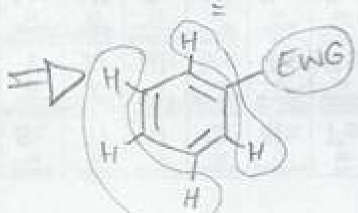
MS ⇒ 148 − 106 = 42
148 − 105 = 43 ← (Pr loss)
(↑ base peak)

−Me = 15
−Et = 29
−Pr = 43

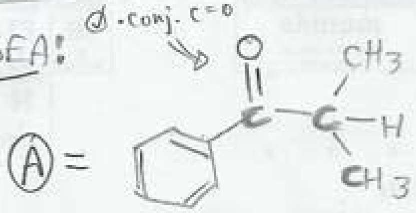
IR: 1675 cm^{-1} (s) ⇒ C=O, weaker than ketone = amide? or conj. C=O?
1220 cm^{-1} s ⇒ C−O?, (not acid, ester)
others? not so useful.

^1H NMR: δ 1.20 d (7Hz) 6H ← 2 CH_3's equiv.
3.53 sept (7Hz) 1H ← one CH seeing them
(↑ nearer to EWG)

farther from EWG ← 7.20 − 7.60 m, 3H
7.80 − 8.08 m, 2H
} 5 phenyl H's
nearer to EWG



IDEA! (✓ conj. C=O)



$C_{10}H_{12}O$ (MM = 148 ✓)

B

148 g/mol ∴ isomers ∴ same formula as A ∴ $C_{10}H_{12}O$

El. Unsat. = $\frac{2(10)+2-12}{2}$ = 10/2 = 5 rings/π-bonds

IR: 1705 cm^{-1} (s) ⇒ C=O — normal ketone? ~~ester?~~ not amide, not conj. C=O since NOT weaker than normal C=O!
no C−O stretch obvious? ∴ not ester... nor ether!

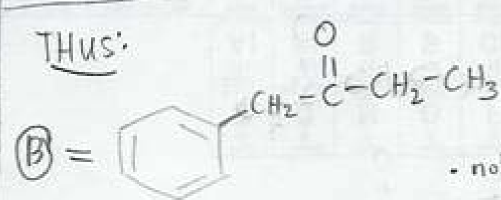
^1H NMR: 0.95 t (7Hz) 3H } see CH_3
2.35 q (7Hz) 2H } CH_2
(↑ nearer to EWG)

EWG − CH_2 − CH_3

3.60 s, 2H (near EWG(s)) isolated CH_2 (X) (EWG)

7.20 mult. 5H (↑ phenyl H's) — phenyl H's don't look extremely different ∴ not close to EWG?

THUS:



- not conj. C=O ✓
- formula ✓
- ^1H splitting ✓
- ^1H integration ✓
- ^1H δ values ✓