Post

Worksheet for February 17

These are the reactions you need to know for exam. I have tried to delineate which mechanisms you are responsible for. Don't forget we started with nomenclature. You will be given a few names.

New material:

Oxidation of primary alcohols, secondary alcohols and tertiary alcohols
With bleach, potassium dichromate with sulfuric acid, chromic acid, potassium permanganate. Oxidation of primary alcohols to aldehydes using CrO3 and pyridine.

The only mechanism for the above you need to know is the reaction with CrO3 and pyridine.

Formation of epoxides with mcpba and formation of epoxides with the treatment of halohydrins with base.

The only mechanism you need from above is the one involving halohydrins and base

The opening of epoxides with aqueous acid and base, general nucleophilic attack on epoxides, especially the attack of alkoxides and "super base"

Need to know all above mechanisms

The formation of Grignard reaction and organolithiums and their reaction with epoxides and acids.

Need to know all above mechanisms.

The Diels Alder and all its associated stereochemistry and regiochemistry.

You do not need to know the mechanism of the DA, but you do need to know the molecular orbitals for a basic diene and dienophile. You need to know the homo and lumo theory for the diels alder in a basic way.

Know in a basic way – the origin of color

You need to know how to identify aromatic compounds and how to do basic EAS reactions – Friedel Crafts, sulfonation, nitration and halogenation of aromatics.

addition of HX and X2 to conjugated systems,

You need the mechanisms of the above

You need to know allylic, and benzylic free radical halogenation, SN2, E2, SN1/E1 reactions. You need to know their mechanisms.

You need to know that NBS is a halogenation reagent , but you don't need to know the mechanism.

You need to know the catalytic hydrogenation of conjugated double bonds and benzene, the oxidation of side chains of aromatics. You do not need to know these mechanisms.

You need to know the formation of cis vicinol diols using KMnO4 and OsO4

Generally, you should review

Free radical substition of alkanes and allylic systems
Addition of HX, HBr (with and without peroxides), water (there are three ways- hydroboration-oxidation, oxymercuration-reduction, and acid catalyzed hydration).
Generally, sn2, sn1, e2 and e1

There may be a little more so, realize you are responsible for everything that was covered in class except the following mechanisms – NBS bromination, chromium reactions except Collins, mcpba epoxidation, KMnO4 addition to double bonds, Osmium tetroxide addition to double bonds.

Note, a lot of the above is abbreviated.

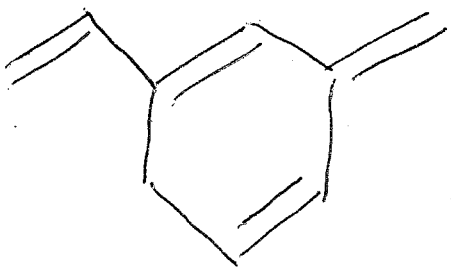
I hope this helps.

My office hours are posted by my door.

Worksheet Scan post | Please Post
Feb 17, 2011

Write Mechanisms leading to major products for each of the following reactions
Include stereochemistry and all resonance forms.
An answer key will be posted Monday.
Where noted, you do not need to include mechanisms.

(1)



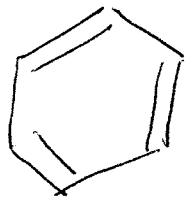
+ HCl

-78°C →

→ +80°C

See attached

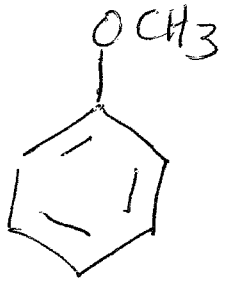
2.

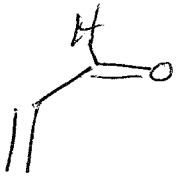


+ Br_2 ⟶ No reaction

Aromatics do not undergo Addition

3.



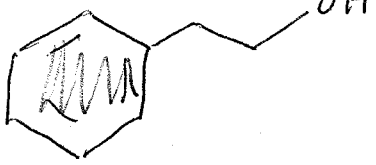


⟶ No rxn

No mechanism required

Aromatic do not undergo DA

4.



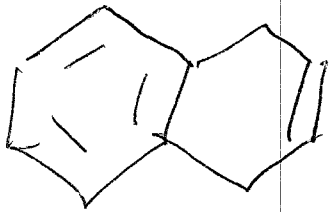
H_2CrO_4 ⟶

No mechanism required

But out line process showing intermediates

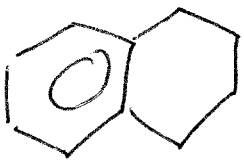
Meant to be a cyclohexene see attached

5.



H_2 / $Pd(C)$ ⟶

No mechanism required



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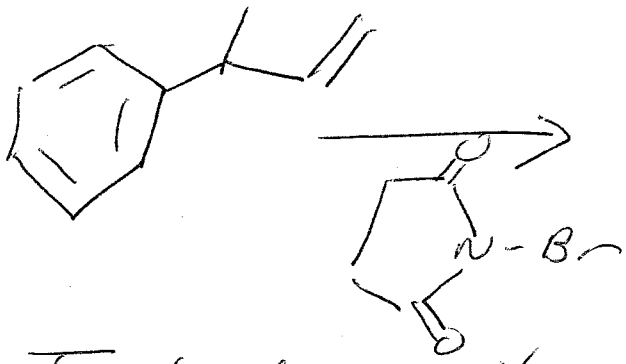

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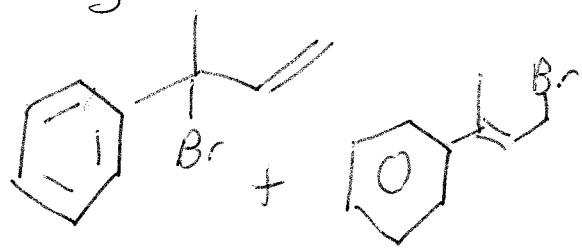
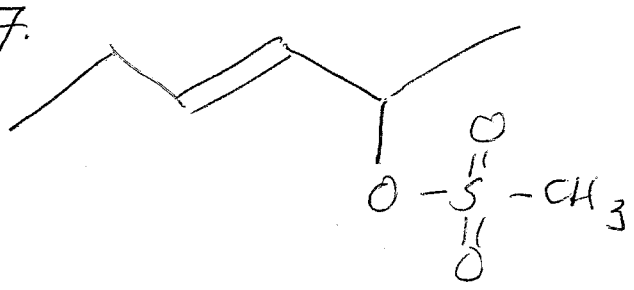


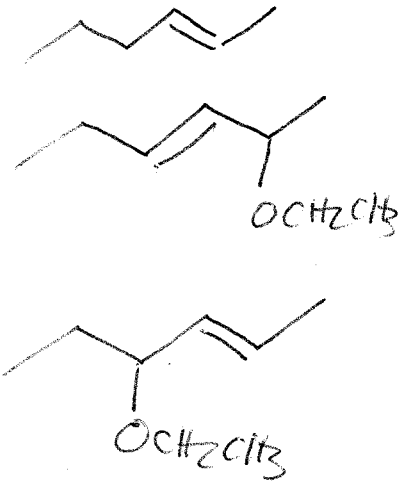
Instructor will give guidance

7.



$HOCH_2CH_3$

S_N1/E_1



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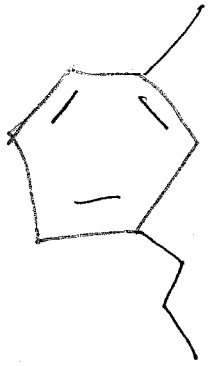
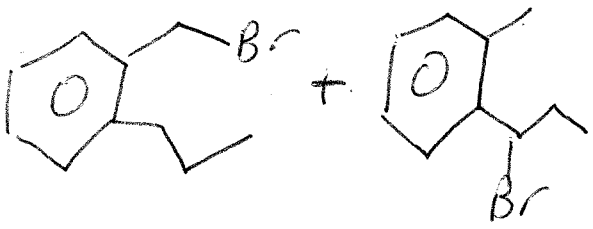


Br_2

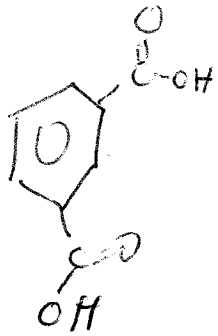
$h\upsilon$



1. $KMnO_4$

2. H_3O^+

No Mechanism Needed



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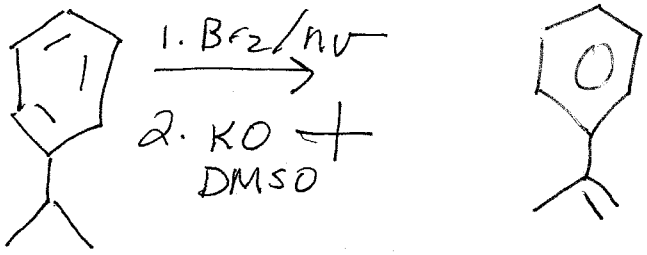
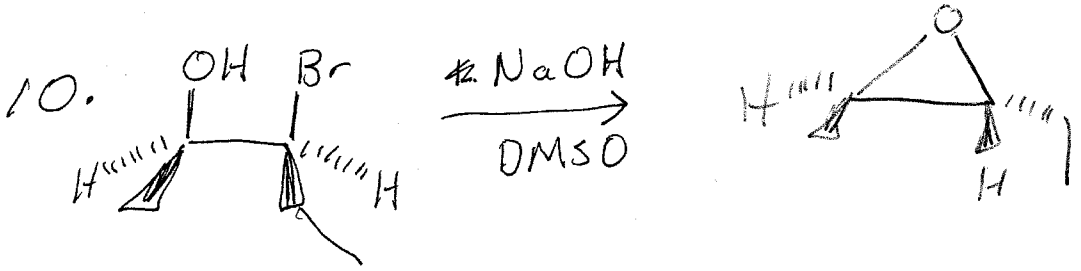
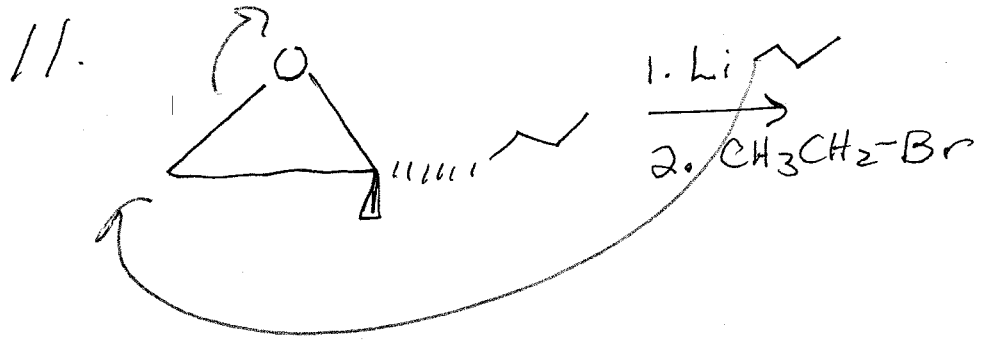
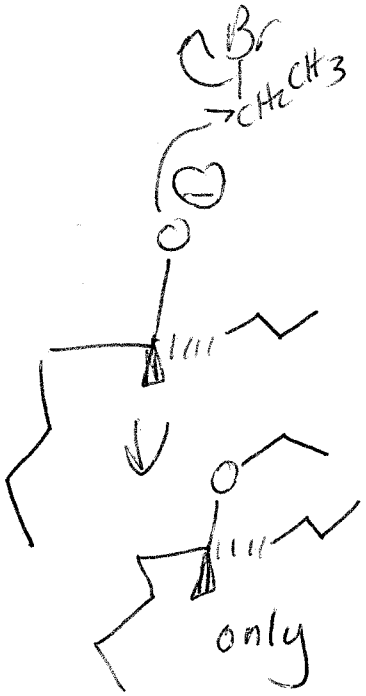

1. Br2/hν
2. KO
DMSO

10.

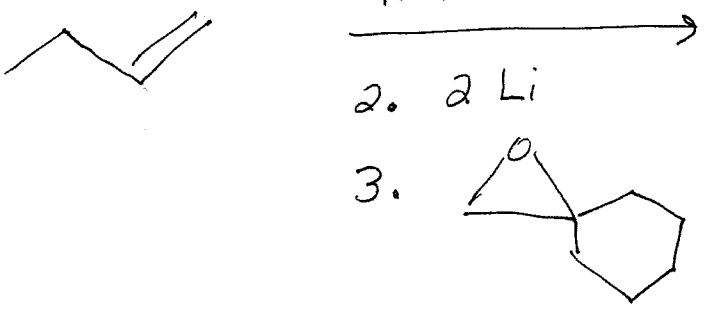

OH
Br
H
H
1. NaOH
DMSO
H
H

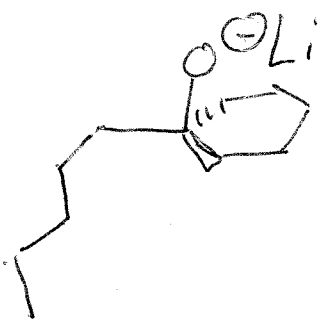
11.


1. Li
2. CH3CH2-Br

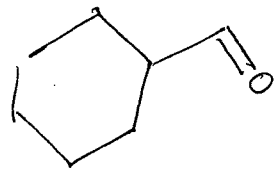

Br
CH2CH3
only

12.

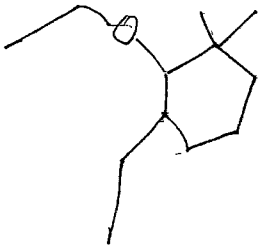
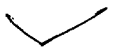

1. HBr ROOR Δ
2. 2 Li
3.

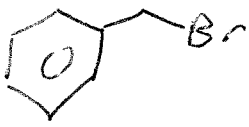
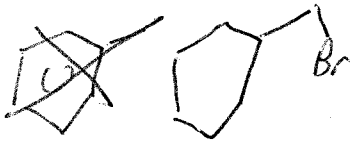

Li

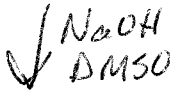
Synthesize the following target molecules from the given starting materials and any needed inorganic reagents

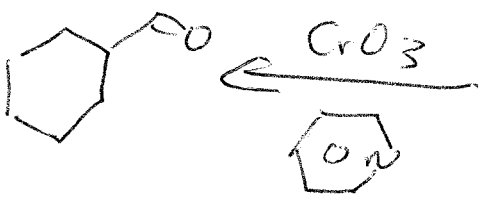
①  from 

(name this) (name this)

 from  and 

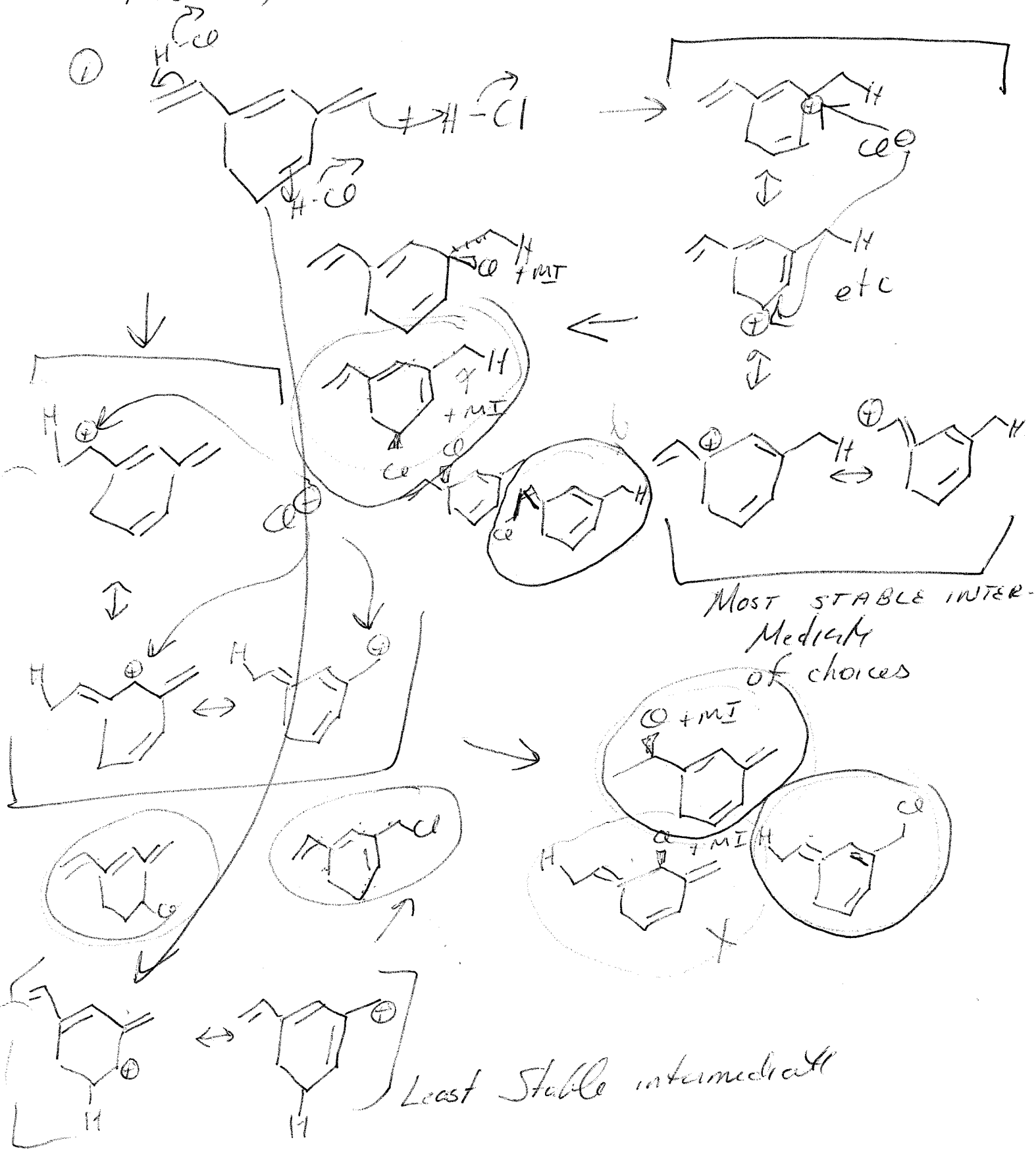
①  $\xrightarrow[h\nu]{Br_2}$  $\xrightarrow[\Delta DDP\ \Delta DDT]{H_2\ Pd/C}$ 





Answer Key

Feb 17, 2011



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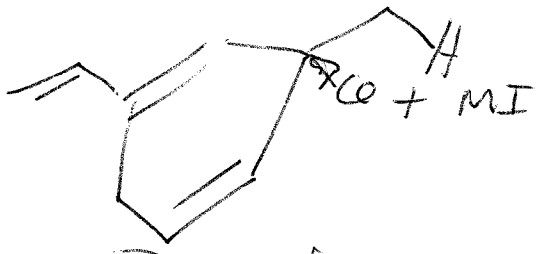
After some reflection, I feel this product would be the kinetic product



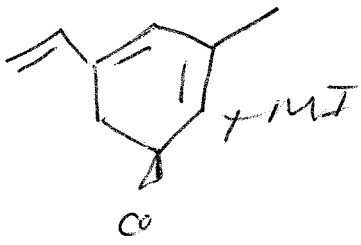
-78°

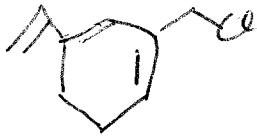
Why? It is the 1,2 product from a substantially more stable intermediate

The others ~~to~~ 1,2 would be the kinetic, do for their respective intermediates, but I feel this 1,2 is significantly faster

At +80

I circled ALL the potential thermodynamic products - picked them because they are the most conjugated OF these I believe these have the greatest # of substituents





7 alkyl substituents

So in this difficult problem 3/8

-78 = Kinetic = $\frac{\text{S}}{\text{t}}$ relates

FASTEST 1, 2 to intermediate

then pick 1, 2 coming from lowest NRG intermediate

+80° Thermo

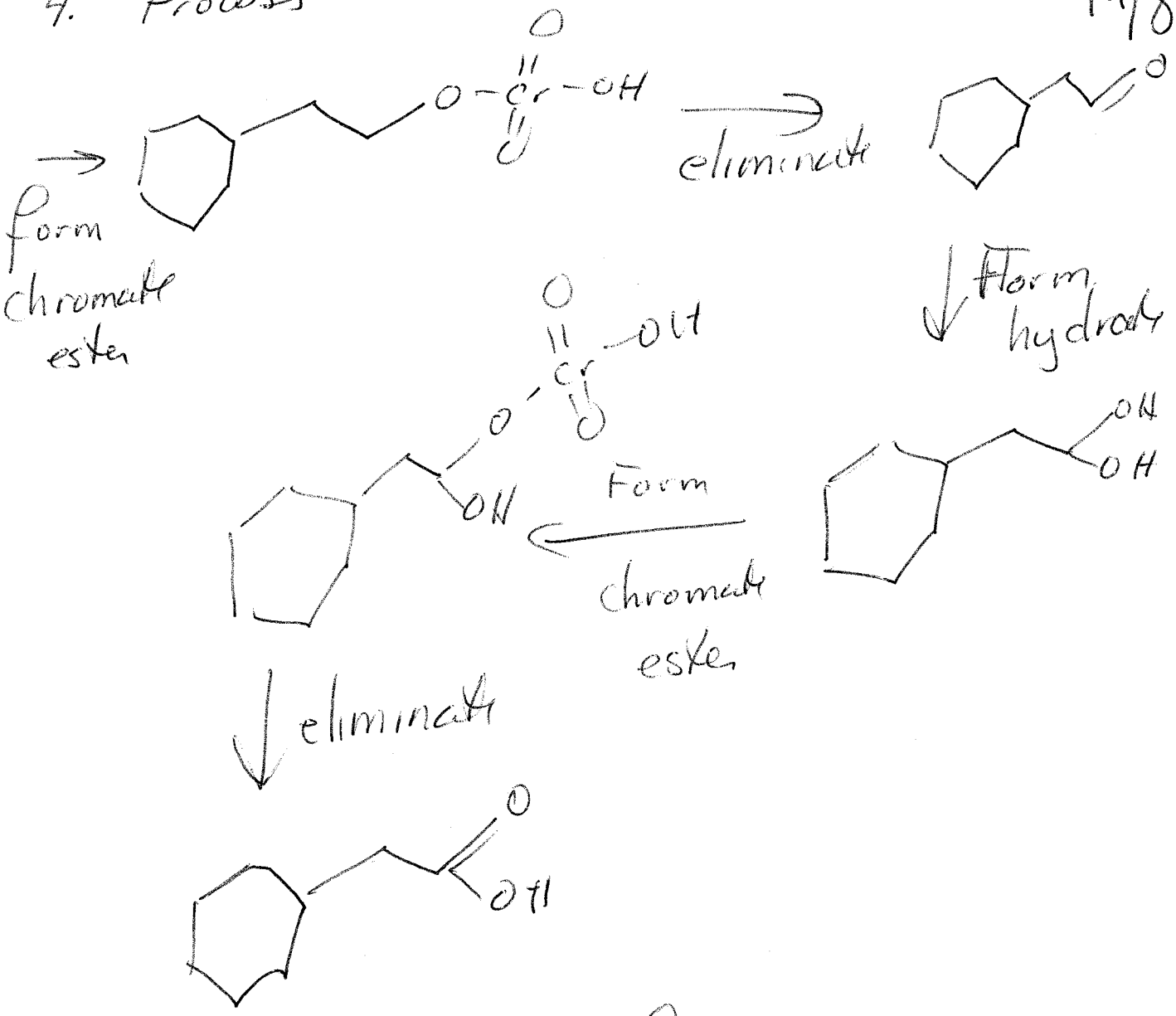
Pick most stable prod ignore intermediate

Criteria —

① Conjugation of double bonds in product

② Substitution of DBs double bonds

4. Process



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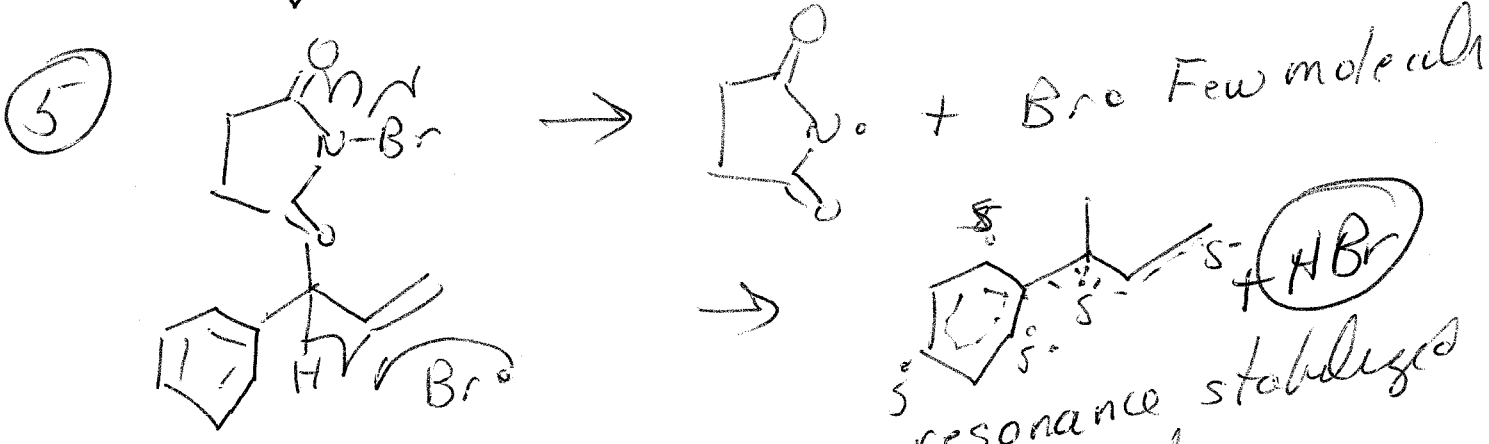
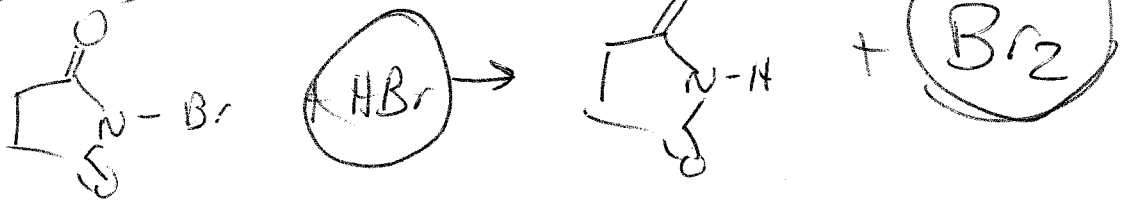


FACTORY



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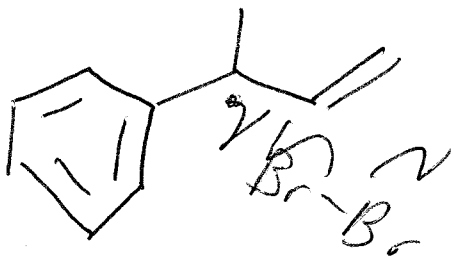
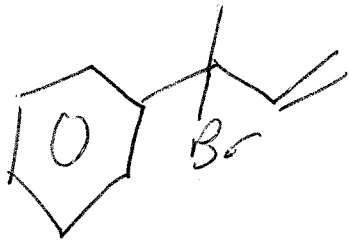
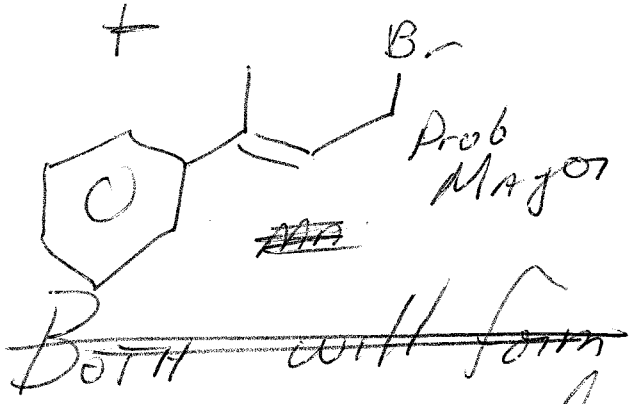
6. cont





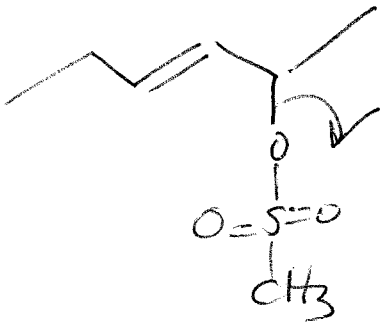


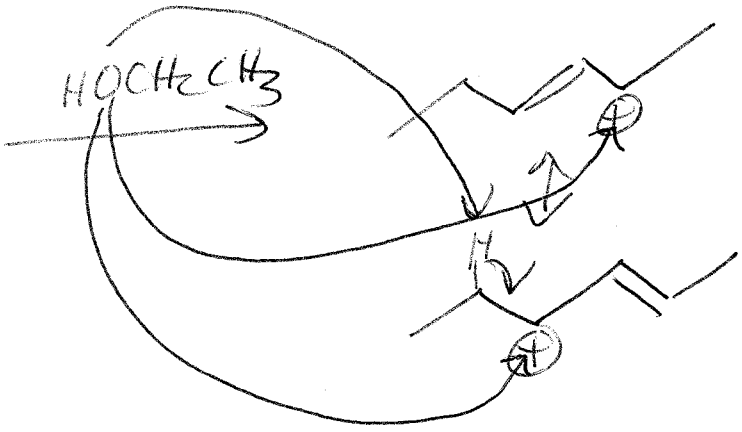
Prob Major

~~Both will form~~

Do not overanalyze write both

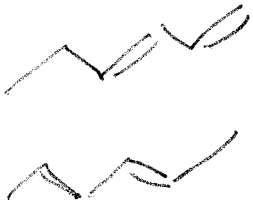
7.

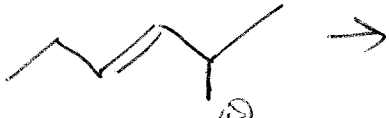


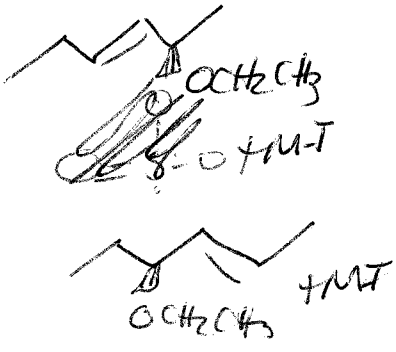


S_N1

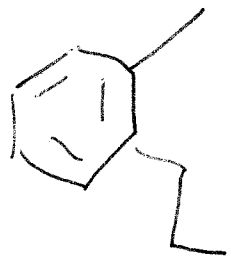
E_1

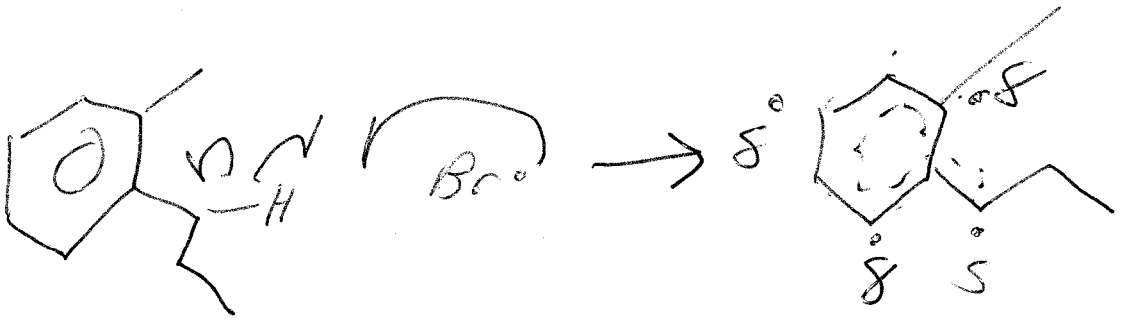


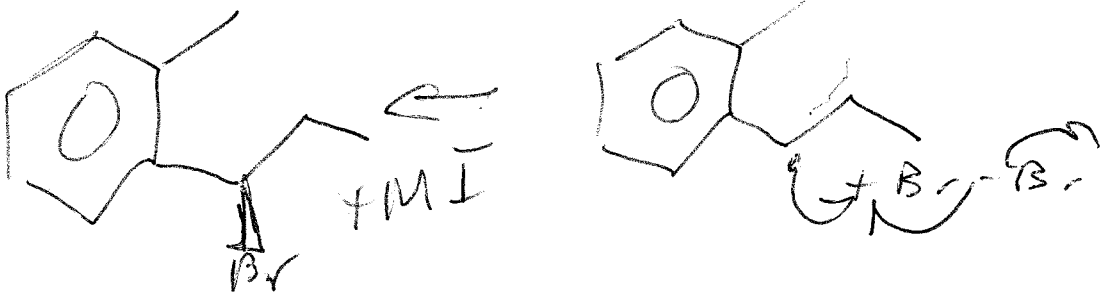


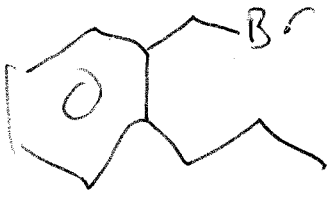


8. Mechanism for Bromination

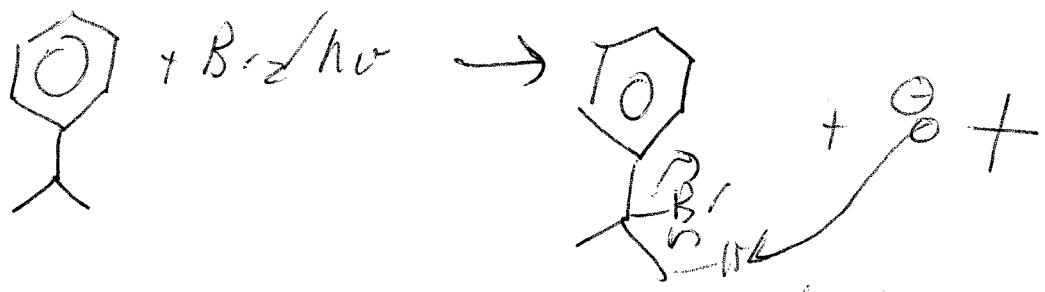




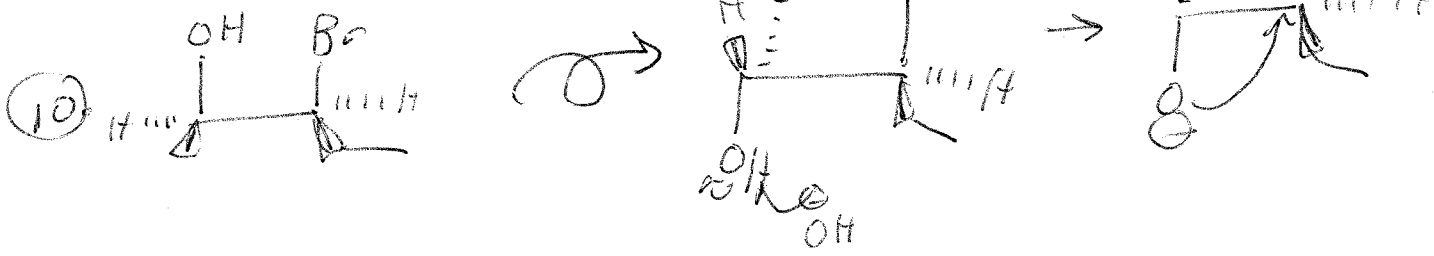


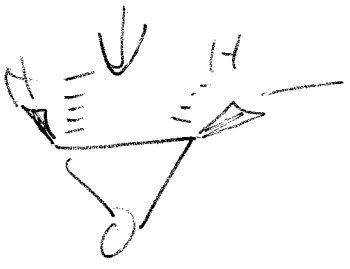


OXIDATION - NO mechanism
Not completely understood

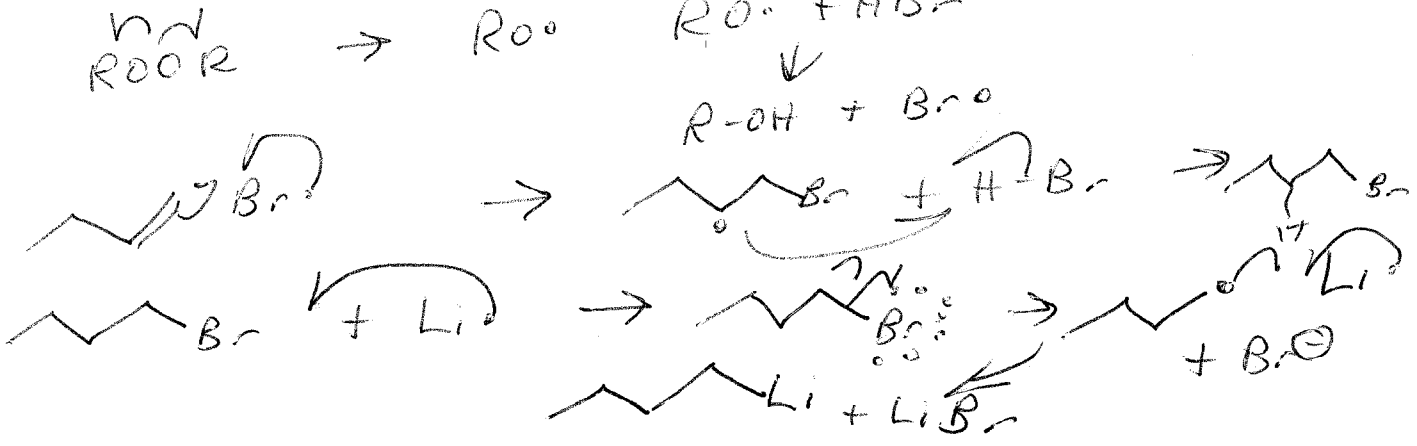
9. 

Mech already shown

(10) 

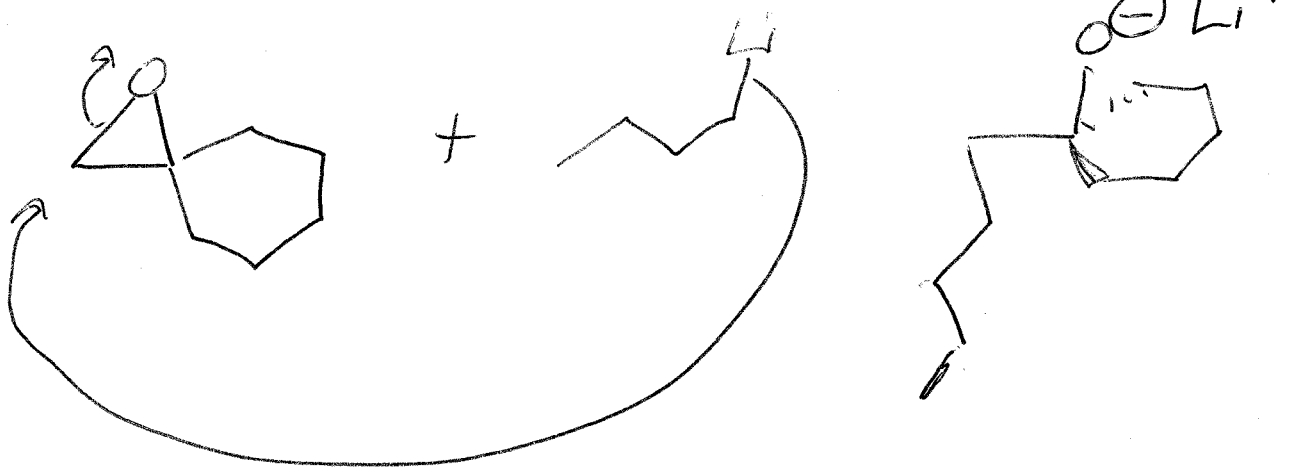


(11) Mech shown

(12) 

12. Cont

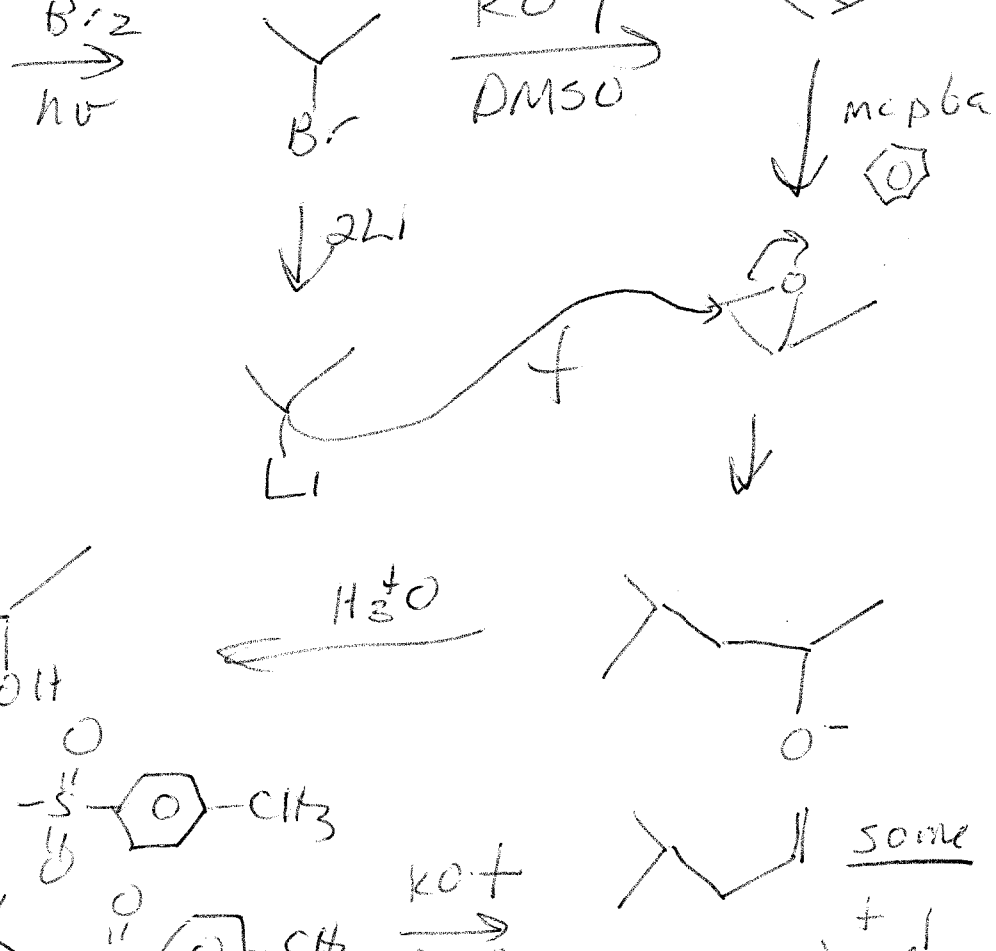
7/8

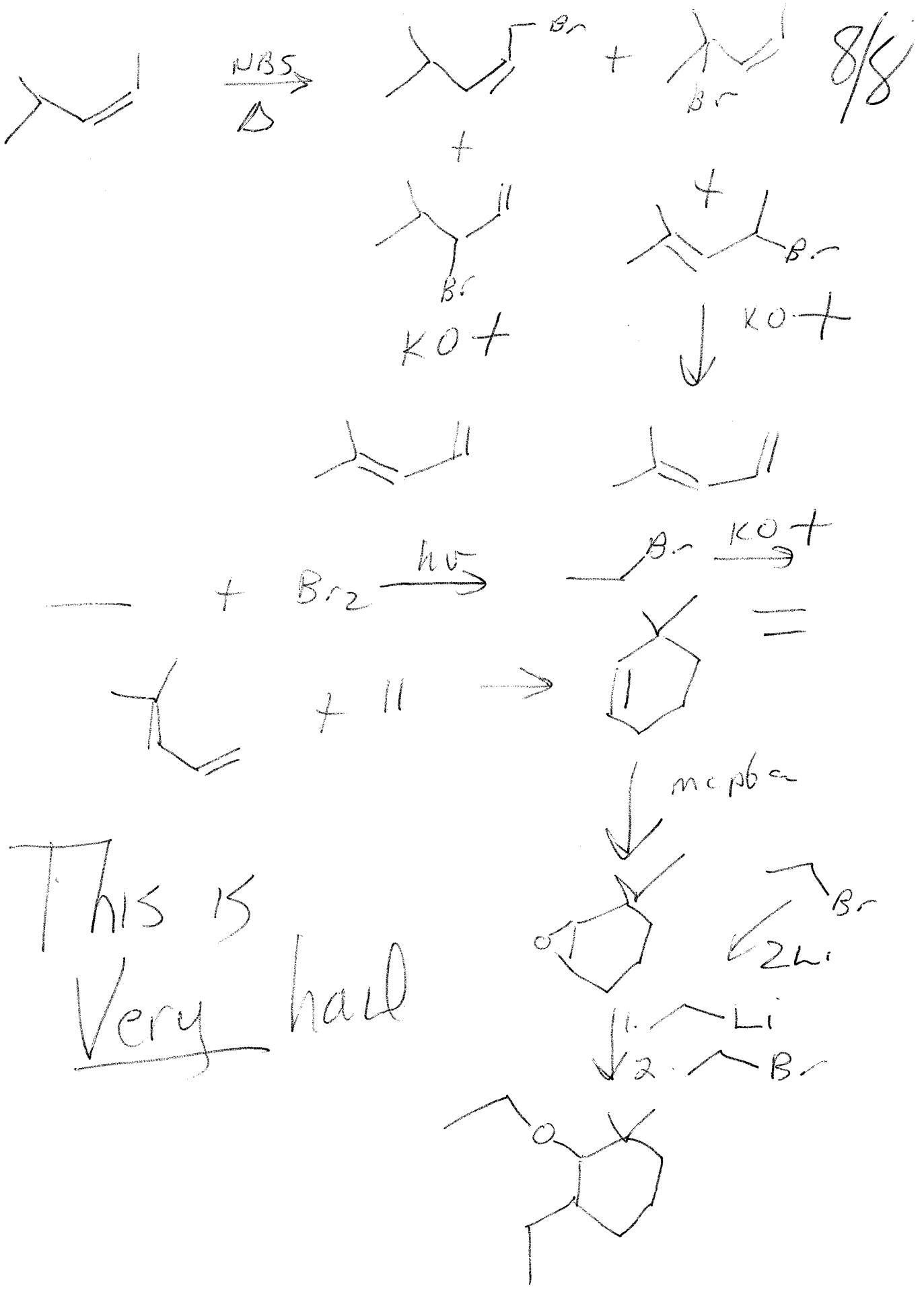


Synthesis

(1) Shown

(2) 





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This is Very hard