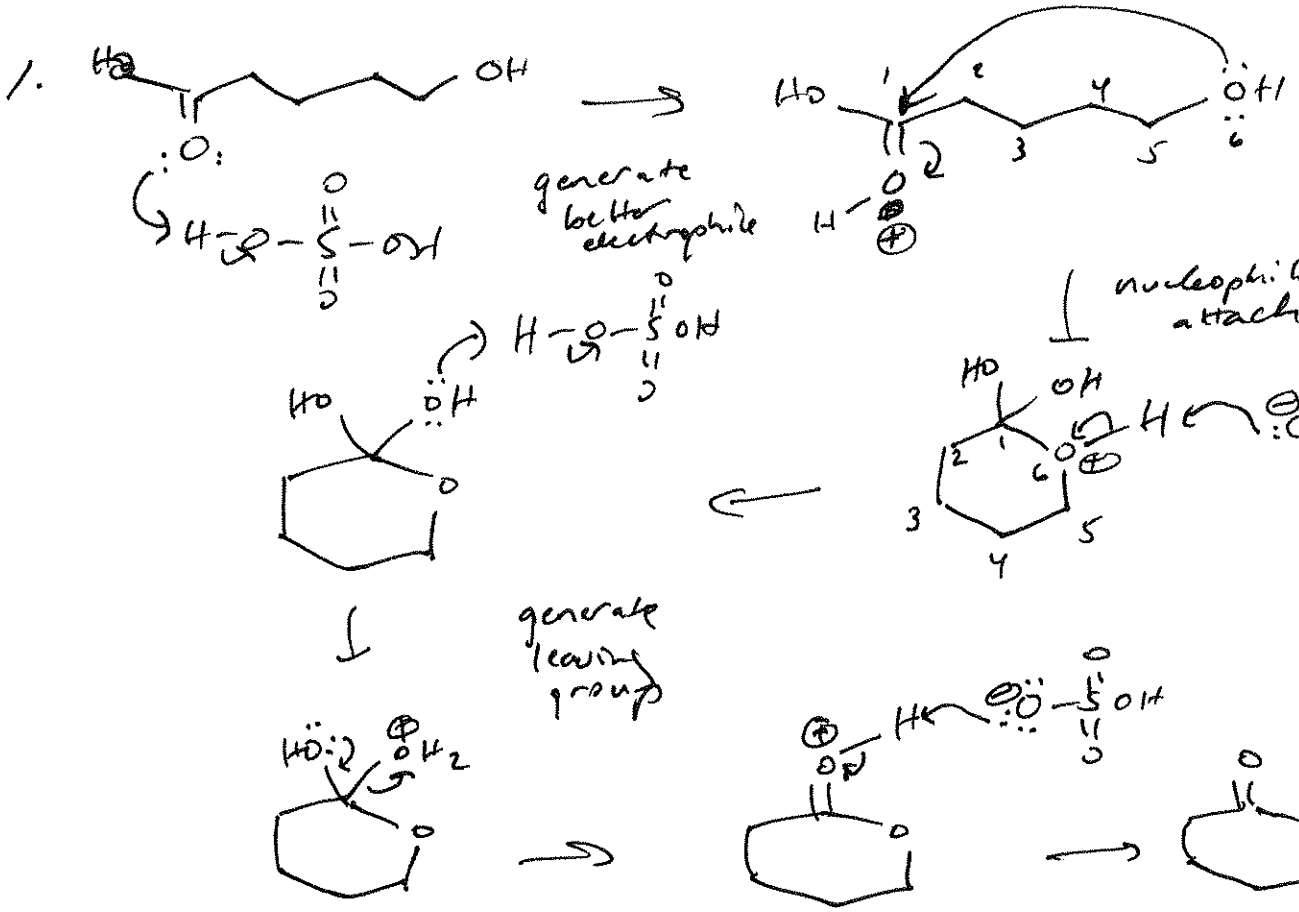
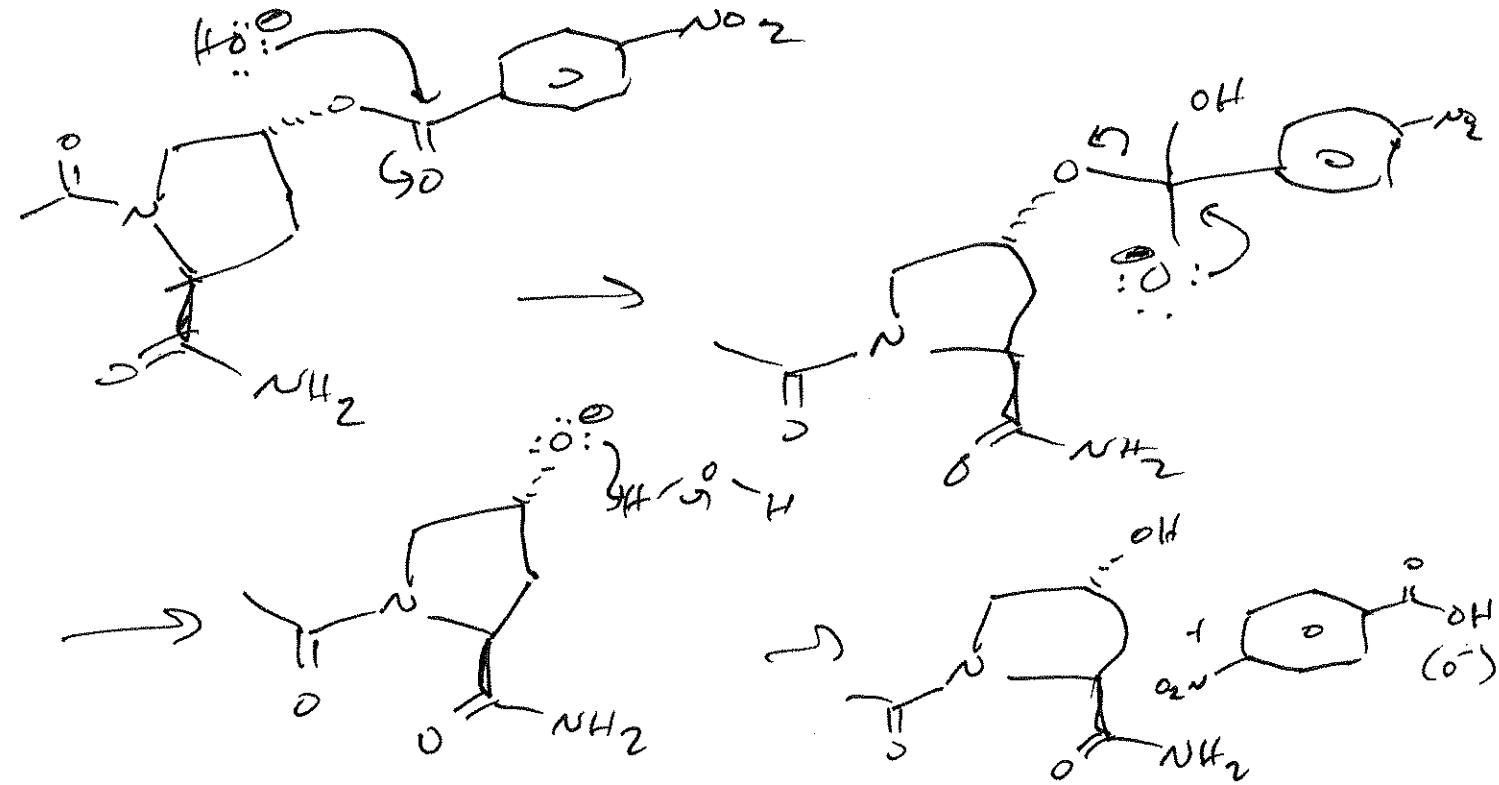
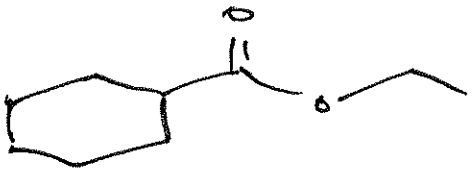
Problem set 7 – Answers

1.





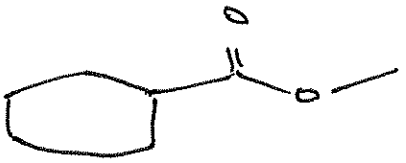
2.



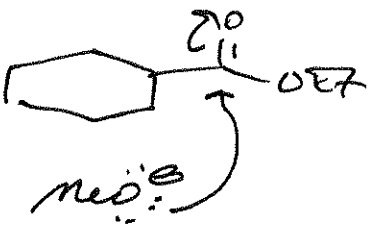
MeOH → no reaction

(insufficient nucleophile/electrophile)

$MeO^{\ominus}/MeOH$ →

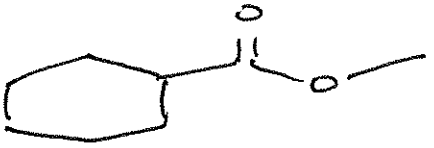


(via

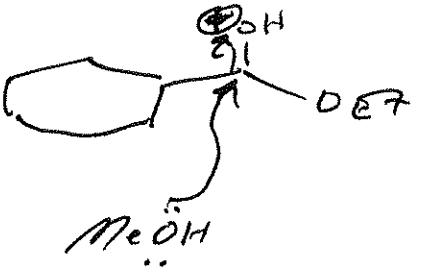


)

$MeOH/H_2SO_4$ →

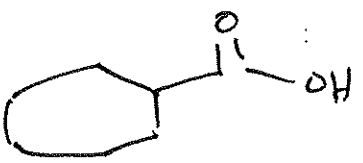


(via



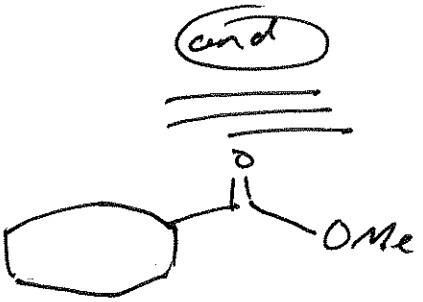
)

$MeOH/H_2O$
HCl →

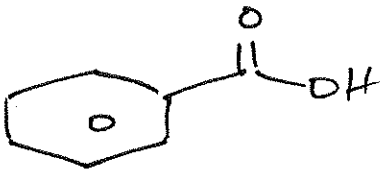


two nucleophiles,

H_2O and MeOH



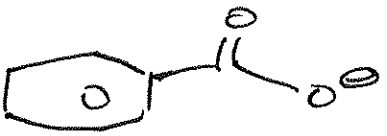
products interconvertible



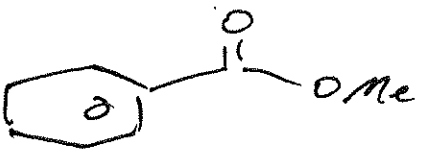
MeOH → no reaction

pKa 4.2

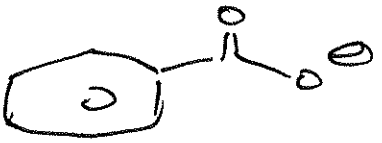
H_2O, pH 7 →



MeOH, H_2SO_4 →

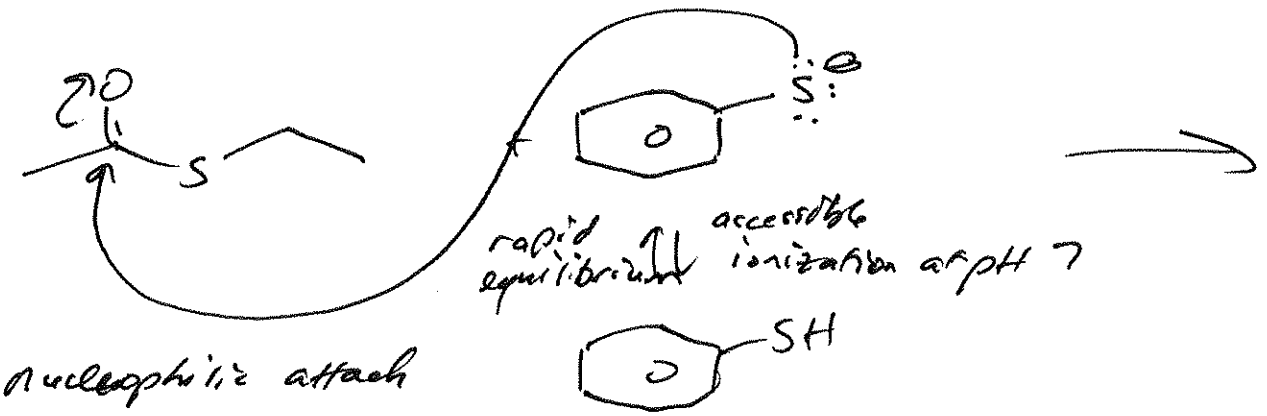


$MeO^{\ominus}$/MeOH →

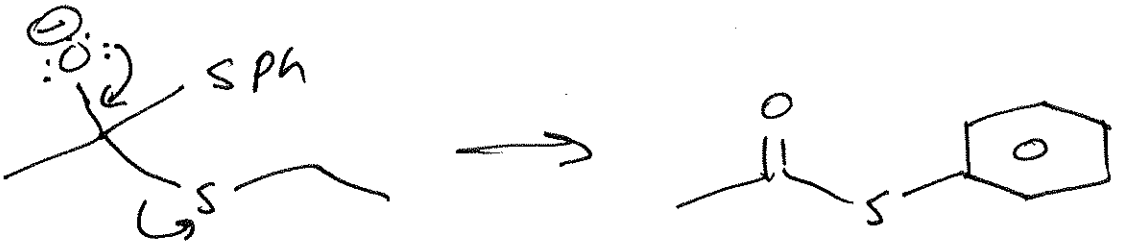


(no leaving group under basic conditions)

3. (a)



nucleophilic attack via thiolate (far more nucleophilic than thiol)



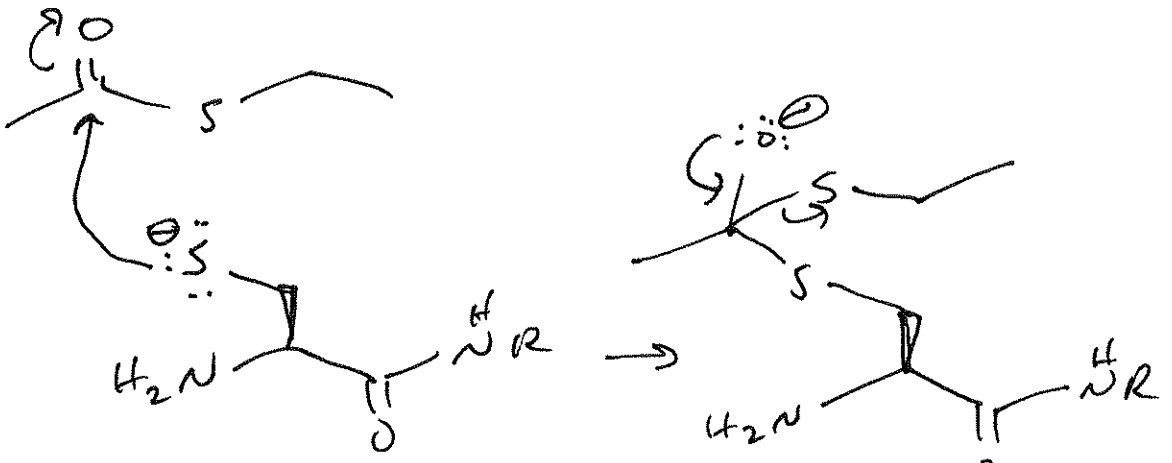
+

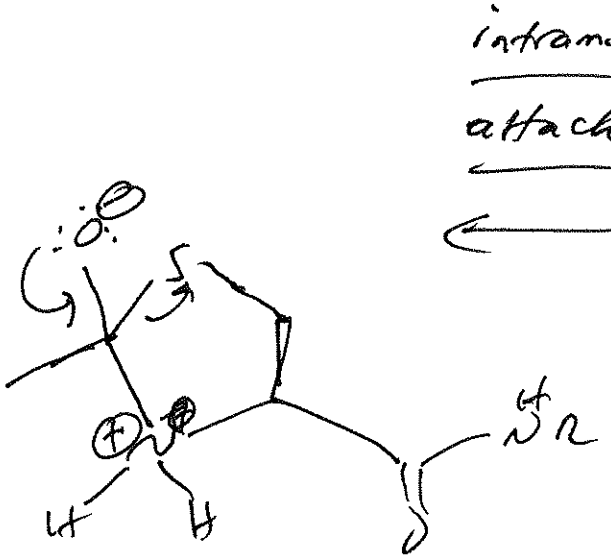
π

better leaving group than alkoxide

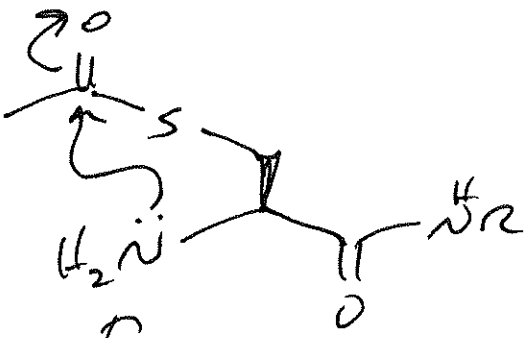
1. Thiolate superb nucleophile, present at pH 7 (~10?; Le Chatelier's principle drives rxn due to rapid equilibrium)
2. Thiolate better leaving group than alkoxide (RSH more acidic than ROH)
3. Because of sp^3 electrons on S being 3s/3p, worse overlap with carbonyl 2p / π orbital; so C=O more electrophilic

(6)





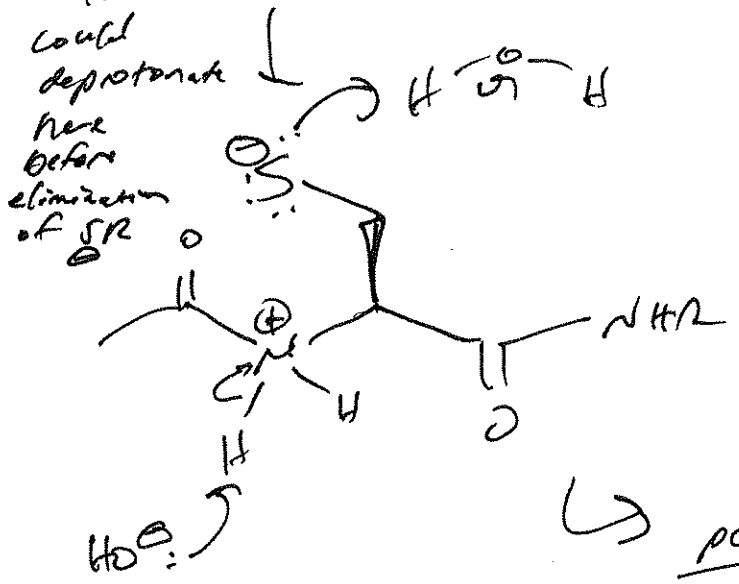
intramolecular attack



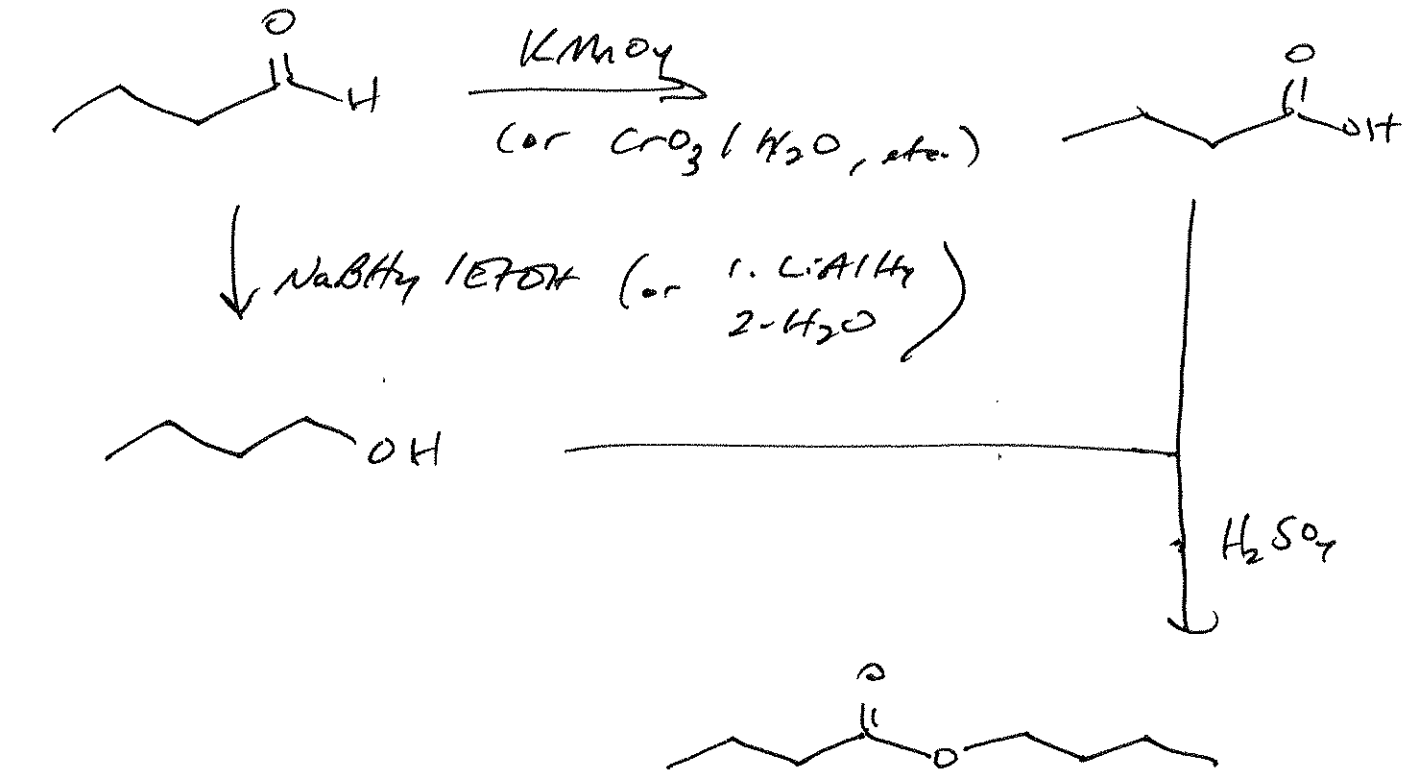
[note: mostly in protonated (R-$\overset{\oplus}{N}H_3$) (non-nucleophilic) form, but rxn occurs via fraction in nucleophilic form; $RNH_2 \rightleftharpoons R\overset{\oplus}{N}H_3$ pKa 10 is rapid equilibrium]

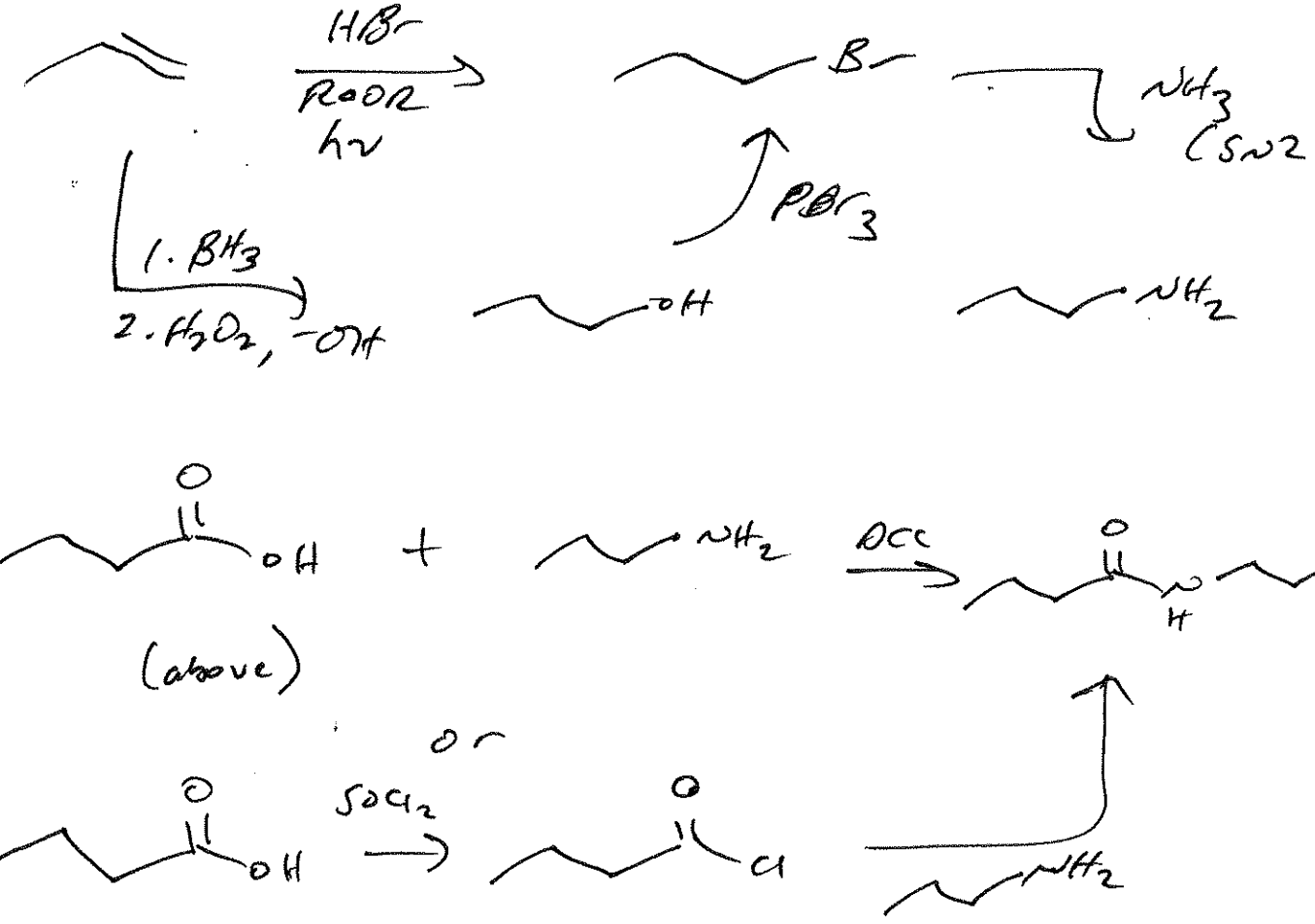
really ~> here, though. Why?

↑ could deprotonate here before elimination of SR

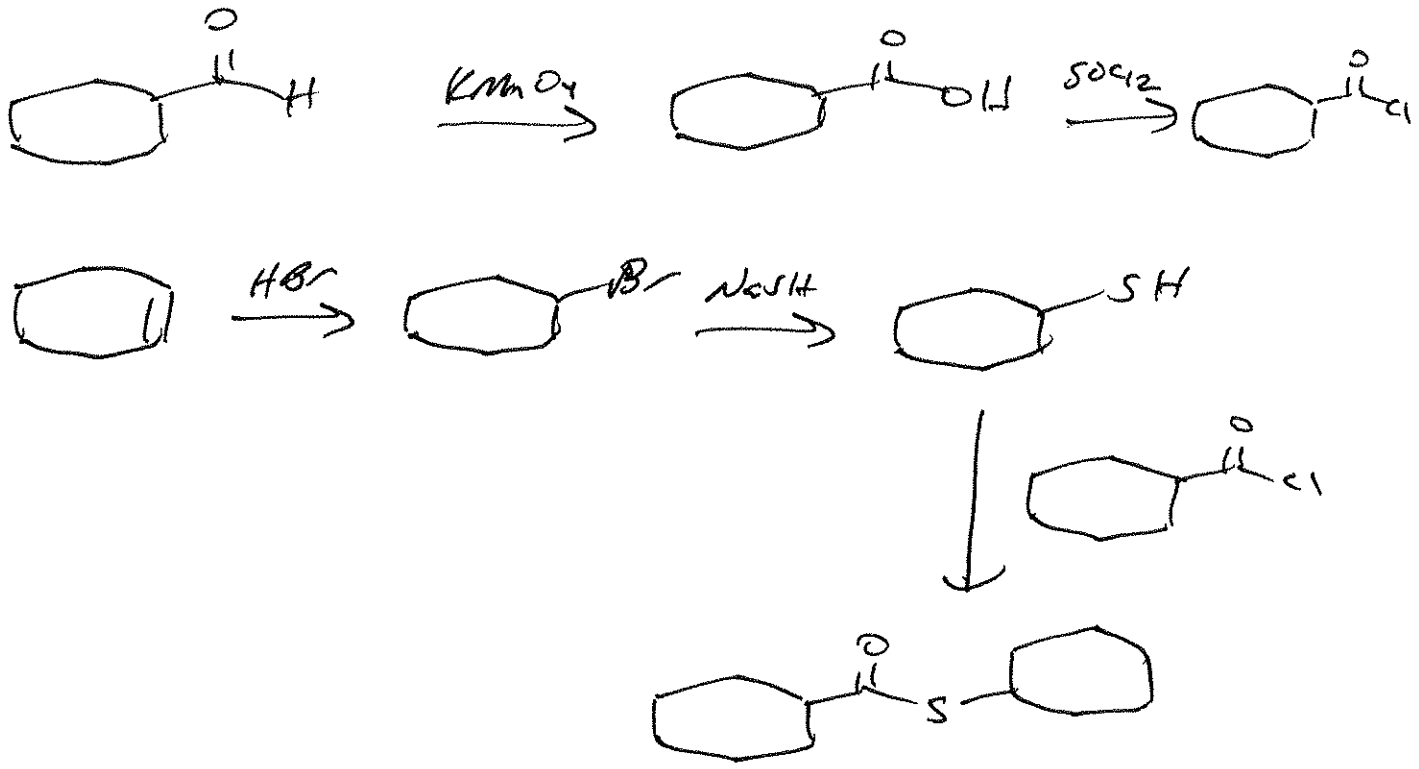


↳ <u>post</u>

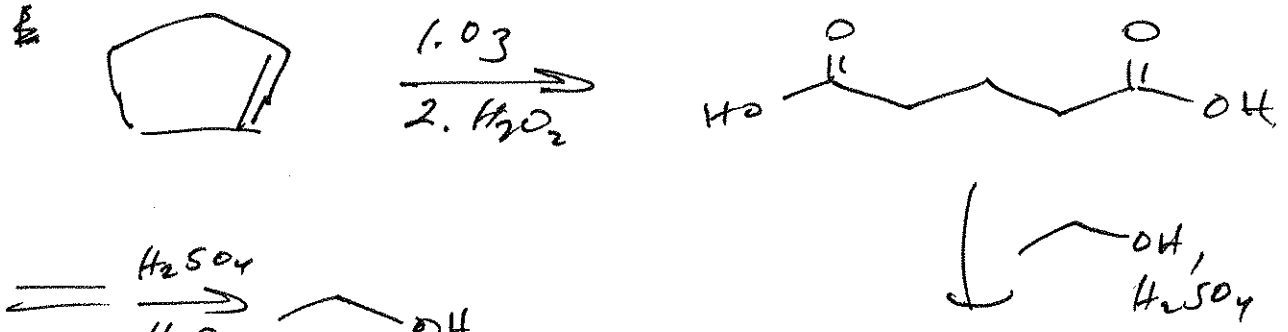

KMnO4
(or CrO3 / H2O, etc.)
NaBH4 / EtOH (or 1. LiAlH4 2. H2O)
H2SO4


HBr
ROOR
hν
PBr3
NH3
(SN2
1. BH3
2. H2O2, -OH

DCC
(above)
or
SOCl2

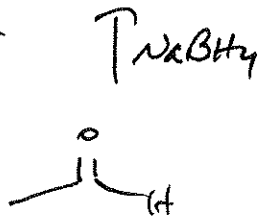

KMnO4
SOCl2
HBr
NaSH
SH
Cl
S

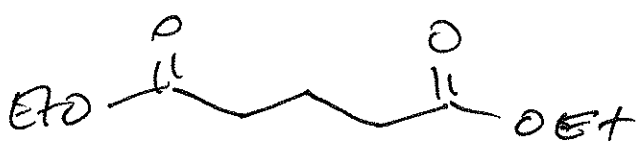
b


1. O3
2. H2O2
HO
OH
OH,
H2SO4

H2SO4
H2O
OH

or


NaBH4
H


EtO
OEt