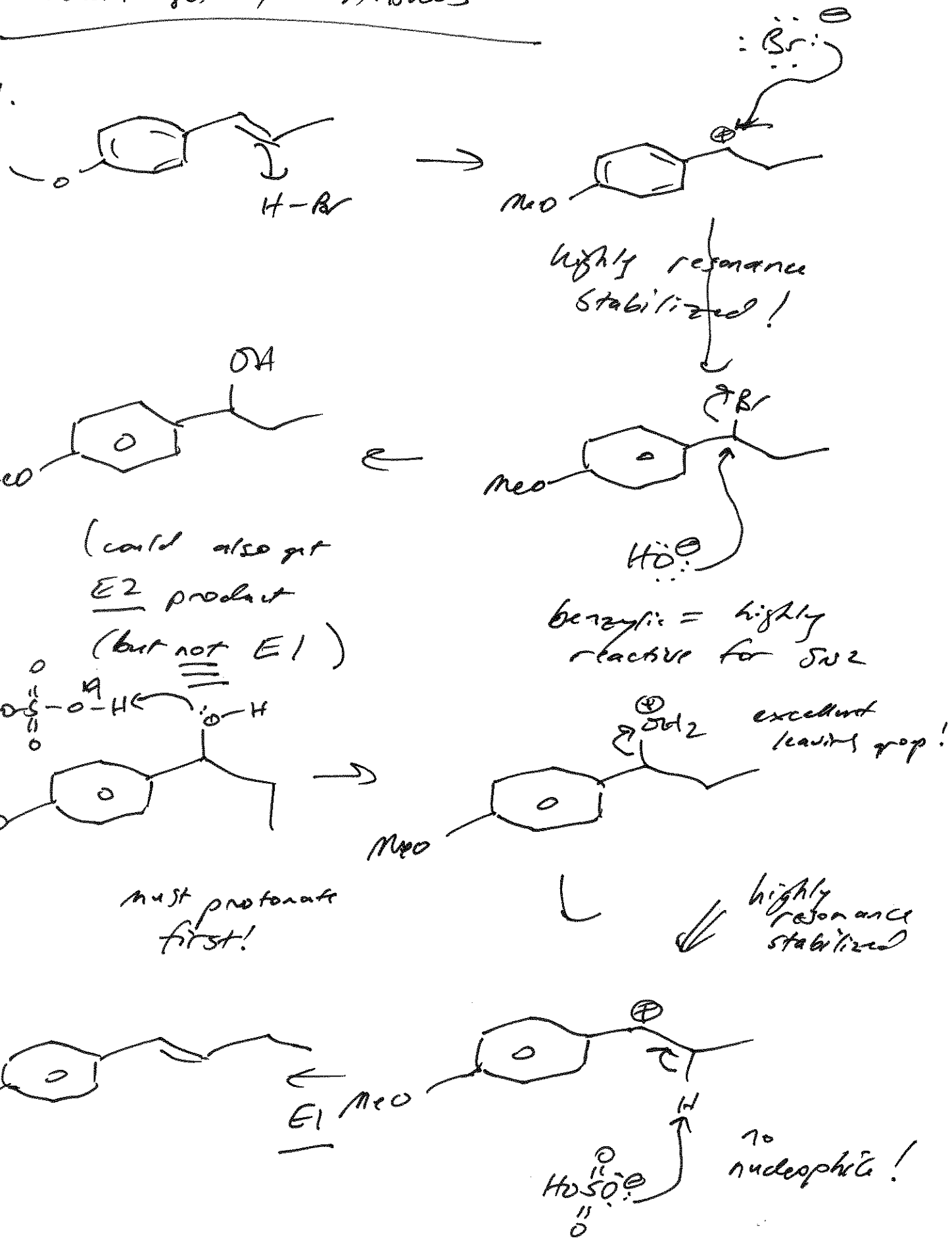
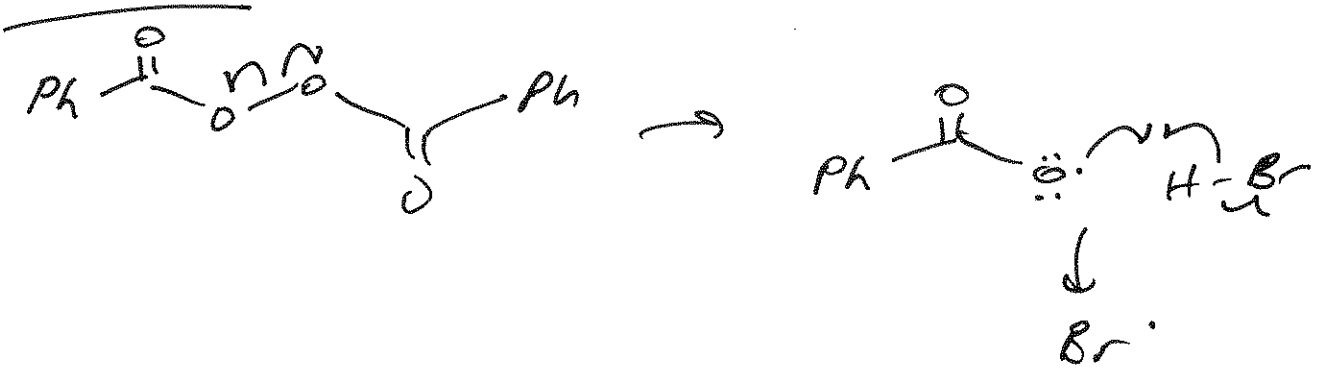
Problem set 4 – Answers

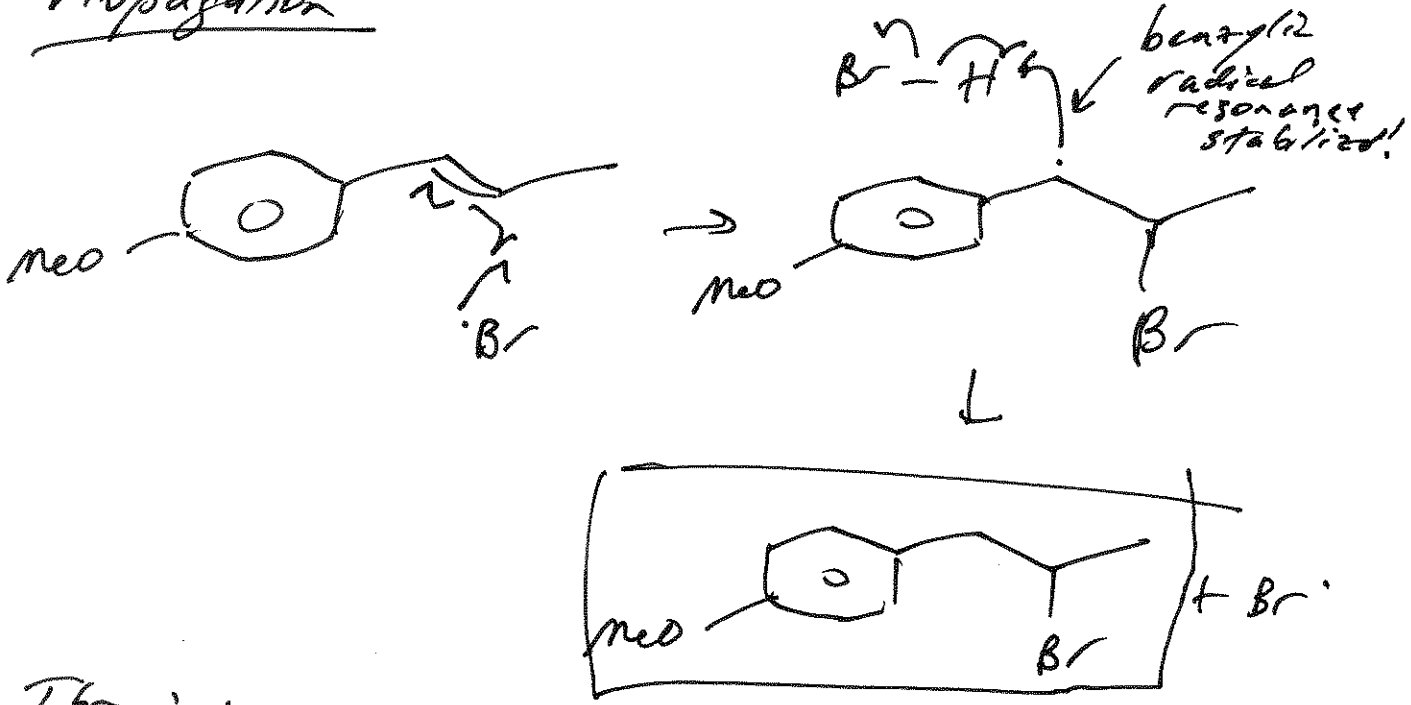
1.



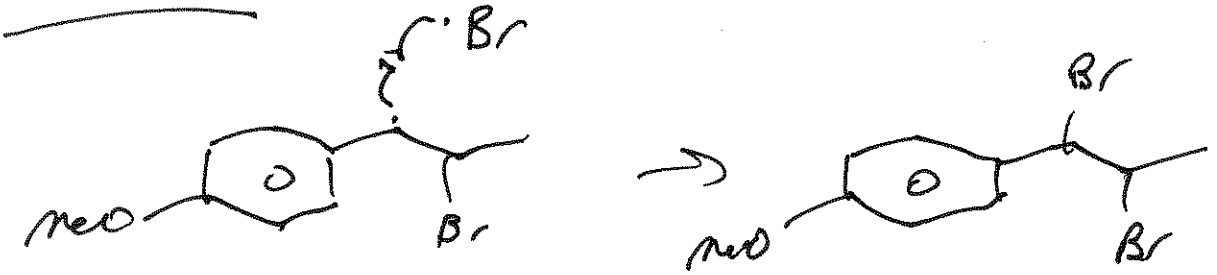
Initiation

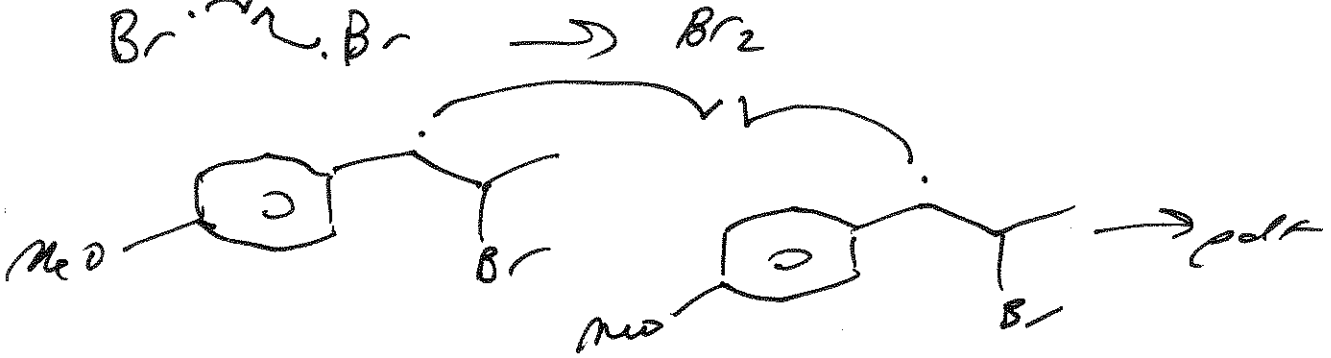


Propagation



Termination





Remember:

Initiation: Generates radical employed in free radical chain (propagation)

Propagation: - Starting material to generate product
- Consumes all reagents (stoichiometric)
- Regenerates radical present at begining of propagation (carries radical)

Termination - Two radicals react with each other to destroy the radical chain

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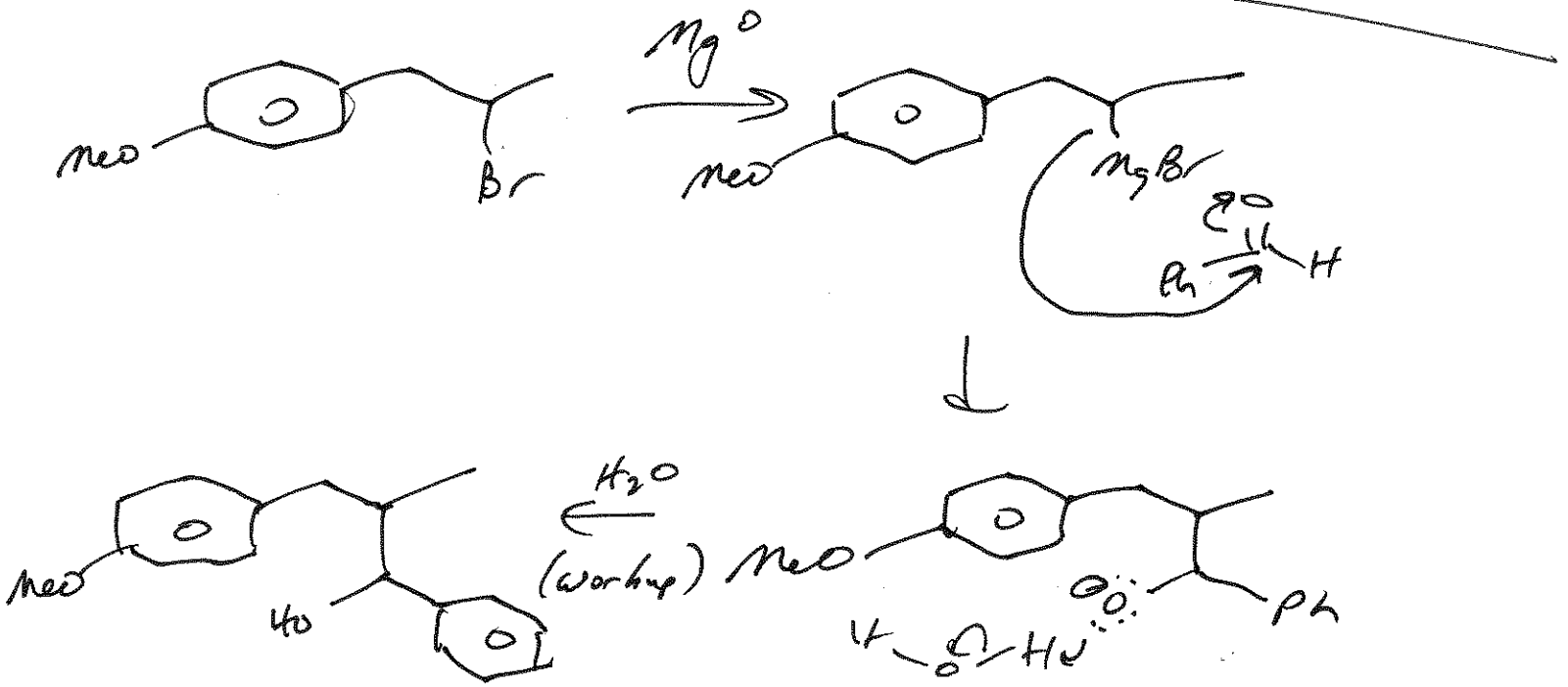
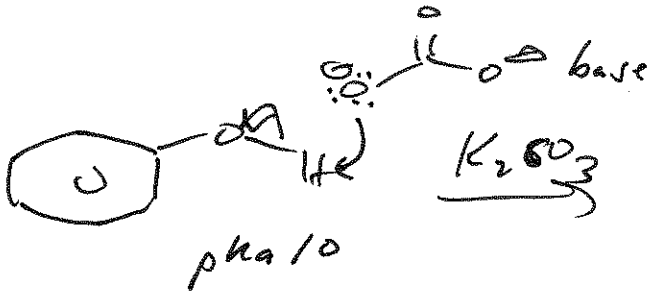
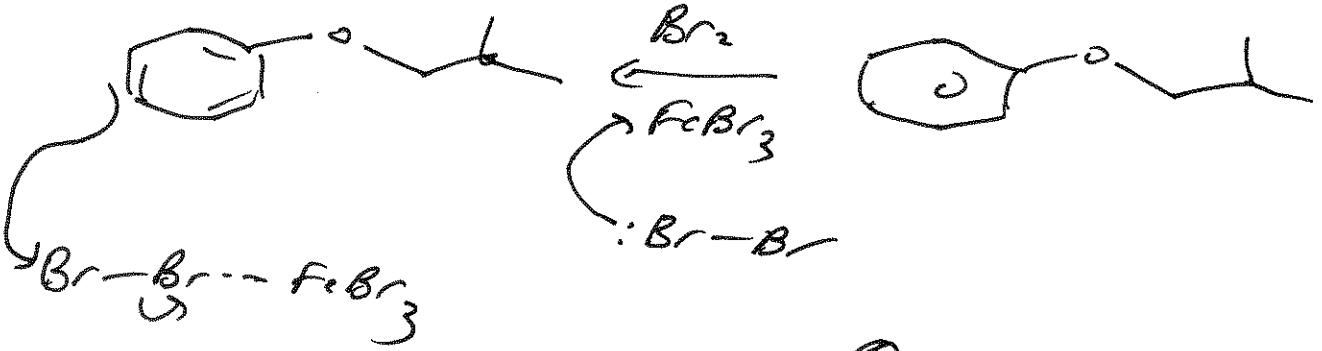
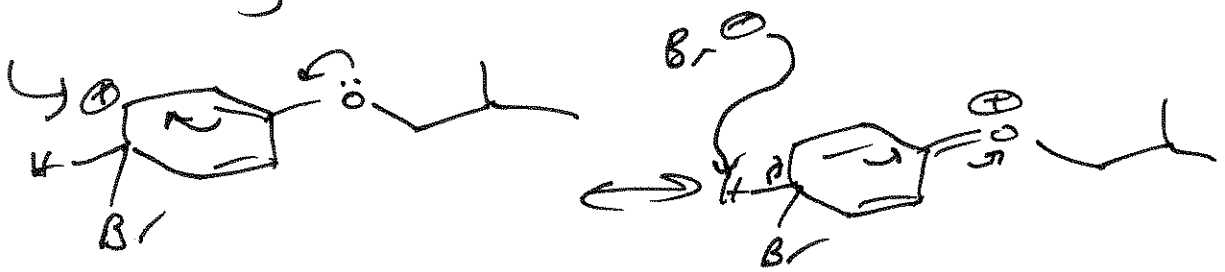
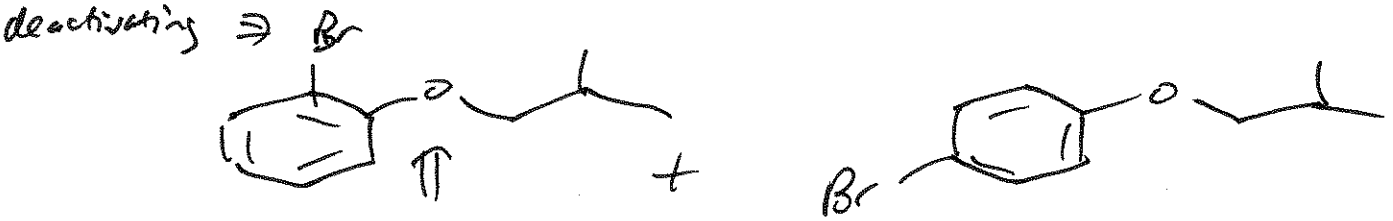






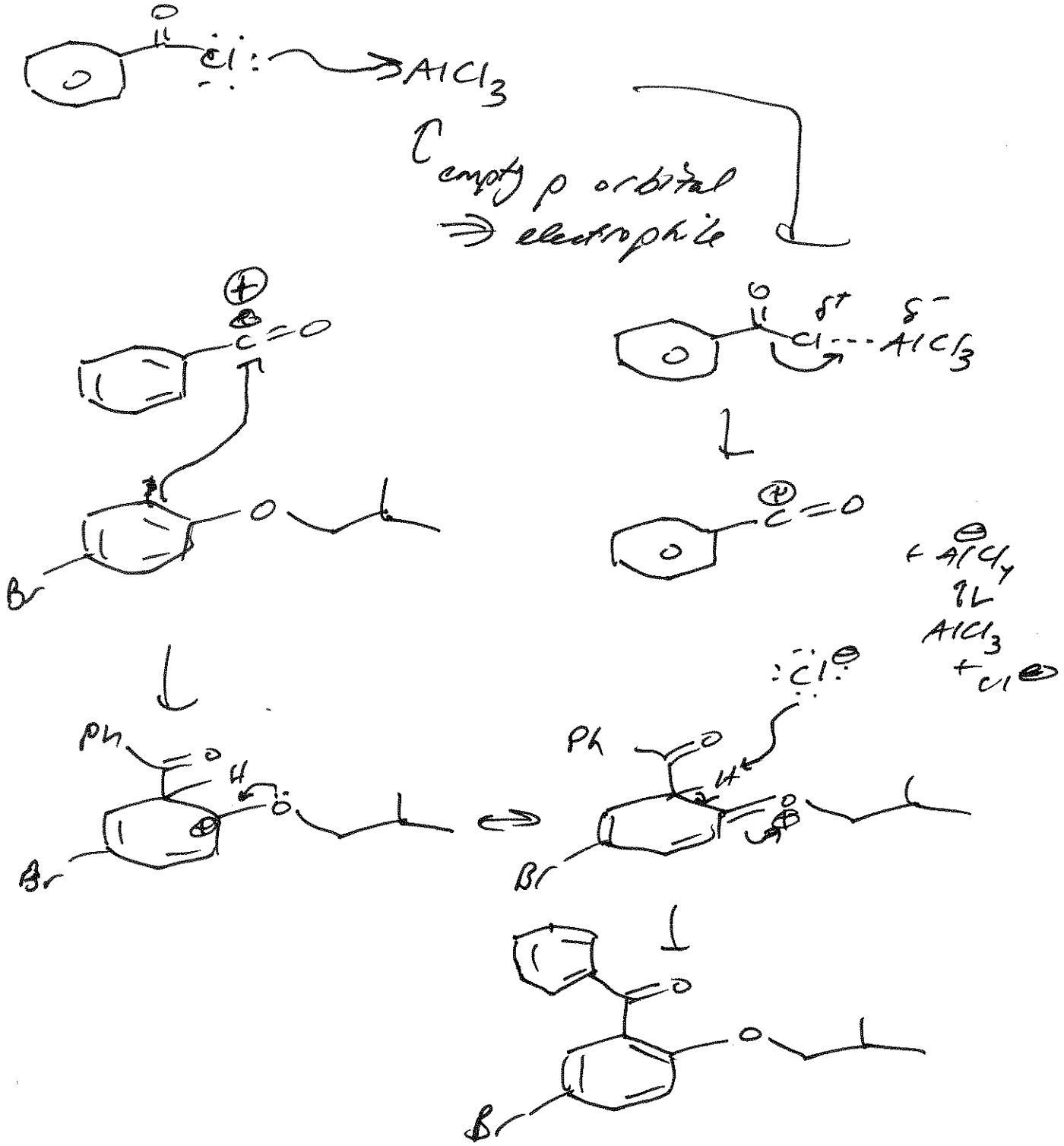


resonance stabilizes ortho, para (show!)

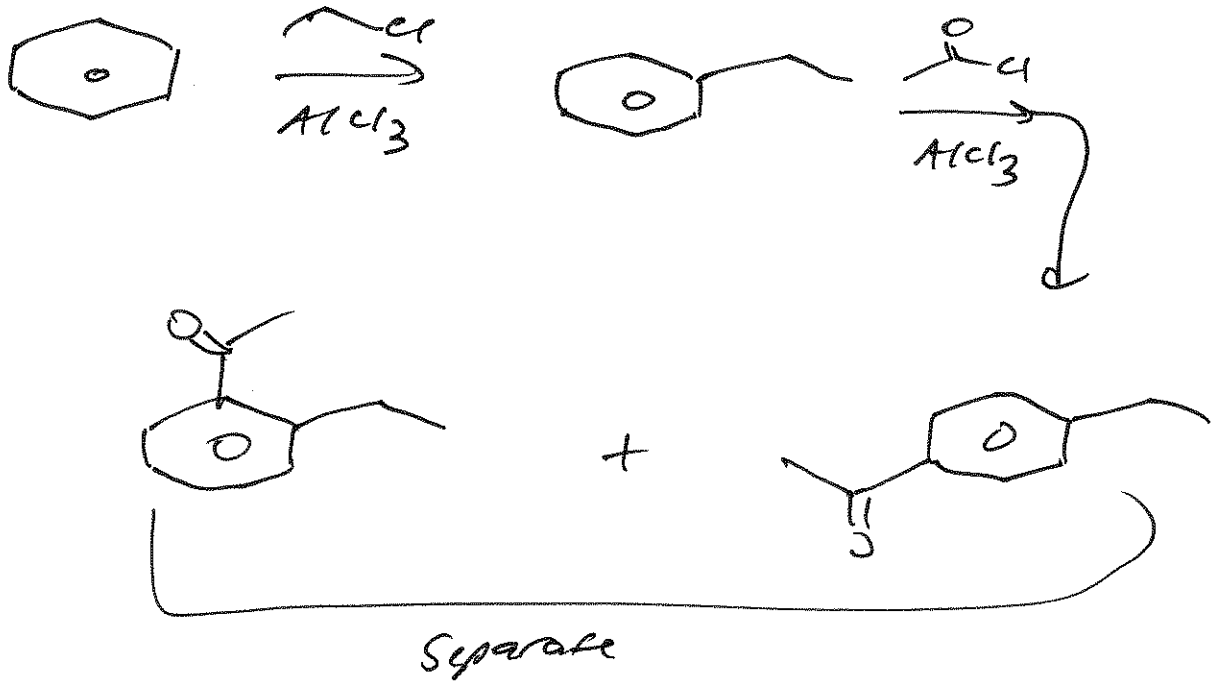


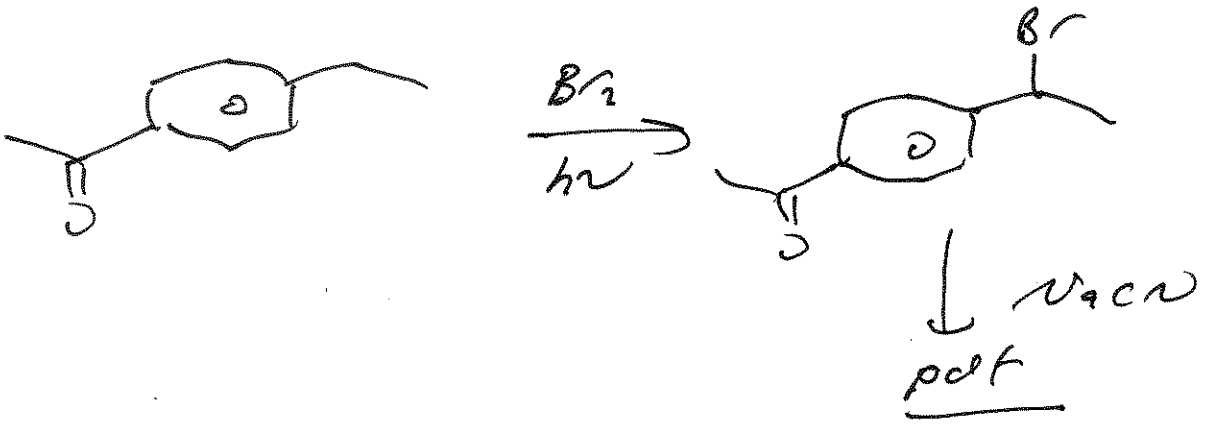
strongly activating

⇒ drives regiochemistry of next E.A.S.

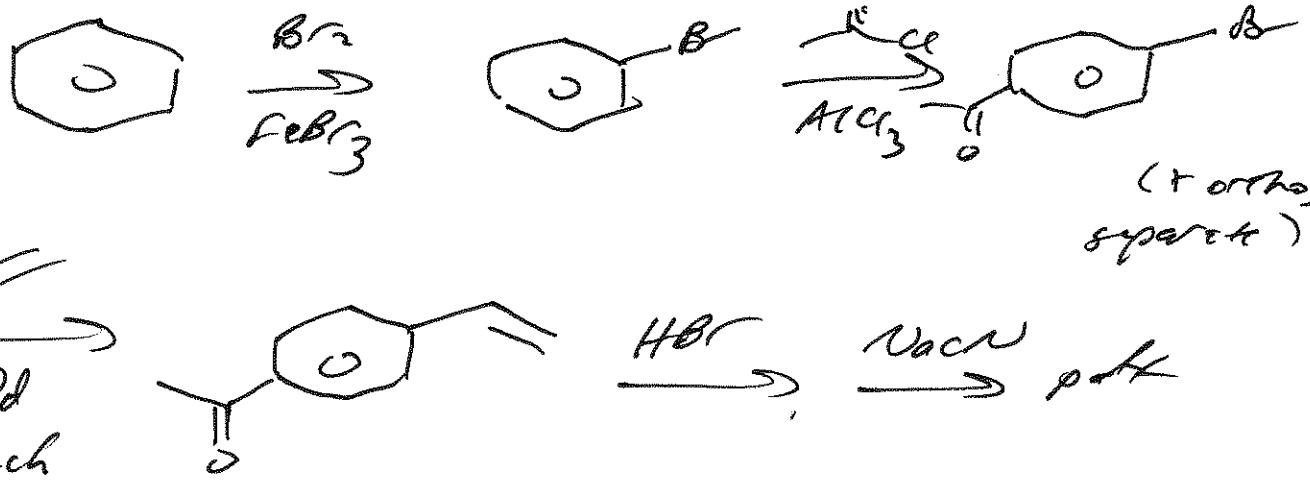

AlCl3
empty p orbital
⇒ electrophile
+ AlCl4⊖
2L
AlCl3
+ Cl⊖
Ph
Br
(from ortho
+
Ph
Br

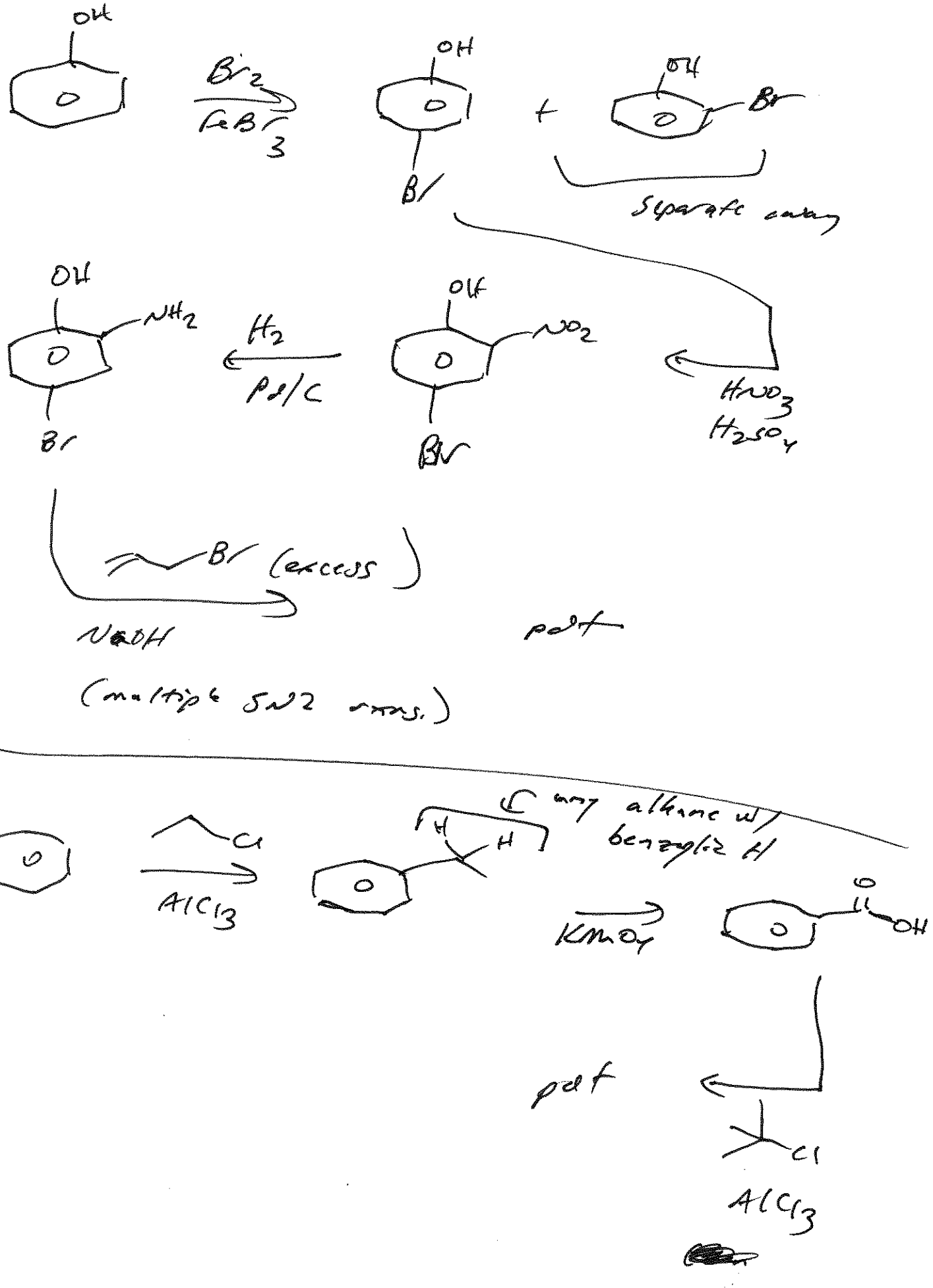
2.

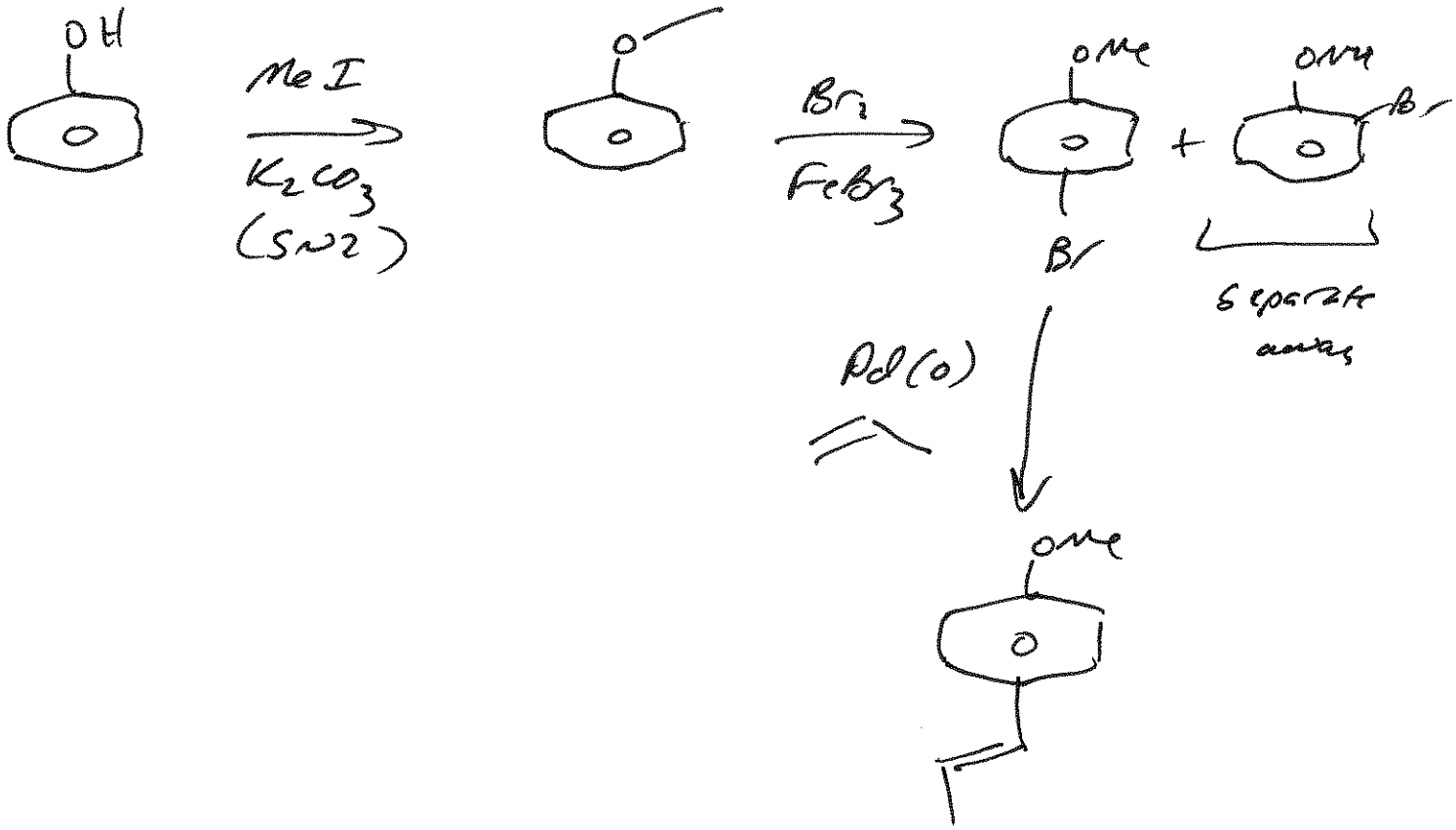




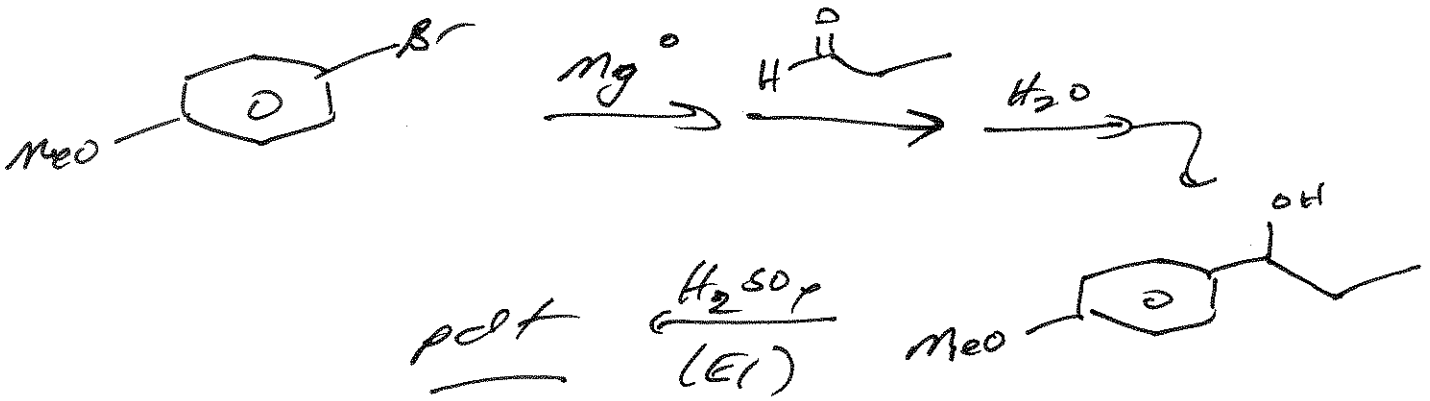
Alternatively

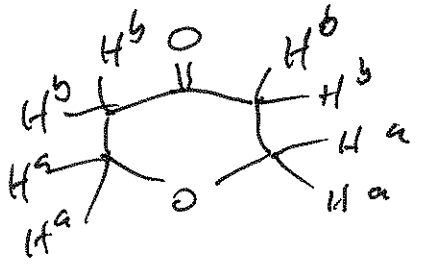



OH
Br_2
$FeBr_3$
Br
+
separate
NH_2
H_2
Pd/C
NO_2
HNO_3
H_2SO_4
excess
NaOH
poly
(multiple SN2 rxns.)
$AlCl_3$
any alkene w/ benzylic H
$KMnO_4$
O
OH
poly
Cl
$AlCl_3$



Alternatively

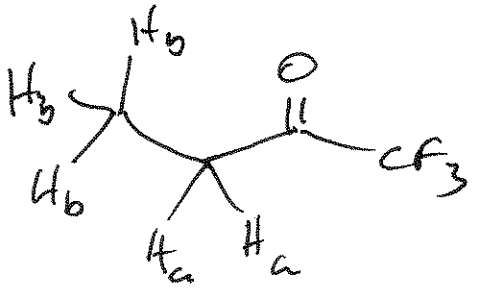




H_a triplet 4 ppm

H_b triplet 2–3 ppm

H_a and H_b integrate 1:1

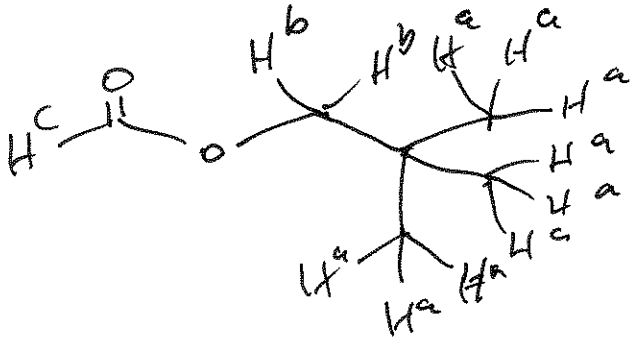


H_a quartet 3 ppm 2H

H_b triplet 1–1.5 ppm 3H

^{19}F: one F, <u>singlet</u>

(~ −75 ppm on the ^{19}F scale...)

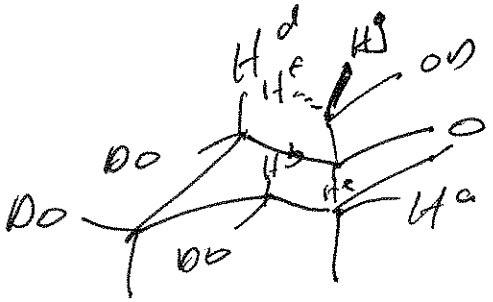


H_a singlet 1 ppm 9H

H_b singlet 4 ppm 2H

H_c singlet 9–10 ppm 1H

Deuterium: do not appear on ^1H NMR spectrum, do not couple to ^1H



= glucose! (as it would be in D_2O)

H_a ~ 4 ppm doublet (d) 1H

H_b ~ 4 ppm doublet of doublets (dd) 1H

H_c ~ 4 ppm dd 1H

H_d ~ 4 ppm dd 1H

H_e ~ 4 ppm dddd (doublet of doublets of doublets) 1H

H_f ~ 4 ppm dd 1H

(one larger ^2J coupling, one smaller ^3J coupling)

H_g ~ 4 ppm dd 1H

Note: H_f and H_g are diastereotopic due to presence of other stereocenters in molecule