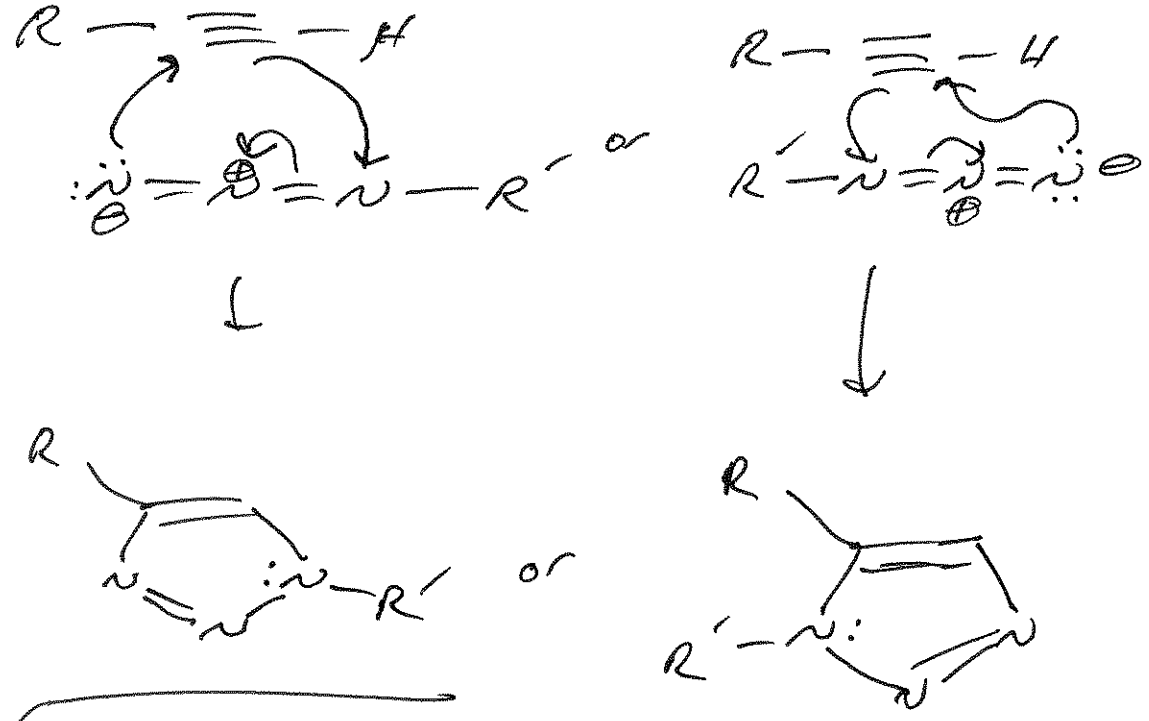
Problem set 3 – Answers

1.



(typical major product (sterics))

Product – fully conjugated
– cyclic
– planar
– 6 π e⁻

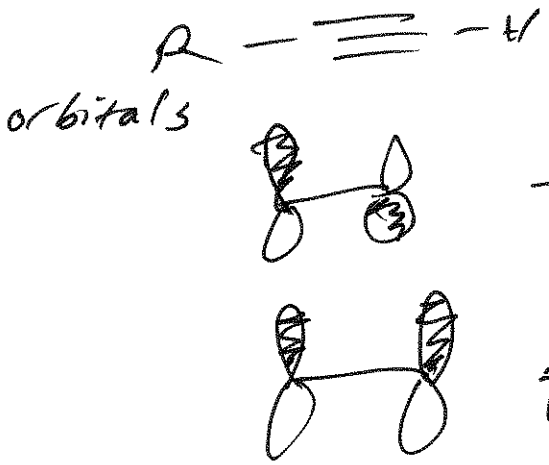
} aromatic!

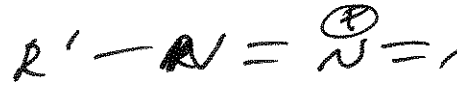
strong driving force for reaction

Also: 2 π bonds → 2 σ bonds

(Alkyne π bond only 55–60 kcal/mol)

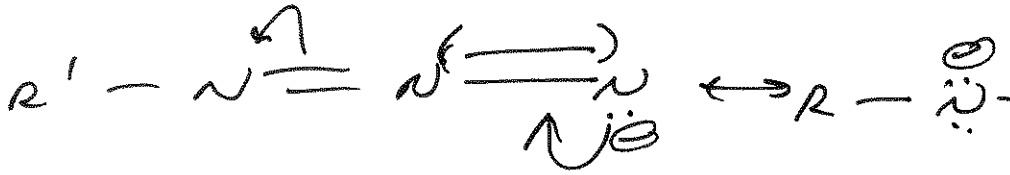
⇒ strong driving force





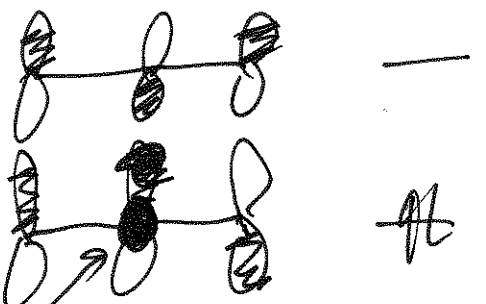
Note that the π bonds here are not conjugated to each other (p orbitals orthogonal)

Conjugated π system



=

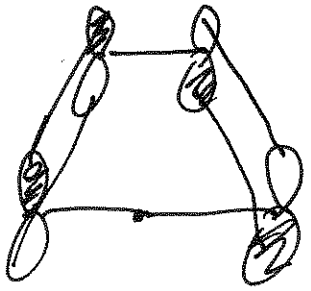
like



So the reaction is driven (as always) by HOMO – LUMO interactions.

LUMO

HOMO

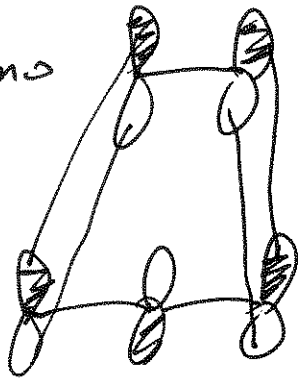


overlap good in both cases in both lobes

Azide nucleophilic character ⇒ HOMO

Could also draw in other mode

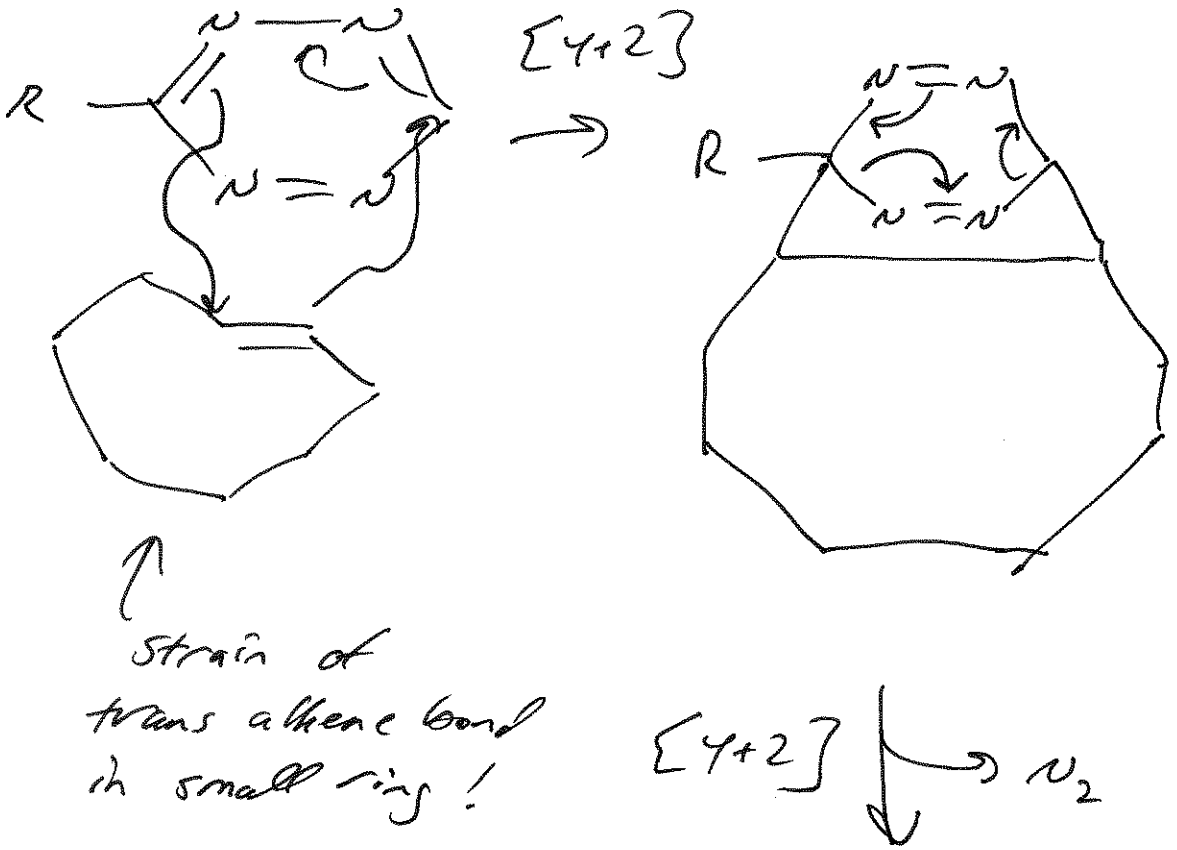
HOMO

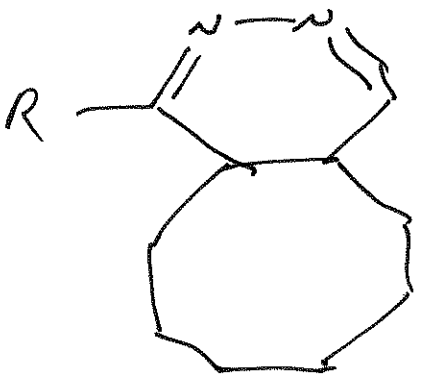


LUMO

Also favorable overlap

2.



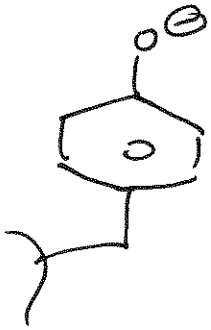


N_2 gas is a spectacular leaving group!

Reaction proceeds rapidly (< 10 minutes) in dilute aqueous conditions.

3. Reaction provides clues about mechanism.

Fast rxn. at pH 10, slower rxn at pH 8, no rxn at pH 3 indicates rxn. via

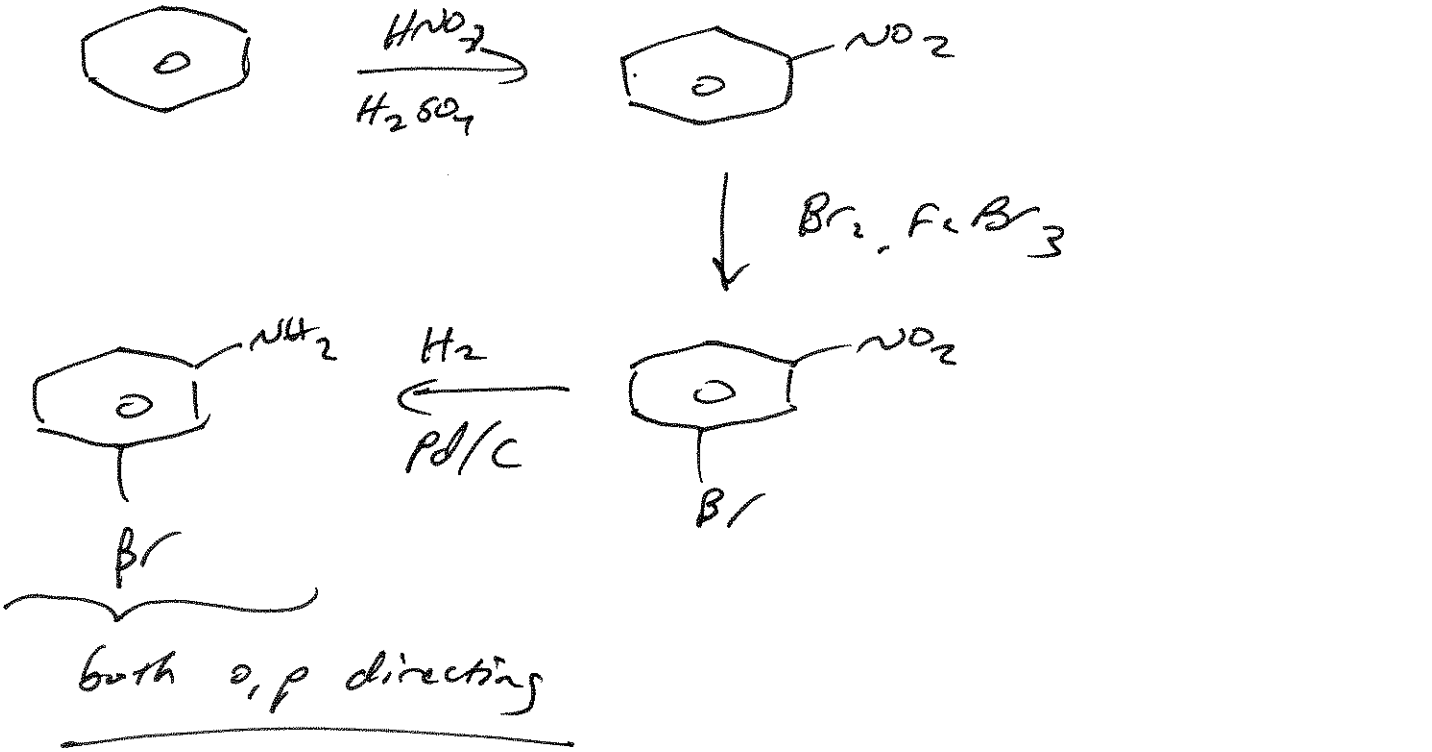


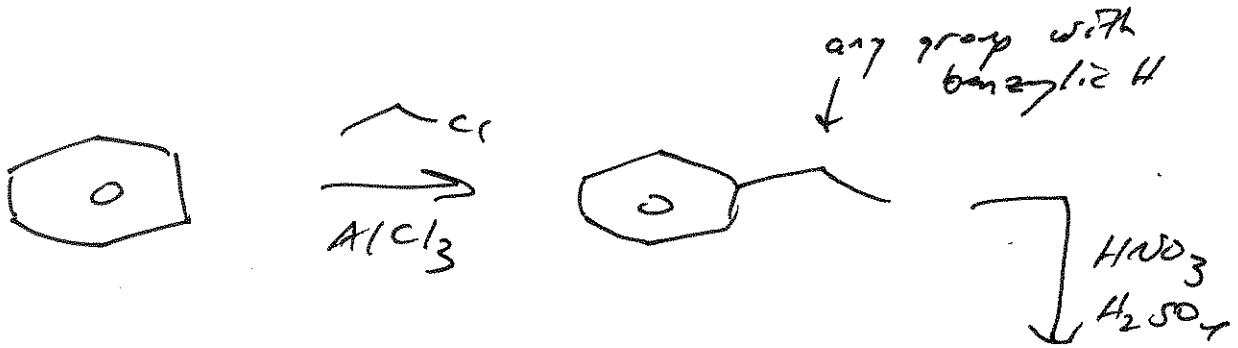
← highly activating for electrophilic aromatic substitution (even better than

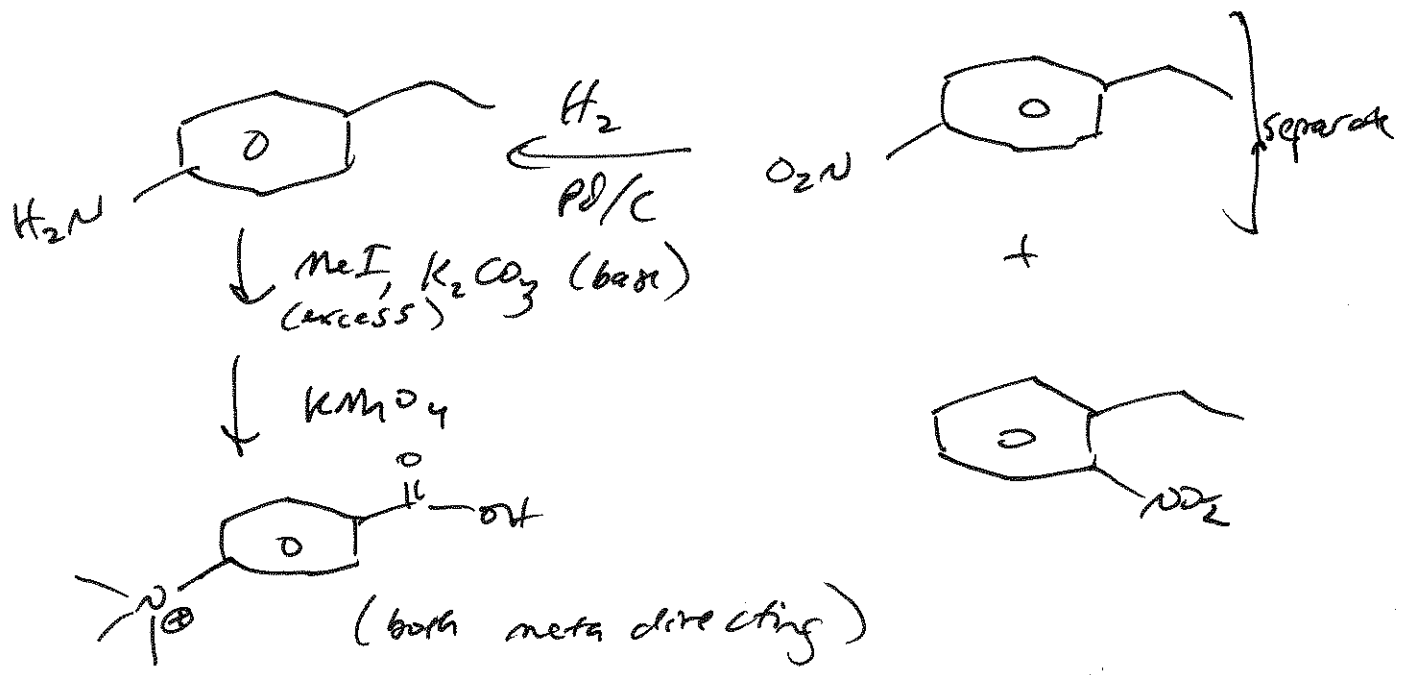
) (far better than

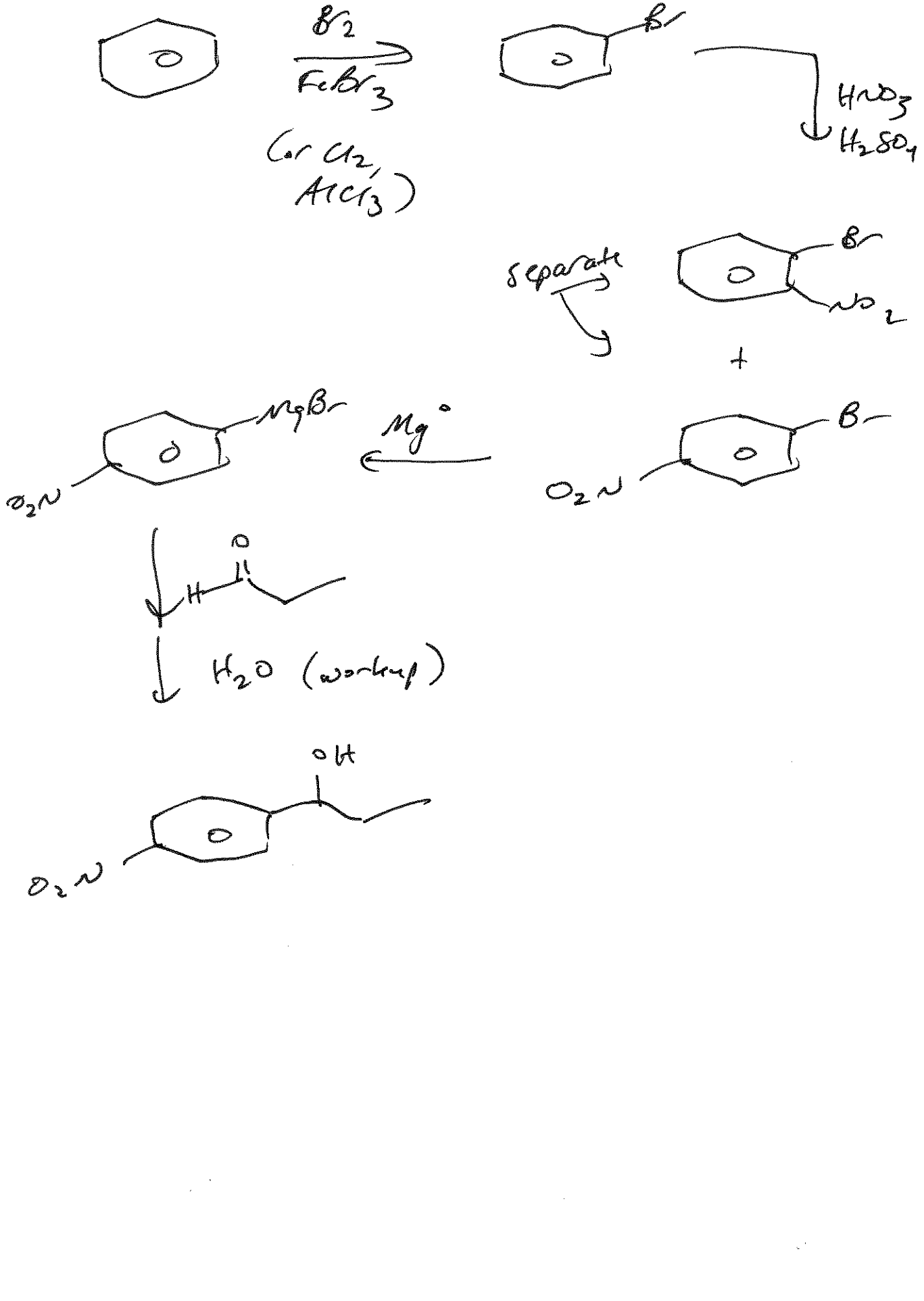
)

4.


HNO3
H2SO4
NO2
Br2, FeBr3
NH2
H2
Pd/C
Br
Br
both o, p directing


Cl
AlCl3
any group with benzylic H
HNO3
H2SO4


H2
Pd/C
H2N
O2N
separate
+
MeI, K2CO3 (base)
(excess)
KMnO4
OH
NO2
(both meta directing)


Br_2
$FeBr_3$
(or Cl_2, $AlCl_3$)
HNO_3
H_2SO_4
separate
Br
NO_2
+
Br
O_2N
MgBr
Mg°
O_2N
O
H
H_2O (workup)
OH
O_2N