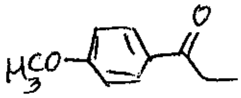
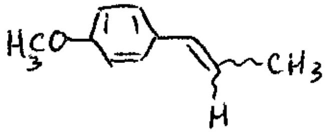
PROBLEM SET #5 SOLUTIONS CHEM 3231

1. A = $H_2N\text{-}NH_2$ / KOH (Wolff-Kishner reduction)
   B = 1. BH_3; 2. H_2O_2, ^{-}OH (Hydroboration / oxidation)
   C = TsCl, pyridine
   D = NaCN, DMF (S_N2)

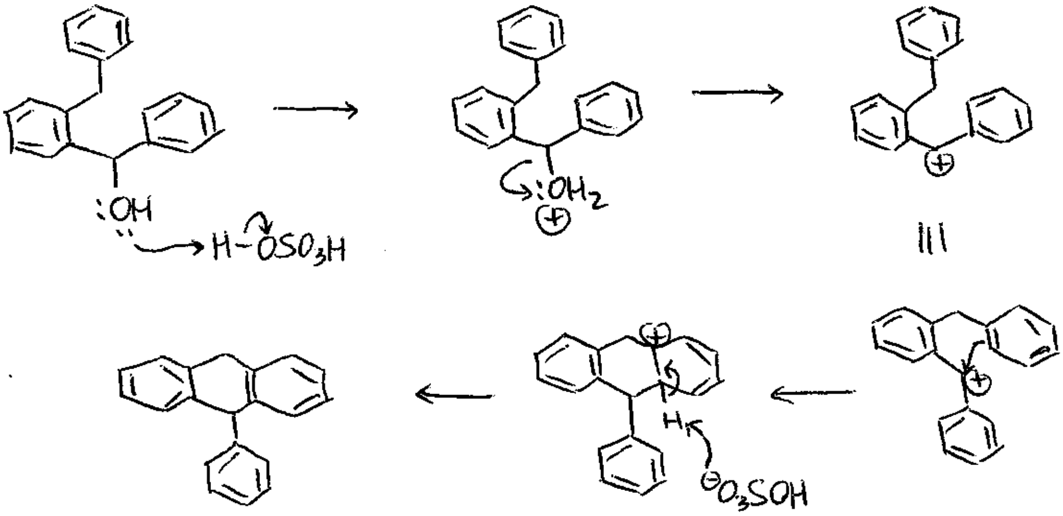
1:



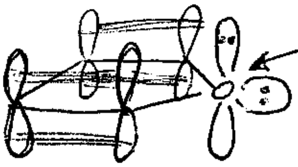
2:



2. This mechanism involves a carbocation rearrangement — good practice in electron-pushing:



3. Draw furan w/ orbitals:

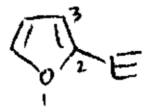


O is sp^2: 2 e^- in sp^2 orbital
2 e^- in p orbital

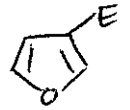
2π e^- from each double bond = 4πe^-
2p e^- from O = 2πe^-
} $\boxed{6}$! AROMATIC

Because the 2 prs. of e^-'s on O reside in different "types" of orbitals, they are technically nonequivalent: one pr. participates in the aromatic system, the other does not.

4. (a) There are two isomers of mono-substituted furan:



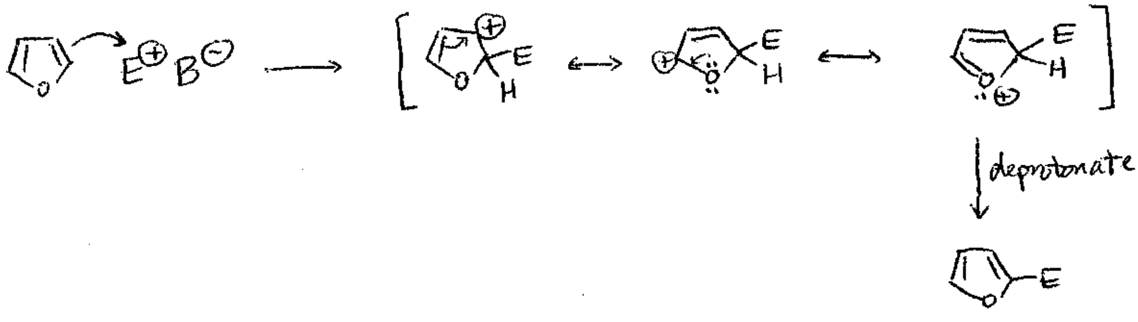
2-substituted furan



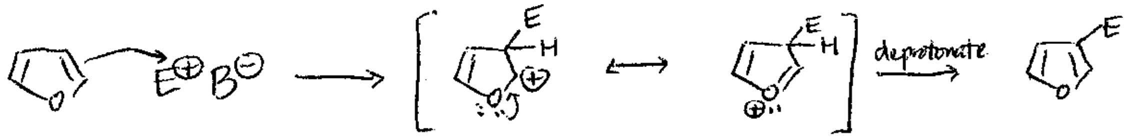
3-substituted furan

(b) To decide which of the above is the major substitution product, we must examine the carbocation IM's here:

2-SUBS'TD:

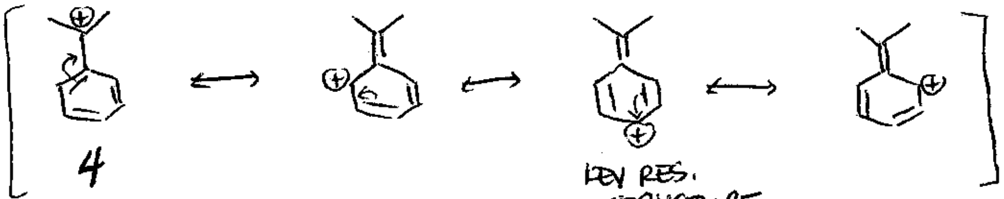


3-SUBS'TD:



There is more resonance stabilization in the cation intermediate for the 2-substituted furan, so this product predominates over its 3-substituted counterpart.

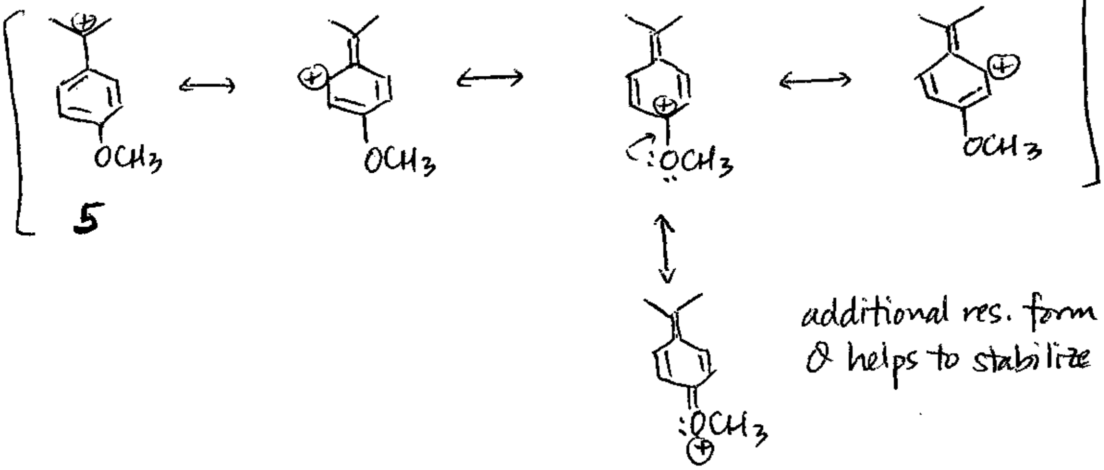
5. Formation of the benzylic cation is key here. Any factors that stabilize the cation will increase the rate of reaction. Of the three substrates, **5** (w/ $-OCH_3$) will react fastest; OCH_3 donates e^-s to stabilize the carbocation. In contrast, the NO_2 group in **6** is a strong e^- withdrawer and will destabilize the carbocation.



4

KEY RES. STRUCTURE ☆

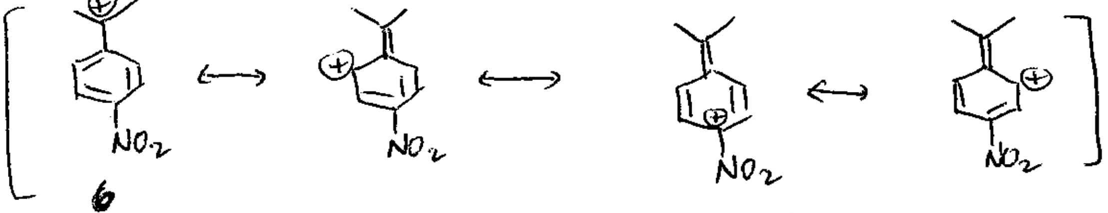
vs



5

additional res. form & helps to stabilize ⊕

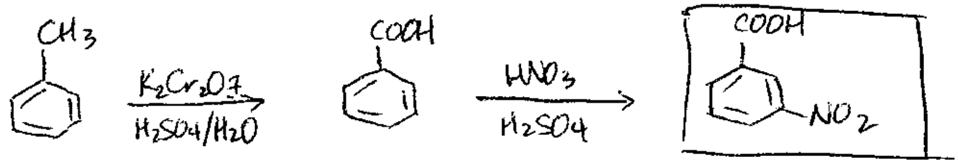
vs



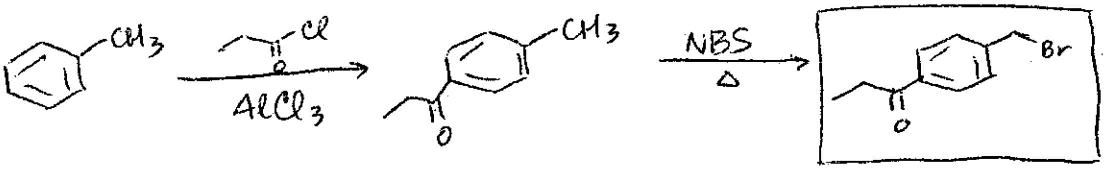
6

this res. form VERY UNSTABLE

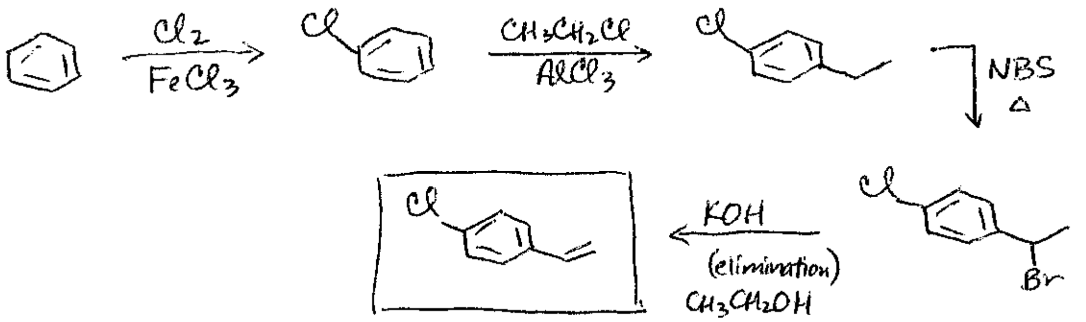
6. (a)


CH3
K2Cr2O7
H2SO4/H2O
COOH
HNO3
H2SO4
COOH
NO2

(b)


CH3
Cl
O
AlCl3
CH3
O
NBS
Δ
Br
O

(c)


Cl2
FeCl3
Cl
CH3CH2Cl
AlCl3
Cl
NBS
Δ
Cl
Br
KOH
(elimination)
CH3CH2OH
Cl