B

CHM 2120
MIDTERM 2
November 9, 2011
8:30-9:50 am

Approximate total number of marks: 70
(subject to slight changes)

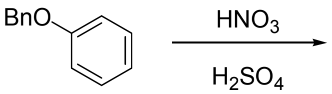
Notes:
- For questions in which mechanisms are not required, part marks might be given for incorrect answers with plausible mechanisms.
- Re-marks requests might not be granted for midterms written in pencil (all questions will be re-graded if a re-mark is requested).
- There is a pK_a table on the last page.

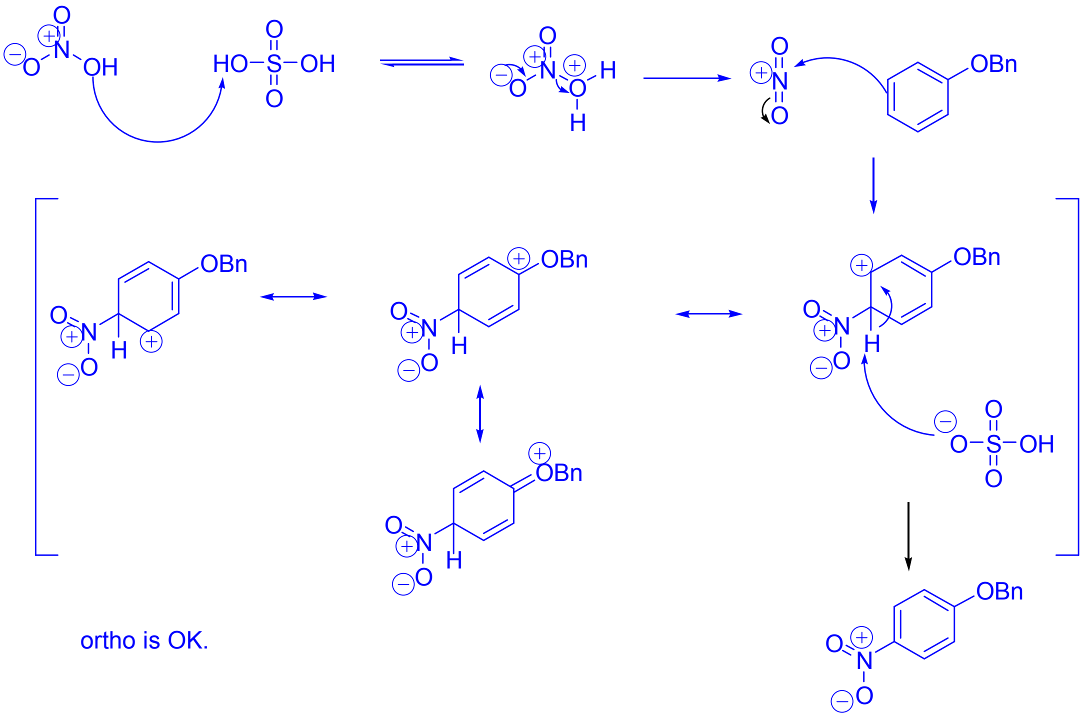
1a	2a	3b	4b	5b	6b	7b	8			1b	2b	3a	4a	5a	6a	7a	0
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Ha	106 106												

B

1.

a. Give the full detailed mechanism for the formation of the major product in the reaction below, including the key resonance structures involved. **(10 pts)**





ortho is OK.

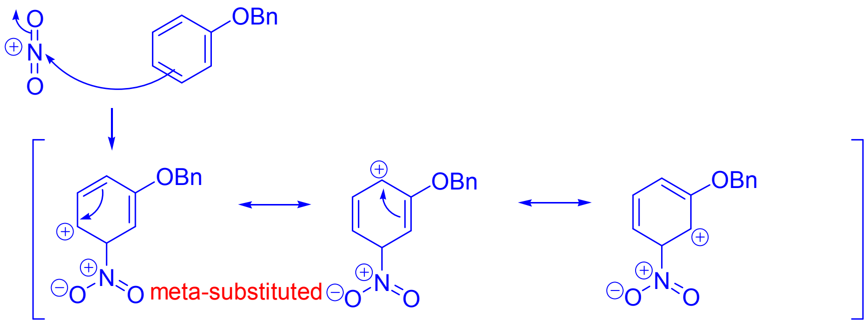
b. Name the reactive electrophile formed in this reaction. **(1 point)**

Nitronium

c. Which aromatic ring is more reactive and why? **(2 points)**

The ring not bonded to the carbonyl group. It is more electronrich than the carbonyl containing ring (which is electron poor) because the oxygen can donate its lone pair of electrons into the aromatic ring. Because it is e- rich it is thus a better nucleophile. Also OK for an answer is that the oxygen can donate a lone pait into the aromatic ring to stabilize the transition state (or intermediate).

d. Clearly explain, *using structures primarily*, the reason for the formation of the favoured regio-isomer ascompared to the unfavoured regio-isomer on the most reactive ring. **(4 points)**



The meta intermediate is stabilized by resonance with the π electrons ONLY, not by resonance with the O's lone pair. Only the ortho and para-substituted intermediates benefit from this additional resonance stabilization with the O's lone pair (see structure above)

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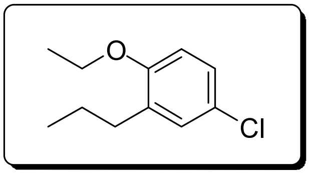
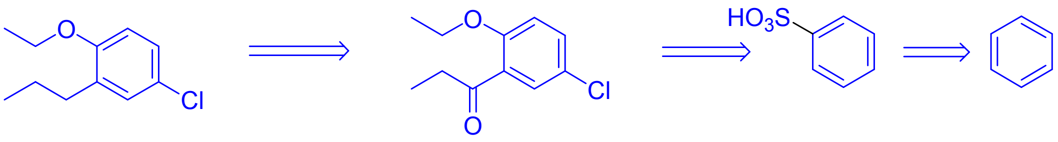
2. Propose a synthesis of the following compound from benzene. Show all required reagents and intermediates. *A retrosynthesis is required.* **(10 points)**

Note: your synthesis must give the compound shown as the major product of the sequence.

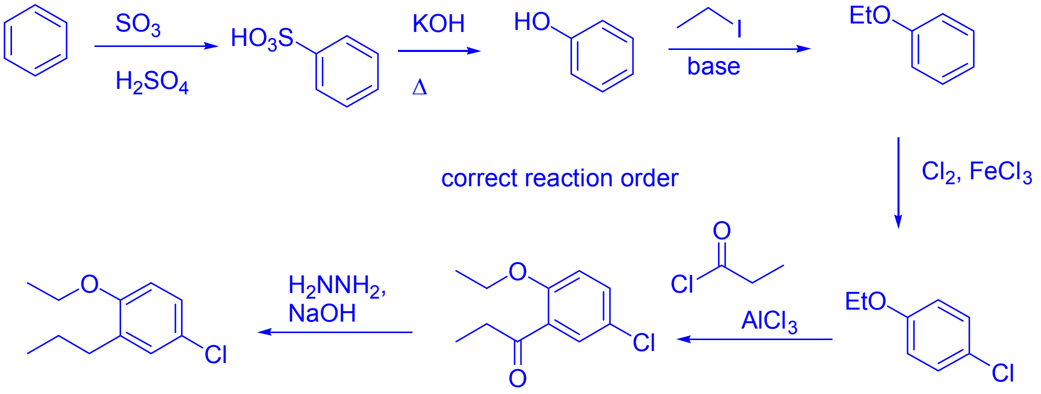




right type of arrow

1 or more reasonable intermediates

go all the way back to benzene

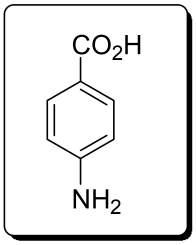


correct reaction order

Max 3 pts out of 7 for a completely different, incorrect route with good chemistry

3. Propose a synthesis of the following compound from the aromatic starting material given. Show all required reagents and intermediates. *A retrosynthesis is required.* **(10 points)**

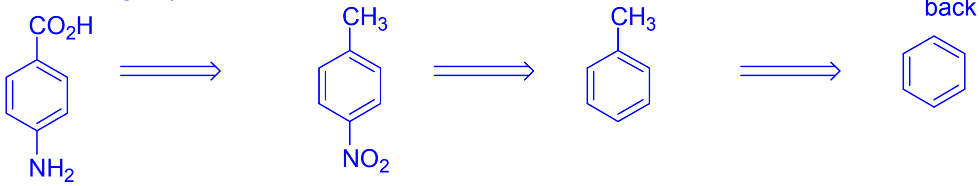
Note: your synthesis must give the compound shown as the major product of the sequence.



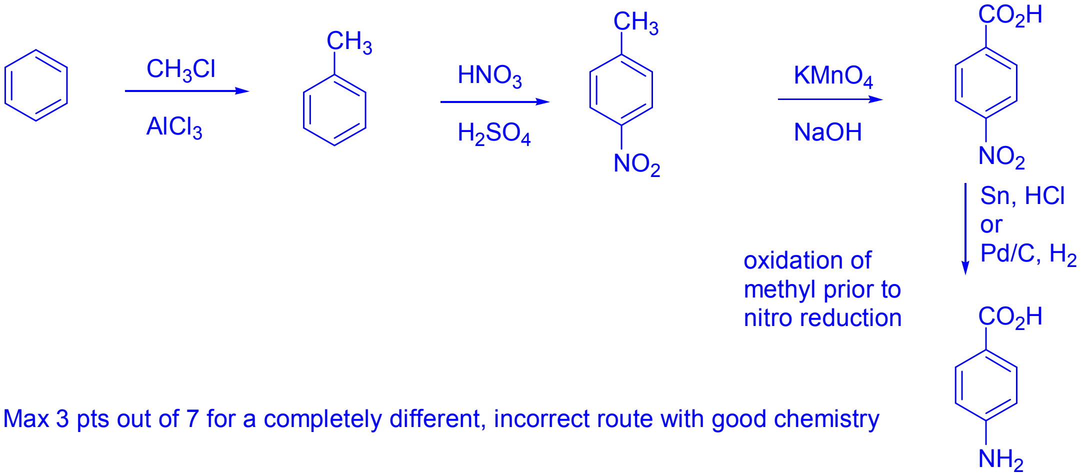
right type of arrow

1 or more reasonable intermediates

go all the way back to benzene



para regiochem (order of EAS)

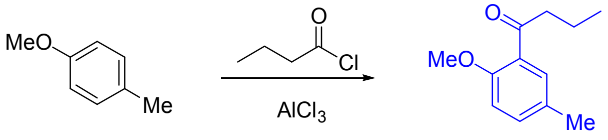


oxidation of methyl prior to nitro reduction

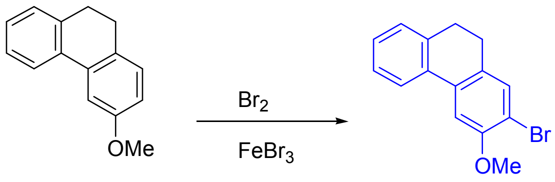
Max 3 pts out of 7 for a completely different, incorrect route with good chemistry

4. Give the major product of each of the following reactions. **(9 points)**

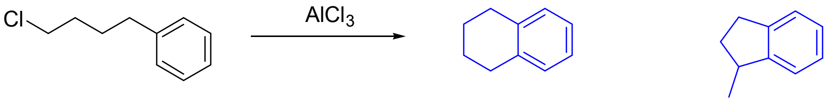
a.



b.



c.



also OK

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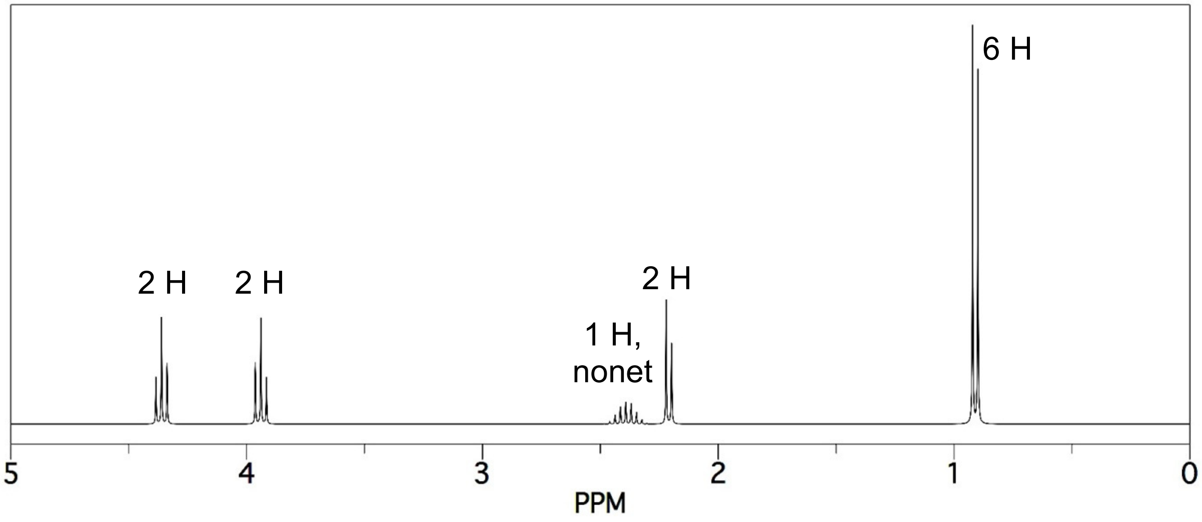
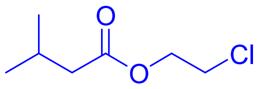
5. Identify the structure of the compound with the moecular formula C7H13ClO2, an intense absorbance in the IR spectrum at 1735 cm^{-1}, and the NMR spectra shown **(2 points)**. Justify your answeer by accounting for all the information provided **(10 points)**.

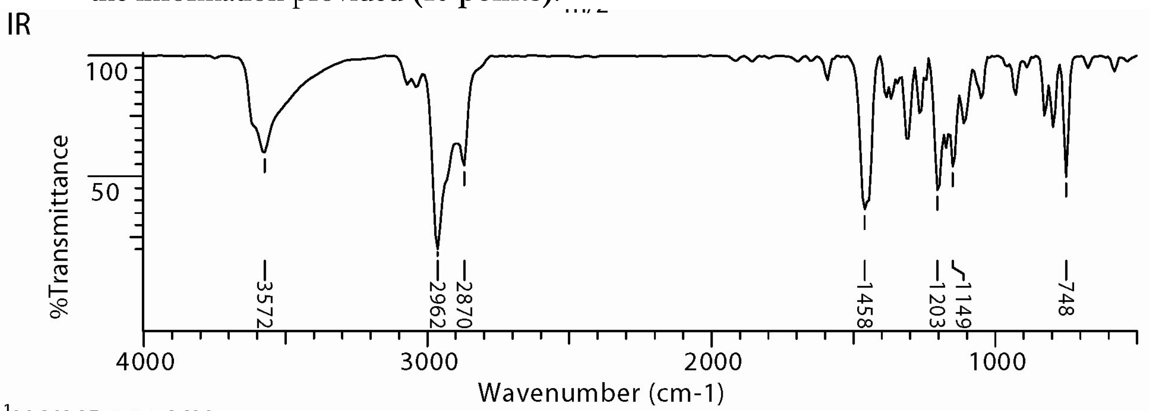


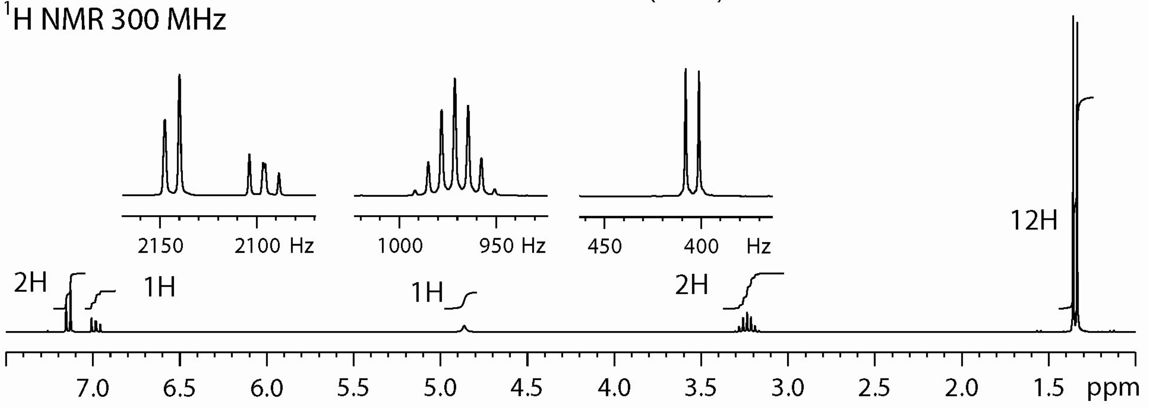
Filling in table with correct data from spectra and proposing a fragment. DU = 1.

Peak	Chemical shift	Integra-tion	Multi-plicity	Comments/Ideas
A	4.4	2H	t	-CH_2- strong EWG, either O or Cl from Mol formula 2 Hs on adjacent atoms
B	3.9	2H	t	-CH_2- strong EWG, either O or Cl from Mol formula 2 Hs on adjacent atoms
C	2.4	1H	nonet	CH no EWG 8 Hs on adjacent atoms Likely bonded to 2 CH_3s and a CH_2
D	2.2	2H	d	-CH_2- mild EWG, likely carbonyl from IR (1735 cm^{-1}) 1 Hs on adjacent atoms
E	0.9	6H	d	2 x -CH_3 no EWG 1 Hs on adjacent atoms



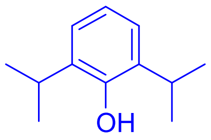
6. Identify the structure of the compound with the moecular formula $C_{12}H_{18}O$ and the IR and NMR spectra shown. **(2 points)** Justify your answeer by accounting for all the information provided **(10 points)**.





Filling in table with correct data from spectra and proposing a fragment. DU = 4.

Peak	Chemical shift	Integration	Multiplicity	Comments/Ideas
A	7.1	2H	d	2 x CH Aromatic hydrogen symmetry to make equivalent 1 H on adjacent carbon
B	7.0	1H	t	CH Aromatic hydrogen 2 H on adjacent carbon
C	4.8	1H	br	-OH Strong EWG likely OH from IR at 3572 cm^{-1} broad signal – in NMR suggest OH also
D	3.2	2H	septet	2 x -CH- mild EWG – possibly bonded to aromatic 6 Hs on adjacent atoms Likely 2 CH_3 attached
E	1.4	12H	d	4 x -CH_3 no EWG 1 Hs on adjacent atoms



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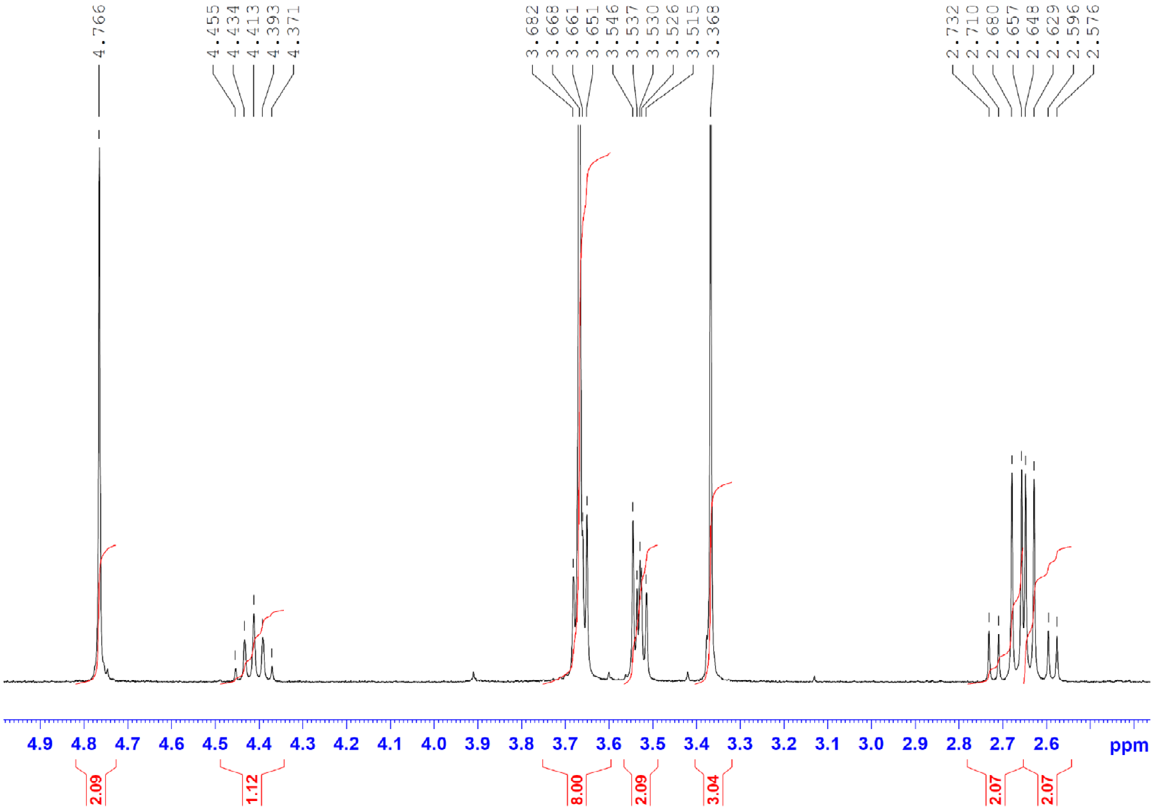
BONUS: **(6 points)**

Provide the structure of the compound with molecular formula $C_{11}H_{20}O_7$ and the NMR spectra below.



Peak	Chemical shift	Integra-tion	Multi-plicity	Comments/Ideas
A	4.8	2H	s	-CH$_2$- Very strong EWG or 2 strong EWGs no Hs on adjacent carbon
B	3.4	1H	p	CH Strong EWG 4 Hs on adjacent atoms Likely bonded to oxygen
C	3.7	6H	s	2 x -CH$_3$ Strong EWG no Hs on adjacent atoms Likely bonded to oxygen / symmetry element
D	3.6	2H	m	-CH$_2$- strong EWG Hs on adjacent atoms Likely bonded to O
E	3.5	2H	m	-CH$_2$- strong EWG Hs on adjacent atoms Likely bonded to O

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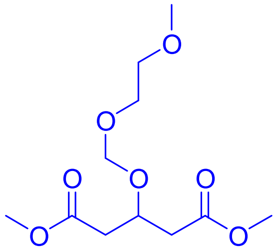
F	3.4	3H	s	-CH_3 Strong EWG no Hs on adjacent atoms Likely bonded to oxygen
G	2.7	4H	m	2 x –CH_2 mild EWG symmetry element



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pK_a table

Acid	pK_a
HCl	-8
ROH_2^+	-2
H_3O^+	-1.75
RCOOH	5
R_3NH^+	10-11
H_2O	15.75
ROH	16-18
H_2	36
RNH_2	35-40
RCH_3	55