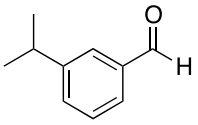
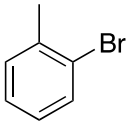
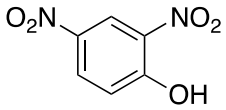
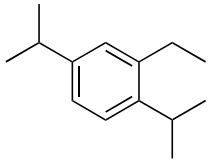
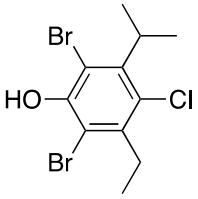
Question 1 – Provide a systematic name for each of the following compounds.

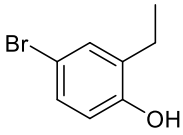
a. 

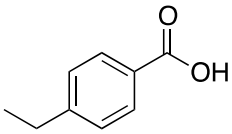
b. 

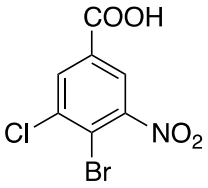
c. 

d. 

e. 

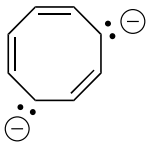
f. 

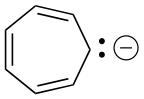
g. 

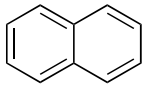
h. 

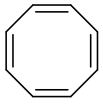
Question 2 – Draw structures for all constitutional isomers with molecular formula C_8H_{10} that contain an aromatic ring.

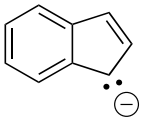
Question 3 – Indicate whether each of the following compounds is aromatic, non-aromatic or anti-aromatic.

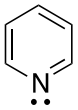
a. 

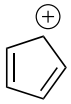
b. 

c. 

d. 

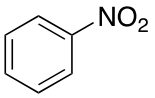
e. 

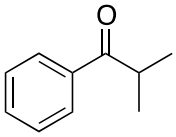
f. 

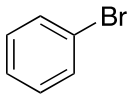
g. 

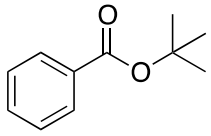
h. 

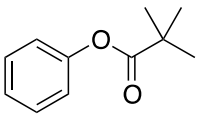
Question 4 – For each of the following compounds, determine whether the ring is activated or deactivated, then determine the strength of activation/deactivation, and finally, determine the expecting directing effects.

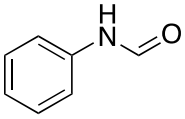
a. 

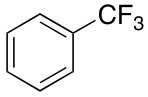
b. 

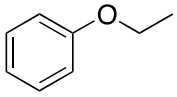
c. 

d. 

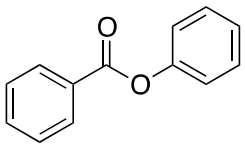
e. 

f. 

g. 

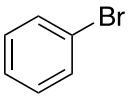
h. 

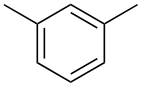
Question 5 – The following compound has two aromatic rings. Identify which ring is expected to be more reactive toward an electrophilic aromatic substitution.

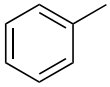


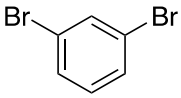
Question 6 – Rank the following compounds in order of increasing reactivity toward electrophilic aromatic substitution:

A 

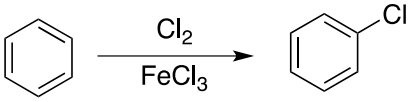
B 

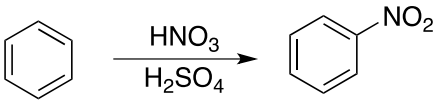
C 

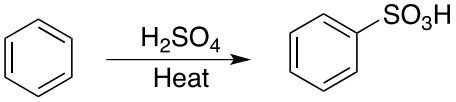
D 

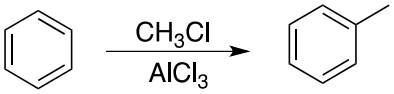
E 

Question 7 – Draw a mechanism for each of the following transformations:

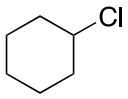
a. 

b. 

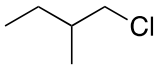
c. 

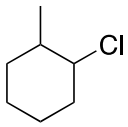
d. 

Question 8 – Predict the expected product(s) when benzene is treated with each of the following alkyl halides in the presence of $AlCl_3$. In each case, assume conditions have been controlled to favour monoalkylation.

a. 

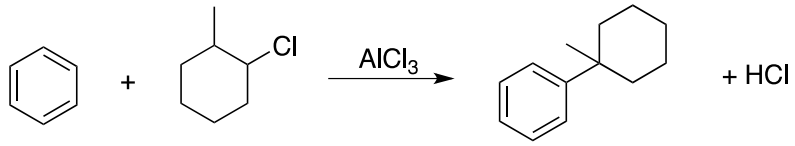
b. 

c. 

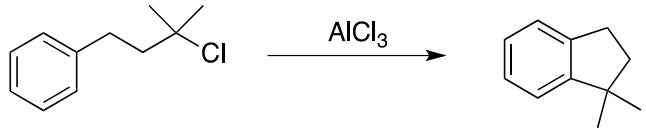
d. 

Question 9 – Provide plausible mechanisms for the following reactions.

a.

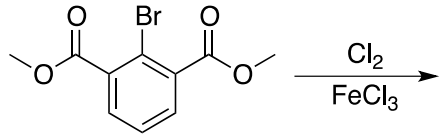


b.

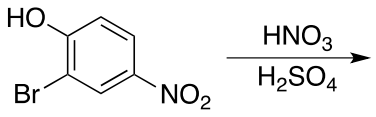


Question 10 – Predict the major product for each of the following reactions:

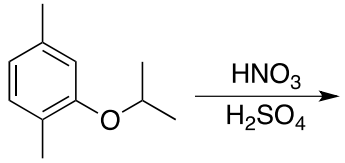
a.



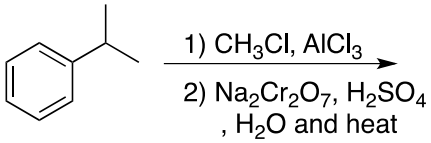
b.



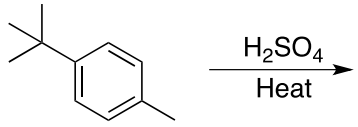
c.



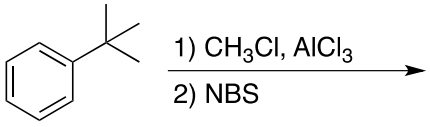
d.



e.

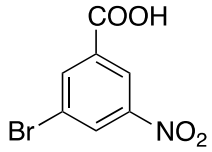


f.

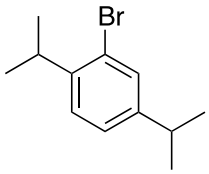


Question 11 – Starting with benzene and using any other necessary reagents of your choice, design a synthesis for each of the following compounds. The synthesis will require more than a single step. In some cases, there may be more than one plausible answer.

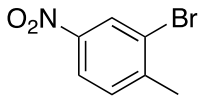
a.



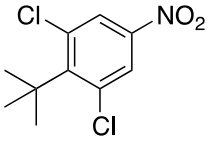
b.



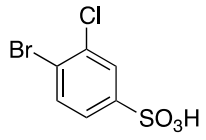
c.



d.



e.



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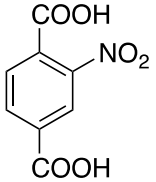
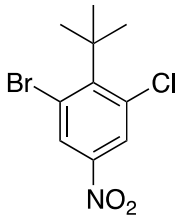
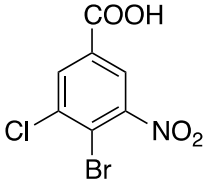


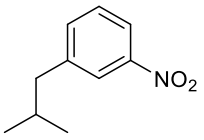
g.



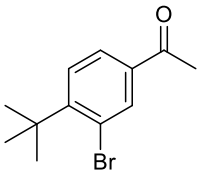
h.



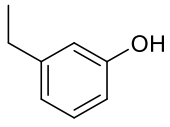
i.



j.



k.



Solutions

Question 1

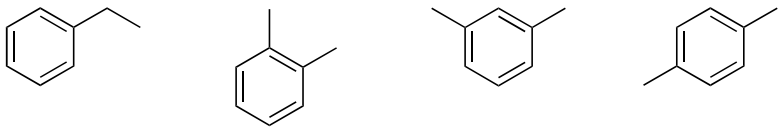
Using common names

a. 3-isopropylbenzaldehyde (or *meta*-isopropylbenzaldehyde)
b. 2-bromotoluene (or *ortho*-bromotoluene)
c. 2,4-dinitrophenol
d. 2-ethyl-1,4-diisopropylbenzene
e. 2,6-dibromo-4-chloro-3-ethyl-5-isopropylphenol
f. 4-bromo-2-ethylphenol
g. 4-ethylbenzoic acid (or *para*-ethylbenzoic acid)
h. 4-bromo-3-chloro-5-nitrobenzoic acid

Using branched names

a. 3-(1-methylethyl)benzaldehyde (or *meta*-(1-methylethyl)benzaldehyde)
d. 2-ethyl-1,4-di(1-methylethyl)benzene
e. 2,6-dibromo-4-chloro-3-ethyl-5-(1-methylethyl)phenol

Question 2



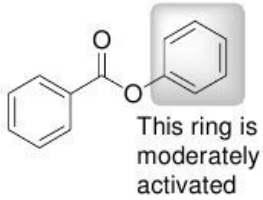
Question 3

a. Aromatic
b. *anti*-aromatic
c. Aromatic
d. Non-aromatic
e. Aromatic
f. Aromatic
g. *anti*-aromatic
h. Non-aromatic

Question 4

a. i) ring is deactivated. Ii) strongly deactivating and iii) meta-directing
b. i) ring is deactivated. Ii) moderately deactivating and iii) meta-directing
c. i) ring is deactivated. Ii) weakly deactivating and iii) ortho, para-directing
d. i) ring is deactivated. Ii) moderately deactivating and iii) meta-directing
e. i) ring is activated. Ii) moderately activating and iii) ortho, para -directing
f. i) ring is activated. Ii) moderately activating and iii) ortho, para -directing
g. i) ring is deactivated. Ii) strongly deactivating and iii) meta-directing
h. i) ring is activated. Ii) moderately activating and iii) ortho, para -directing

Question 5



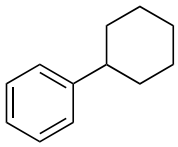
Question 6

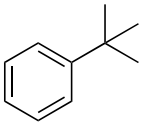
(least reactive toward EAS) **E < B < A < D < C** (most reactive toward EAS)

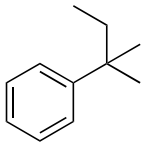
Question 7

Refer to textbook/course notes for the solutions.

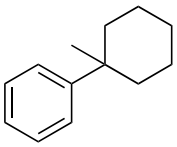
Question 8

a. 

b. 

c. 

involved rearrangement of alkyl carbocation

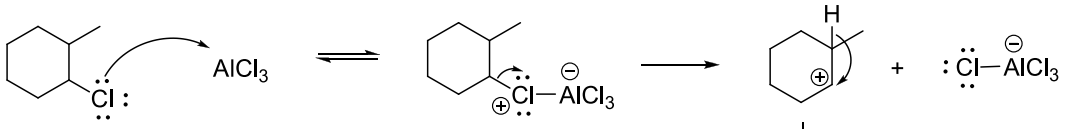
d. 

involved rearrangement of alkyl carbocation

Question 9

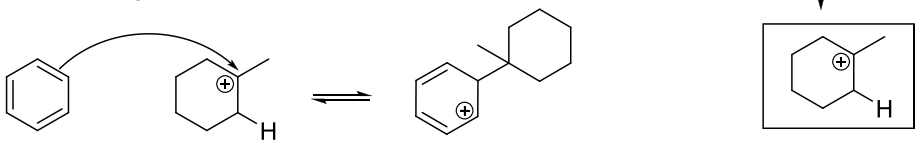
a.

Step 1 - alkyl halide activation

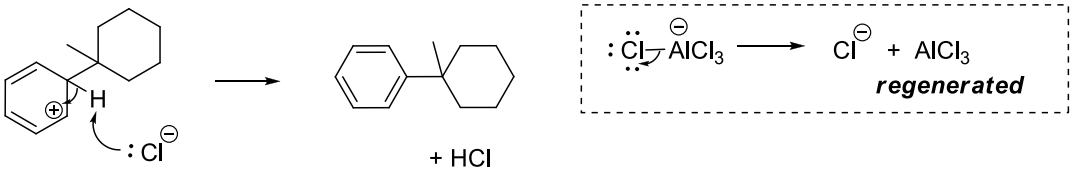


1,2-hydride shift

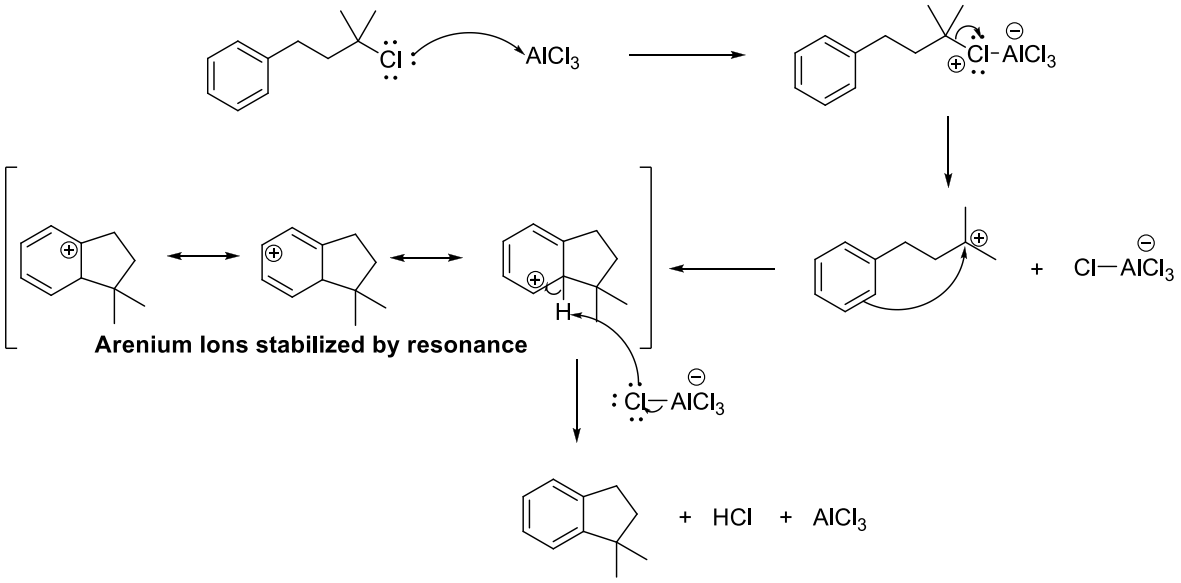
Step 2 - Attack by pi-electrons of benzene



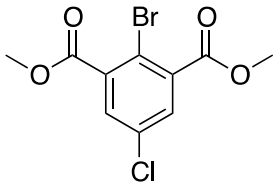
Step 2 - Elimination to restore aromaticity

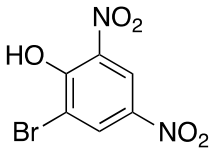


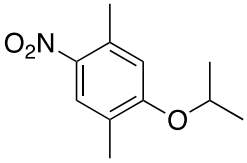
b.

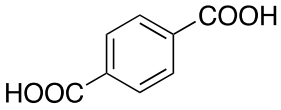


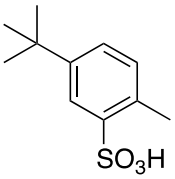
Question 10

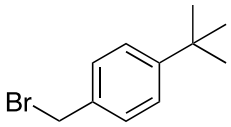
a. 

b. 

c. 

d. 

e. 

f. 

Question 11 (Note: Normally you would be expected to draw out each intermediate during a synthesis**)**

a. 1. $AlCl_3$ and CH_3Cl
   2. $Na_2Cr_2O_7$, H_2SO_4, H_2O and heat
   3. HNO_3 and H_2SO_4
   4. Br_2 and $FeBr_3$

b. 1. $AlCl_3$ and $(CH_3)_2CHCl$
   2. $AlCl_3$ and $(CH_3)_2CHCl$
   3. Br_2 and $FeBr_3$

c. 1. $AlCl_3$ and CH_3Cl
   2. HNO_3 and H_2SO_4
   3. Br_2 and $FeBr_3$

d. 1. $AlCl_3$ and $(CH_3)_3CCl$
   2. HNO_3 and H_2SO_4
   3. excess Cl_2 and $FeCl_3$

e. 1. Br_2 and $FeBr_3$
   2. SO_3, H_2SO_4
   3. Cl_2 and $FeCl_3$

f. 1. $AlCl_3$ and $(CH_3)_2CHCl$
   2. $AlCl_3$ and $(CH_3)_2CHCl$
   3. HNO_3 and H_2SO_4
   4. $Na_2Cr_2O_7$, H_2SO_4, H_2O and heat

g. 1. $AlCl_3$ and $(CH_3)_3CCl$
   2. HNO_3 and H_2SO_4
   3. Br_2 and $FeBr_3$
   4. Cl_2 and $FeCl_3$

h. 1. $AlCl_3$ and $(CH_3)_2CHCl$
   2. Br_2 and $FeBr_3$
   3. $Na_2Cr_2O_7$, H_2SO_4 and H_2O
   4. HNO_3 and H_2SO_4
   5. Cl_2 and $FeCl_3$

i. 1. $(CH_3)_2CHC(O)Cl$, $AlCl_3$
   2. H_2O
   3. HNO_3, H_2SO_4
   4. NH_2NH_2, NaOEt, heat

j. 1. $(CH_3)_3CCl$, $AlCl_3$
   2. $CH_3C(O)Cl$, $AlCl_3$
   3. H_2O
   4. Br_2, $FeBr_3$

k. 1. $CH_3C(O)Cl$, $AlCl_3$
   2. H_2O
   3. HNO_3, H_2SO_4
   4. H_2, Pd/C
   5. $NaNO_2$, HCl

6. Cu_2O, Cu^{2+}, H_2O