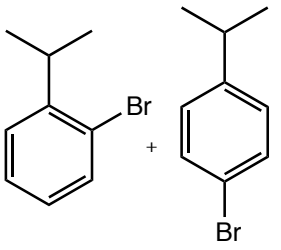
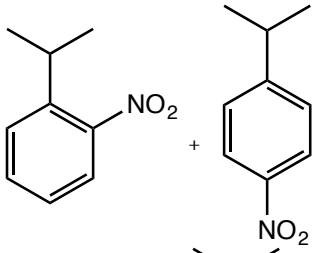
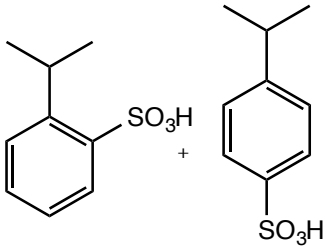
Chapter 19 Practice Problems
Solutions

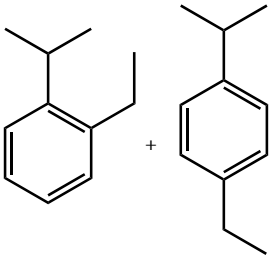
1

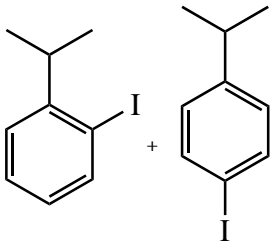
A. 1-isopropyl-2-methylbenzene *or* ortho-isopropylmethylbenzene *or* 2-isopropyltoluene
B. 1-bromo-4-chloro-2,5-dimethylbenzene
C. 4-bromo-2-nitro-1-n-propylbenzene
D. 4-ethyl-3-methylphenol
E. 3-bromo-5-methylaniline
F. 3,4-dimethylbenzoic acid
G. 2,5-difluorobenzaldehyde

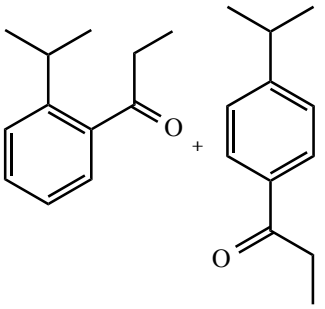
AI 

AII 

AIII 

AIV 

AV 

AVI 

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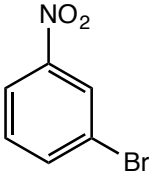
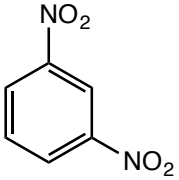
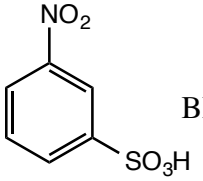
BI 

BII 

BIII 

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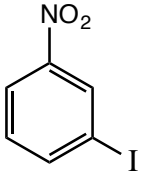
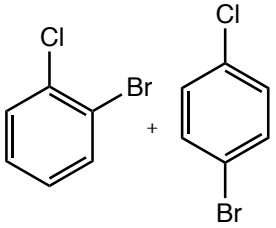
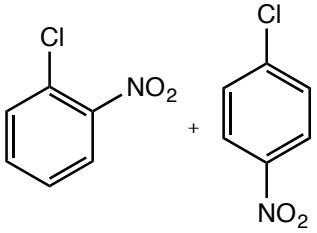
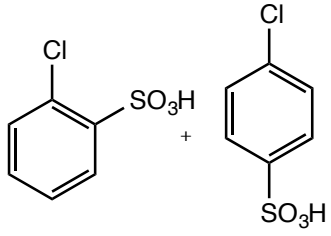
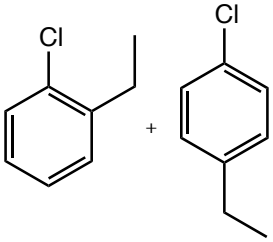
BV 

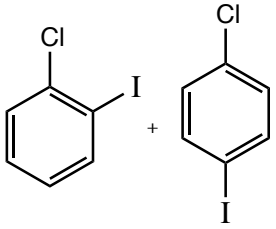
BVI NR

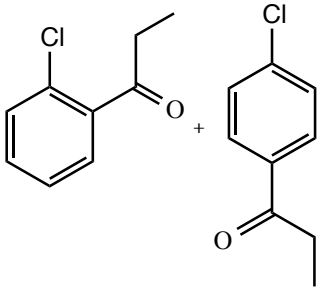
CI 

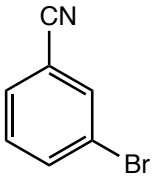
CII 

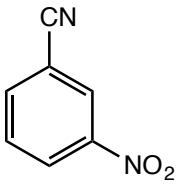
CIII 

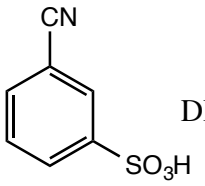
CIV 

CV 

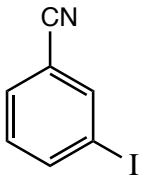
CVI 

DI 

DII 

DIII 

DIV NR

DV 

DVI NR

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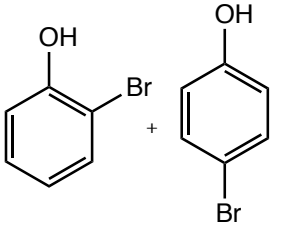
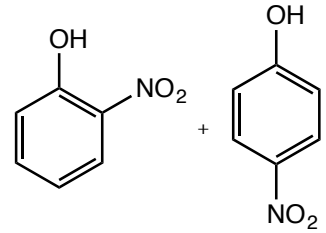
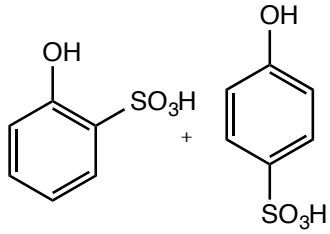
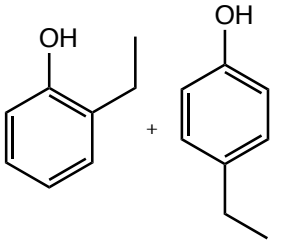
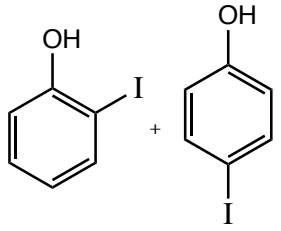
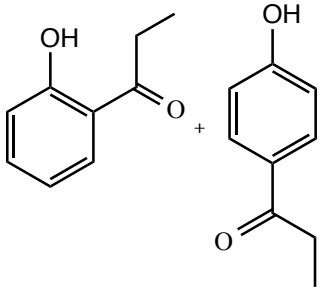
EI 

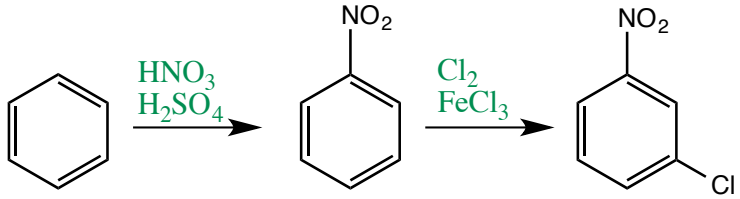
EII 

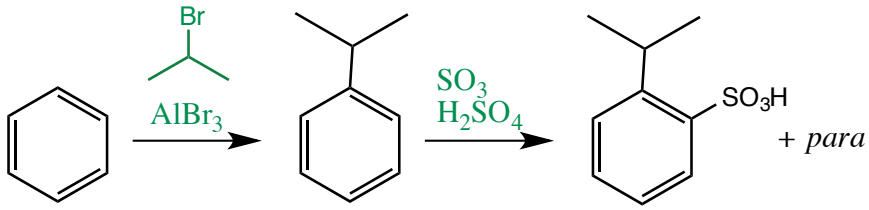
EIII 

EIV 

EV 

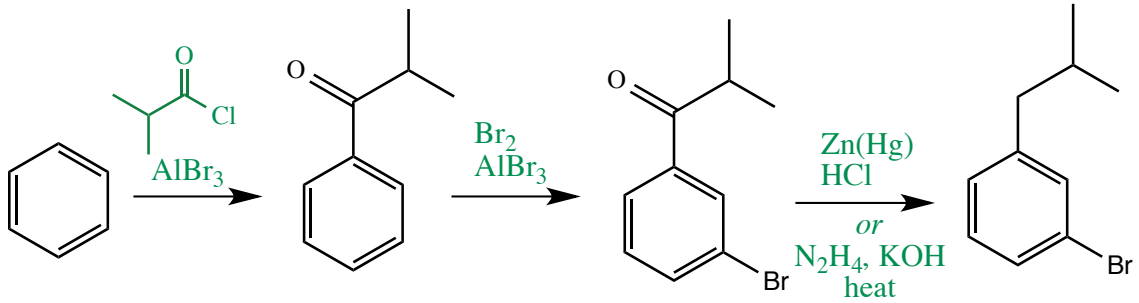
EVI 

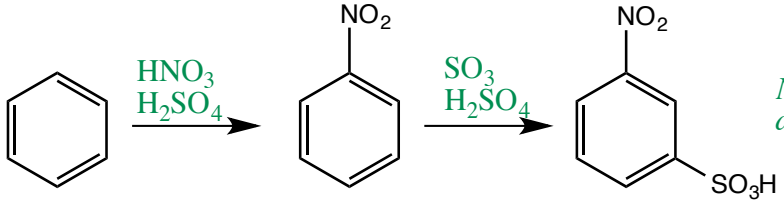
A 

B 

+ *para*

3

C 

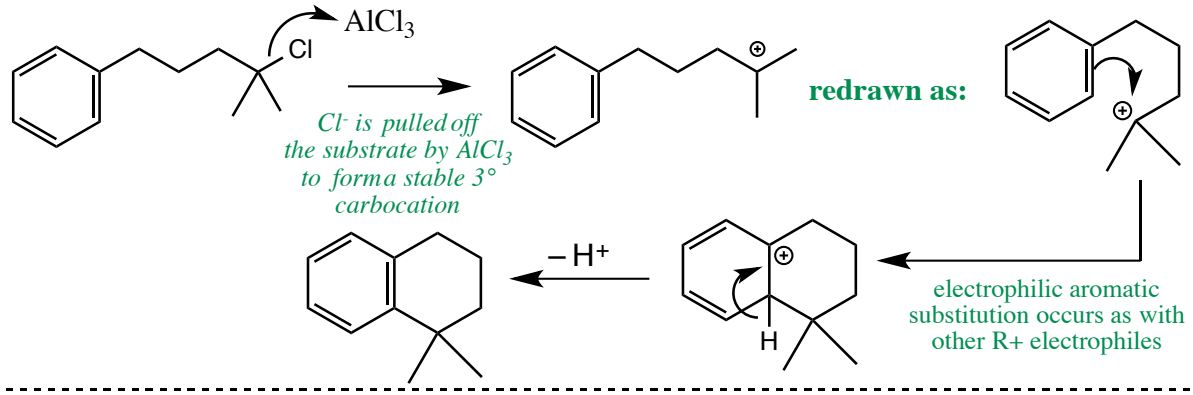
D 

NOTE: reverse order works as well

4

• The nitro group is a strong electron-withdrawing group and meta-director so it is not surprising that compound **1** results in 95% bromination at the meta site
• Compound **2** differs from compound **1** in that the nitro group is not attached directly to the benzene ring, but instead to a CH_2 group that is ***then*** attached to the benzene ring.
• In that situation, the nitro group is not able to exert as strong an electron-withdrawing effect and is therefore a weaker meta-director, resulting in less bromination at the meta site.

5



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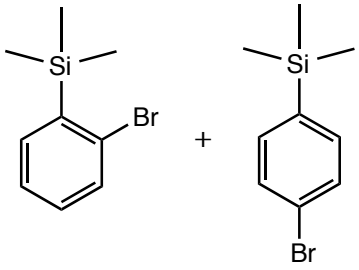
i • if the electrophilic aromatic substitution reaction is occuring faster than that of benzene, the attached group must be an activating group which means it is acting as an electron-donating group

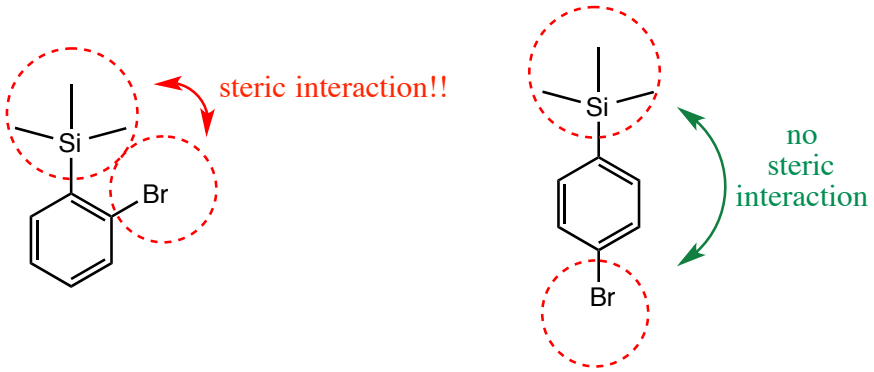
ii • we know that the *tert*-butyl group is an electron-donating group (it is an "R" group)
• because reaction with *tert*-butylbenzene is faster than that of trimethylsilylbenzene, the *tert*-butyl group must be a stronger activating group which means it is a stronger electron-donating group

iii • since we have established that the trimethylsilyl group is electron donating, it is likely an ortho, para-director, therefore, the products would be:

6



iv • the trimethylsilyl group is a large group. Substitution at the ortho position with the large Br atom would create a lot of steric strain that is NOT present in the para-substituted compound
• therefore, more bromination occurs at the less sterically strained para-position.



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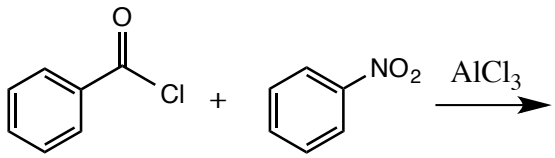
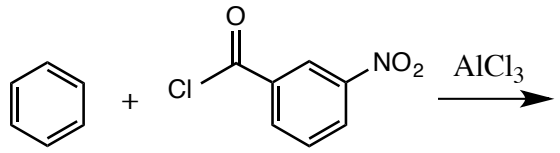


- both reactions will theoretically lead to the same product
- however, Fridel-Crafts reactions are not possible on a benzene ring substituted with an electron-withdrawing group stronger than a halide
- therefore, only the bottom reaction is practically feasible

or



8

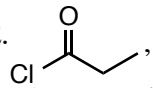
A 1. HNO_3, H_2SO_4
2. Cl_2, $FeCl_3$

B 1. Br_2, $AlBr_3$
2. SO_3, H_2SO_4
(some ortho also formed)

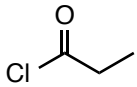
C 1. CH_3Cl, $AlCl_3$
2. $KMnO_4$ or Jones
3. Br_2, $FeBr_3$

D 1. CH_3Br, $AlBr_3$
2. SO_3, H_2SO_4 *(some ortho also formed)*
3. Br_2, $AlBr_3$
4. $K_2Cr_2O_7$, H_2SO_4, H_2O

E 1. HNO_3, H_2SO_4
2. I_2, $CuCl_2$
3. Sn°, HCl

F 1. CH_3Cl, $AlCl_3$
2. 

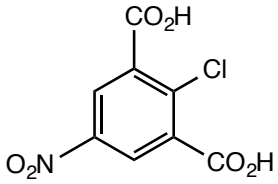
(some ortho also formed)

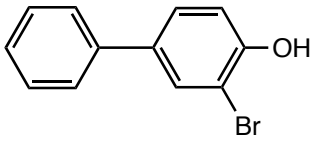
G 1. 

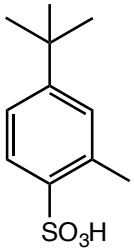
2. N_2H_4, KOH, Δ
3. Cl_2, $AlCl_3$
(some para also formed)

H 1. HNO_3, H_2SO_4
2. I_2, $CuCl_2$
3. Fe°, HCl
4. SO_3, H_2SO_4

9







10

parasite **metabolic**

http:// = url for a website