

PHA284

Organic Chemistry II

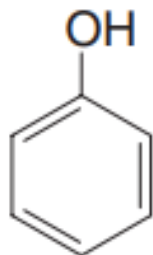
Ankara University
Faculty of Pharmacy
Department of Pharmaceutical Chemistry



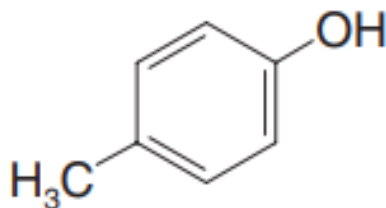
Phenols

Phenols

Compounds that have a hydroxyl group directly attached to a benzene ring are called **phenols**.



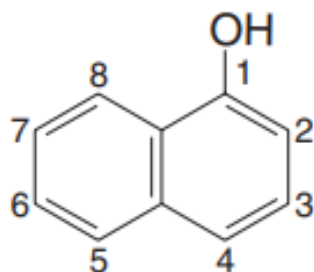
Phenol



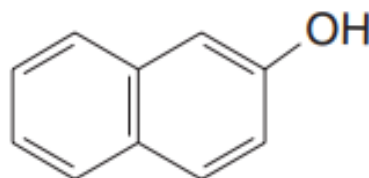
**4-Methylphenol
(a phenol)**

Phenols

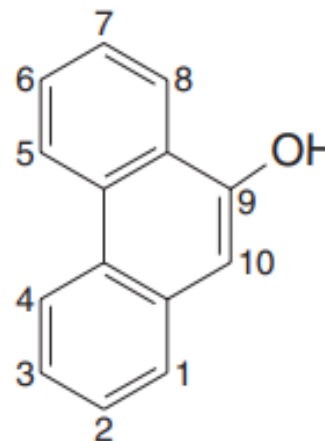
Compounds that have a hydroxyl group attached to a polycyclic benzenoid ring are chemically similar to phenols, but they are called naphthols and phenanthrols. For example:



1-Naphthol
(α -naphthol)



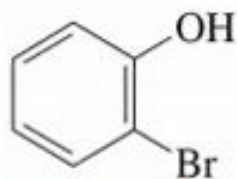
2-Naphthol
(β -naphthol)



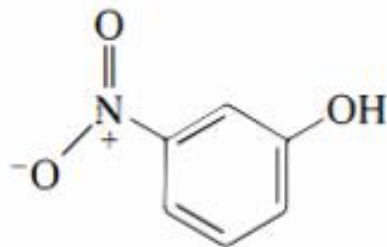
9-Phenanthrol

Nomenclature

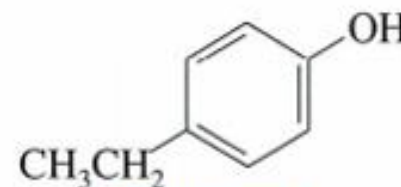
IUPAC name:
common name:



2-bromophenol
ortho-bromophenol



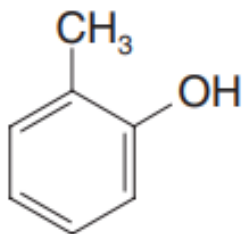
3-nitrophenol
meta-nitrophenol



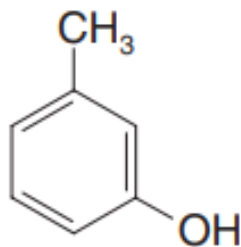
4-ethylphenol
para-ethylphenol

Nomenclature

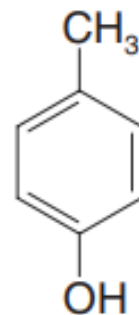
- The methylphenols are commonly called cresols:



2-Methylphenol
(*o*-cresol)



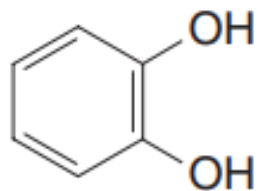
3-Methylphenol
(*m*-cresol)



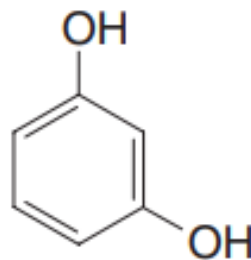
4-Methylphenol
(*p*-cresol)

Nomenclature

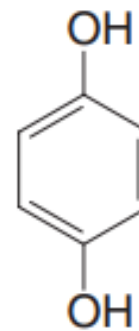
- The benzenediols also have common names:



1,2-Benzenediol
(catechol)

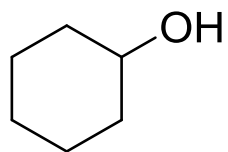


1,3-Benzenediol
(resorcinol)

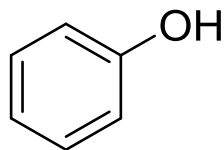


1,4-Benzenediol
(hydroquinone)

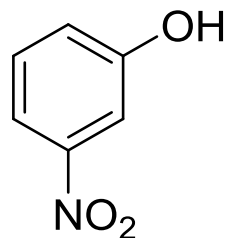
Strength of Phenols as Acids



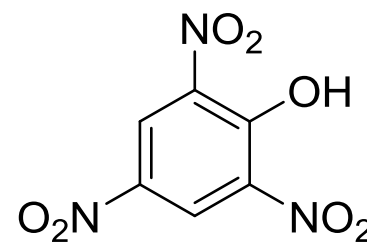
cyclohexanol
 $pK_a = 18$



phenol
 $pK_a = 9.89$

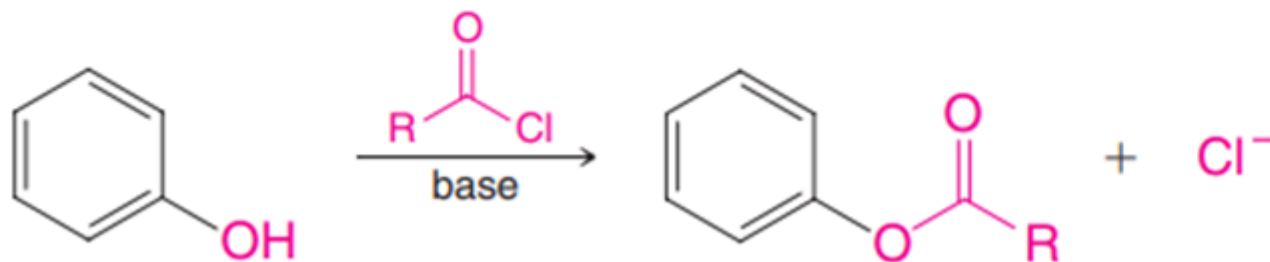
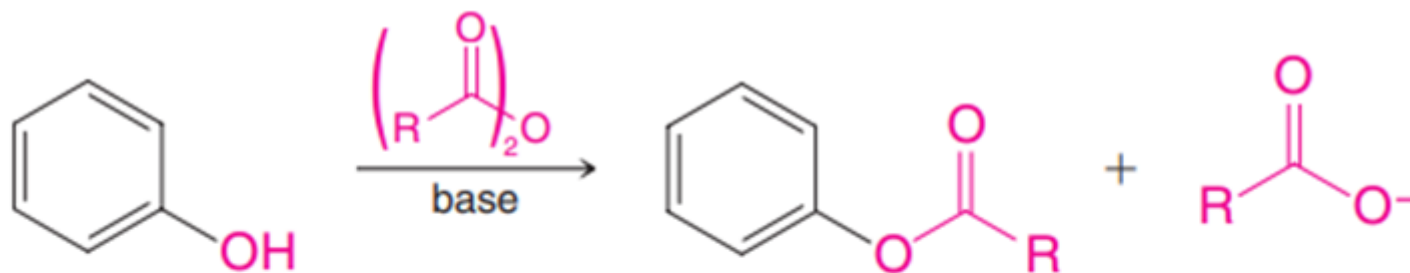


3-nitrophenol
 $pK_a = 7.15$

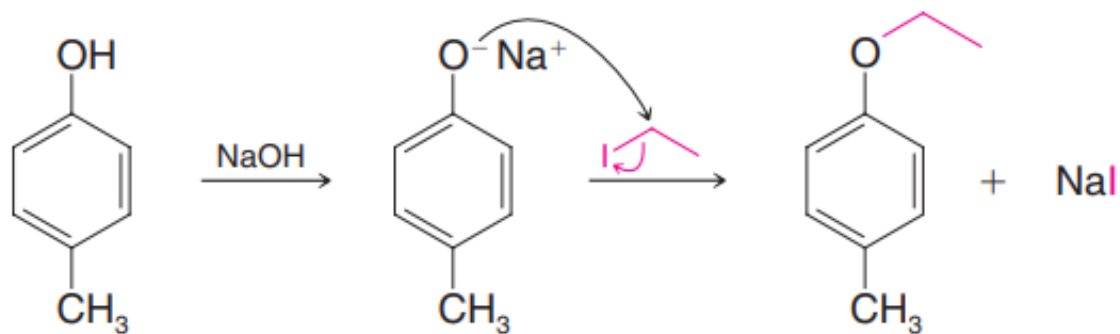
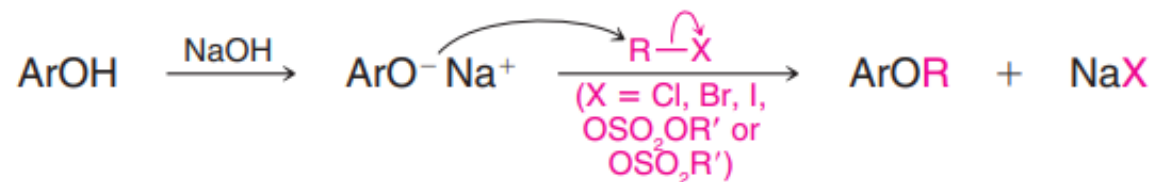


2,4,6-trinitrophenol
picric acid
 $pK_a = 0.38$

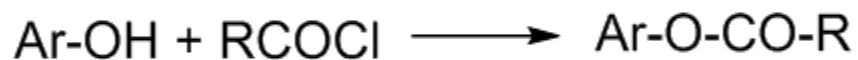
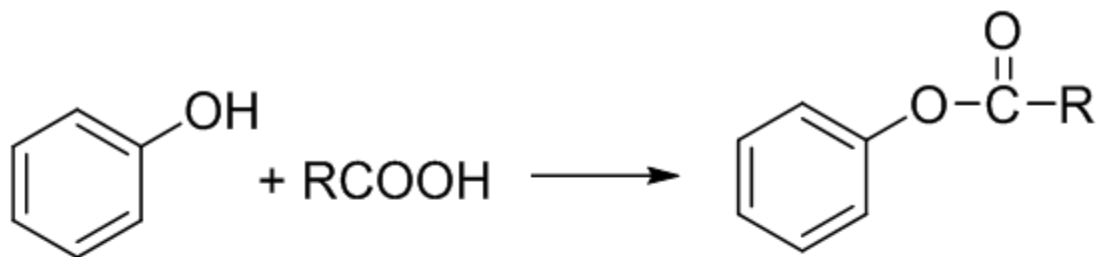
Reactions of Hydroxy Group of Phenols



Reactions of Hydroxy Group of Phenols

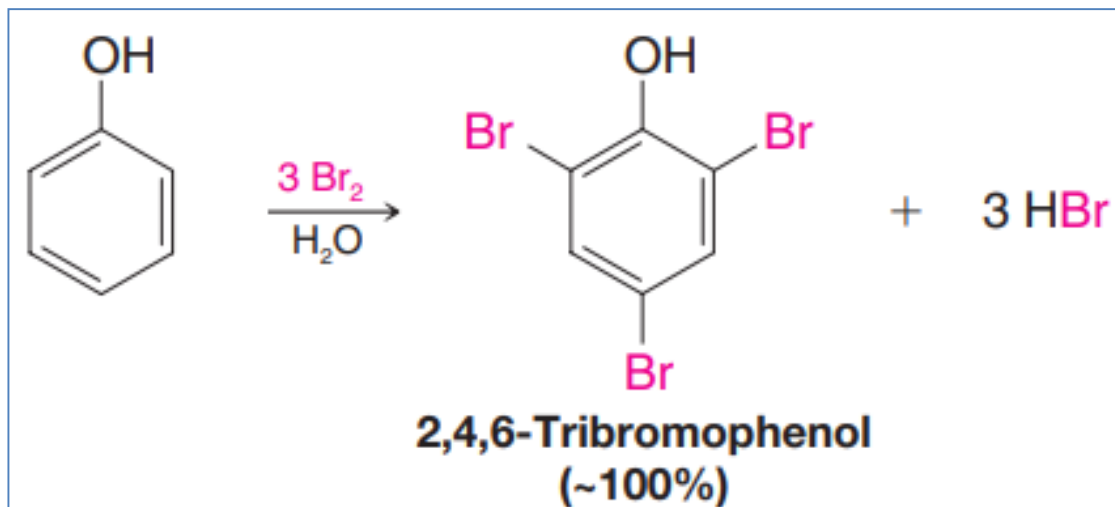


Reactions of Hydroxy Group of Phenols:



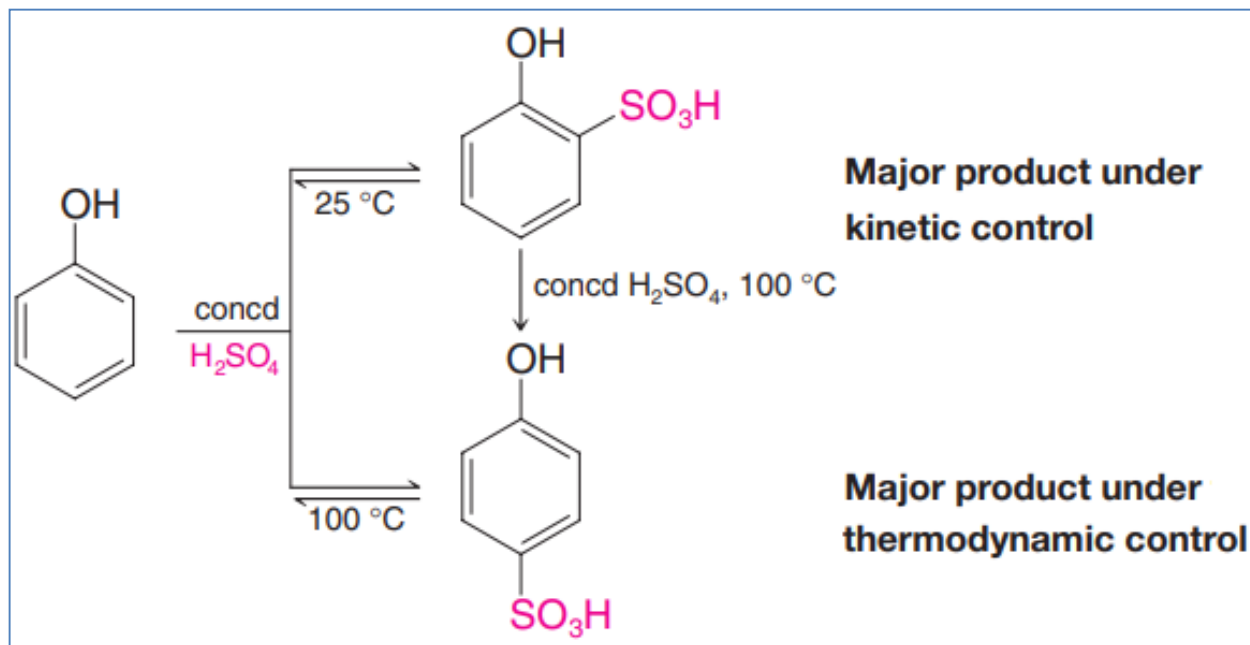
Reactions of the Benzene Ring of Phenols

- Bromination



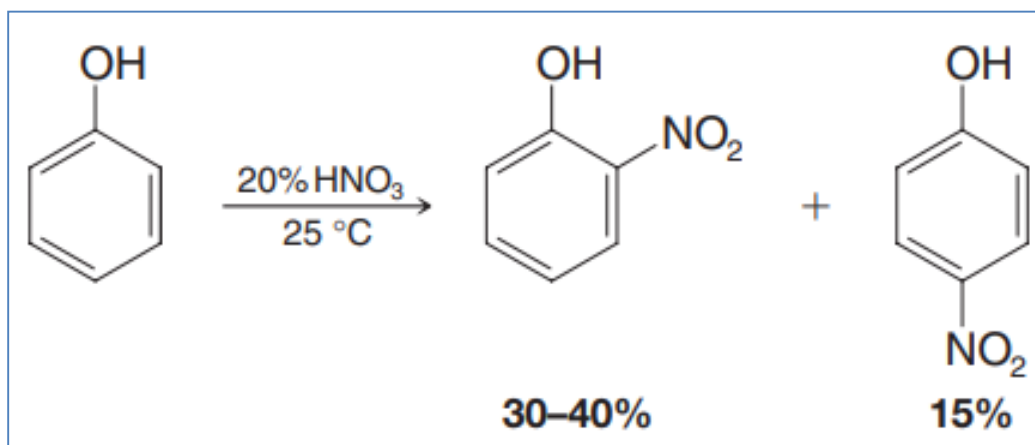
Reactions of the Benzene Ring of Phenols

- Sulfonation



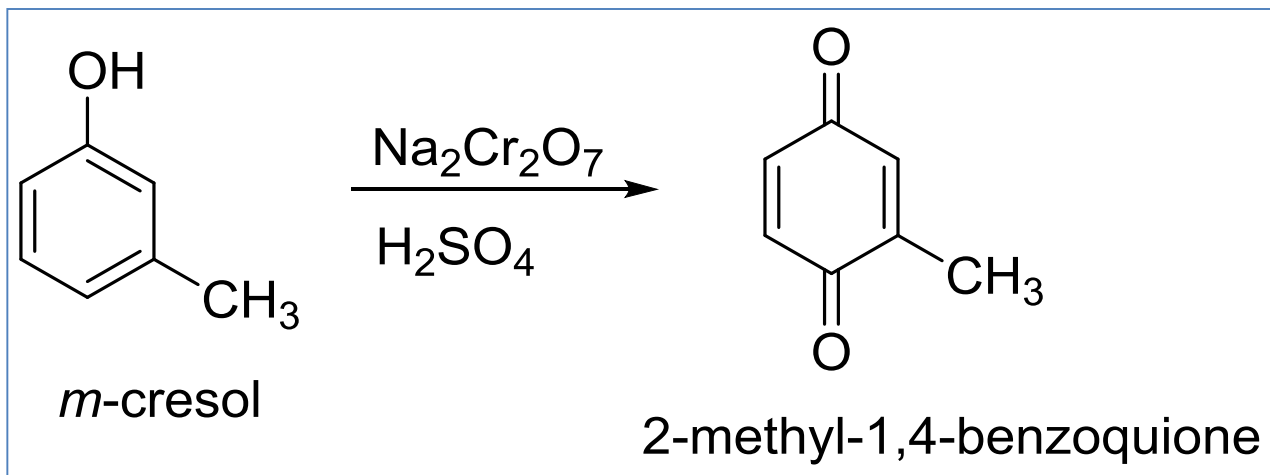
Reactions of the Benzene Ring of Phenols

- Nitration



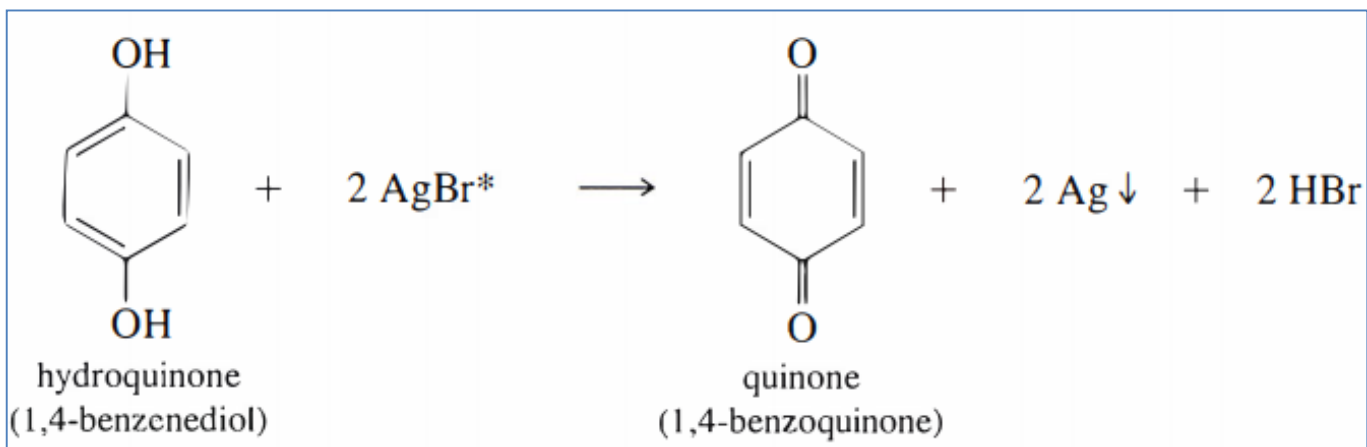
Reactions of Phenols

- Oxidation



Reactions of Phenols

- Oxidation



Synthetic Applications

Synthetic Applications

- ★ The substitution reactions of aromatic rings and the reactions of the side chains of alkyl and alkenyl benzenes, when taken together, offer us a powerful set of reactions for organic synthesis. By using these reactions skillfully, we shall be able to synthesize a large number of benzene derivatives.
- ★ Part of the skill in planning a synthesis is deciding in what order to carry out the reactions.
- ★ A substituent group already present on a benzene ring can affect both the reactivity of the ring toward electrophilic substitution and the orientation that the incoming group takes on the ring.

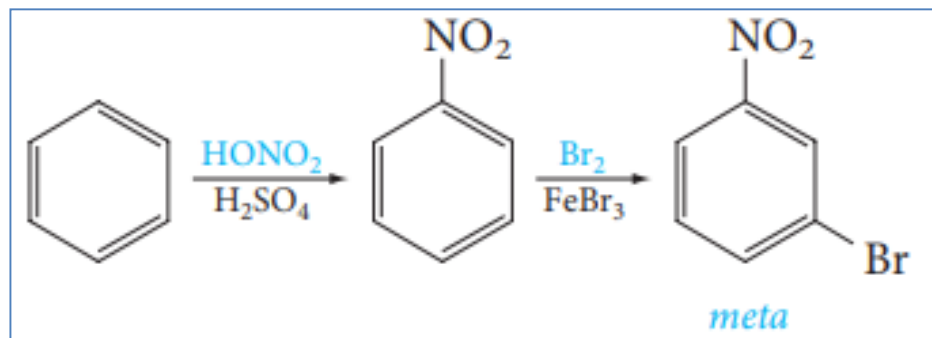
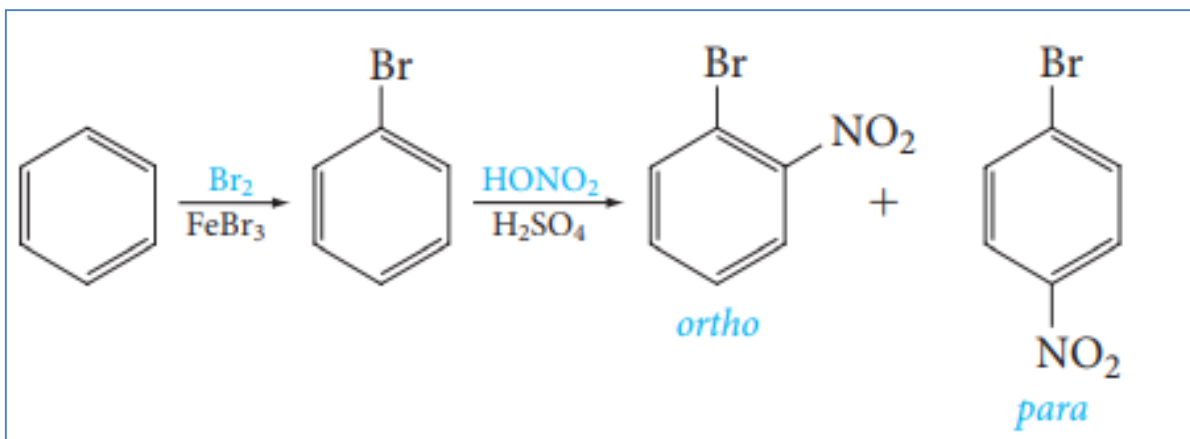
Substituent Effect on Reactivity

Substituents not only affect the position of substitution, they also affect the rate of substitution, whether it will occur slower or faster than for benzene.

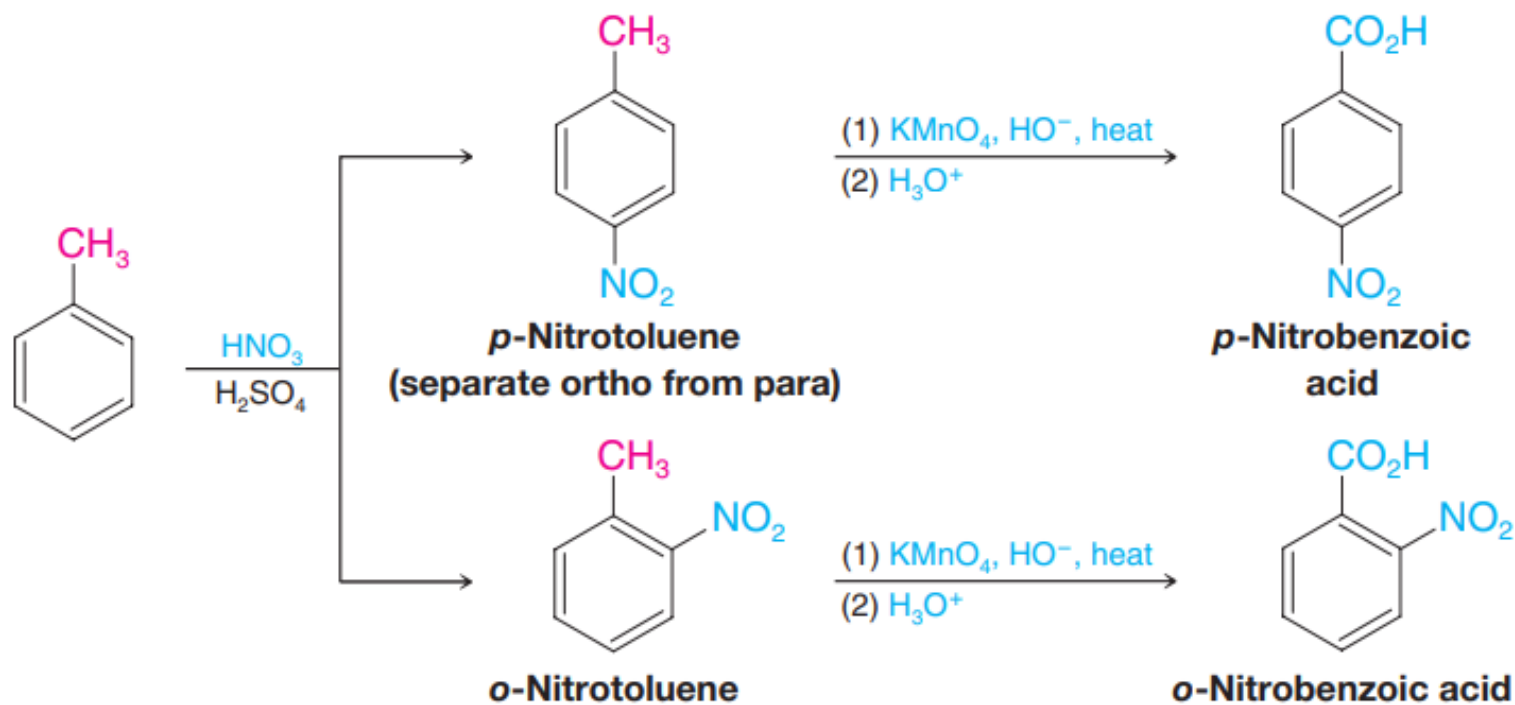
If a substituent is **activating**, the rate of electrophilic aromatic substitution is faster for the substituted benzene than for unsubstituted benzene. Likewise, if a substituent is **deactivating**, the rate of reaction is slower than for benzene.

With the halogens (F, Cl, Br, and I), two opposing effects bring about the only important exception to these rules. Because they are strongly electron withdrawing, the halogens are ring deactivating; but because they have unshared electron pairs, they are ortho,para directing.

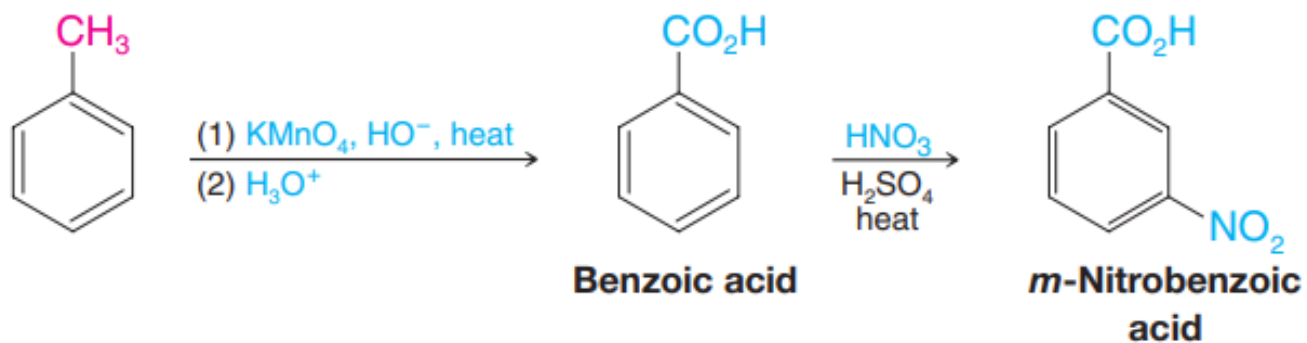
The importance of directing effects in synthesis



The importance of directing effects in synthesis



The importance of directing effects in synthesis



References

- ***Organic Chemistry 11e***, T.W. Graham Solomons, Craig B. Fryhle, Scott A. Snyder, John Wiley & Sons, Inc., 2014, ISBN 978-1-118-13357-6 (cloth) Binder-ready version ISBN 978-1-118-14739-9
- ***Organic Chemistry: A Short Course, 13th Ed.***, D.J. Hart, C.M. Hadad, L.E. Craine, H. Hart, Brooks/Cole, Cengage Learning, 2012, ISBN-13: 978-1-111-42556-2
- ***Organic Chemistry, 6th Ed.***, L. G. Wade, Pearson Education, Inc., 2006, ISBN 0-13-147871-0
- ***Organic Chemistry, 2nd Ed.***, Jonathan Clayden, Nick Greeves, and Stuart Warren,, Oxford University Press, 2012, ISBN: 9780199270293
- ***Organic Chemistry***, Mukherjee, S.M., et al., New Age International Ltd, 2008. ProQuest Ebook Central, <http://ebookcentral.proquest.com/lib/ankara/detail.action?docID=3017383>.