

TUTORIAL NINE: AROMATIC CHEMISTRY

Keywords:

Reactivity of Ar-X; Evidence of aromaticity; Huckel Rule; Electron rich and deficient aromatics.

Electrophilic aromatic substitution (E.A.S) with D_3O^+ , HNO_3/H_2SO_4 , FeX_3/X_2 , SO_3/H_2SO_4 , $Hg(OAc)_2$, $Tl(OCOCF_3)_3$, $CH_3Cl/AlCl_3$, $CH_3COCl/AlCl_3$; Formylation by - Vilsmeier and Reimer Tiemann reactions; Use of isotopes to investigate mech; Activating o,p-directing; Deactivating m-directing; halobenzene as deactivating o,p-directing E.A.S. sigma-complex reaction profiles; reactivity when more than one substituent; reactivity of Naphthalene, Anthracene (esp nitration and sulphonation - kinetic vs thermodynamic products)

Aromatic Nucleophilic substitution; Benzyne; Birch reduction of electron rich/deficient aromatics; oxidation to dimers (radical) and to benzoic acids; reduction of nitroaromatics; Oxidation of anilines to aryl nitro compounds; diazonium salts; Sandmeyer reaction; Gatterman reaction Azocoupling to azobenzene dyes; phenols quinones; acylation-reduction for controlled alkylation; benzylic radicals, carbonium ions.

Reading:

CGWW Chapters 22, 43

Sykes, Chapter 6

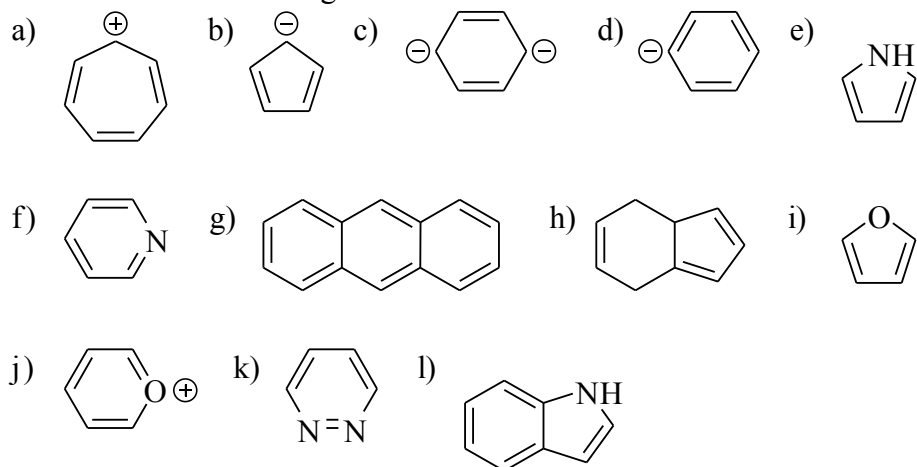
(Others, March, (3rd Ed.) Chapters 10-13)

Tutorial problems are attached.

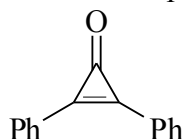
Note: the prelims exam does not require a comprehensive knowledge of all aromatic chemistry - but you should know all the basic concepts and mechanistic types.

TUTORIAL PROBLEMS NINE

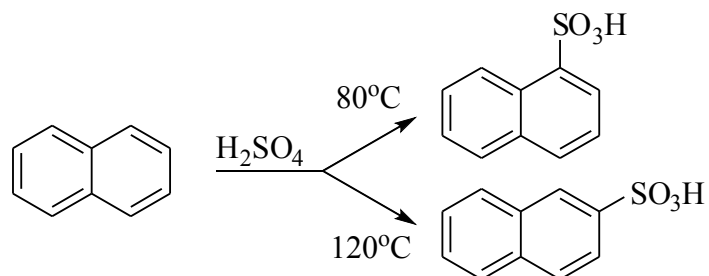
1. Which of the following are aromatic?



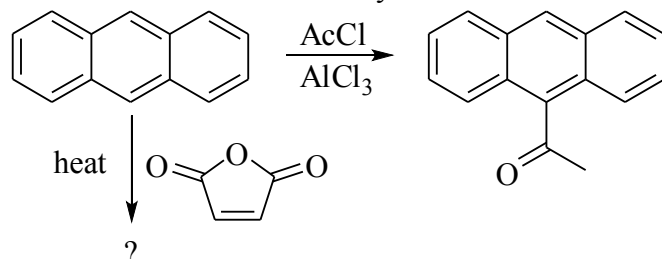
2. 2,3-Diphenylcyclopropanone (below) has a dipole moment $>5D$ and undergoes facile nucleophilic substitution. Comment.



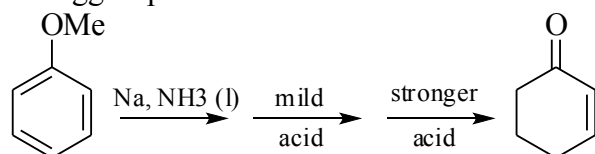
3. Explain what is meant by kinetic and thermodynamic control using the following example:



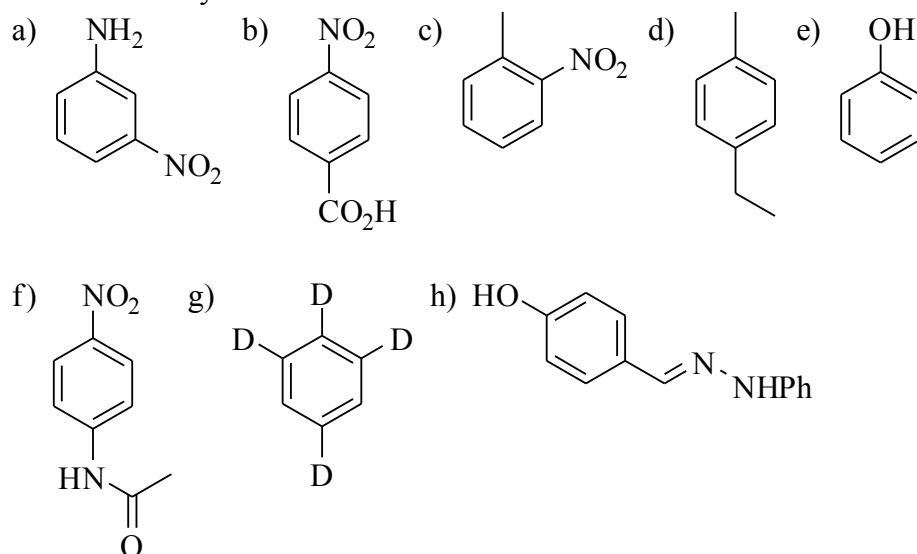
4. Explain the following observation and suggest a product for the reaction of anthracene with succinic anhydride.



5. Suggest plausible mechanisms for the following reaction sequence:



6. The synthesis of substituted benzenes is a good place to learn the importance of planning in synthesis. Describe the most efficient synthesis of the following molecules that you can devise:



7. Predict the major product for each of the following reactions, explaining your choice in each case:

