
CHEM2201: Section 2 - Aromatic & Heteroaromatic Compounds

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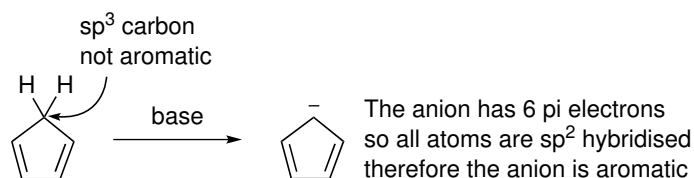
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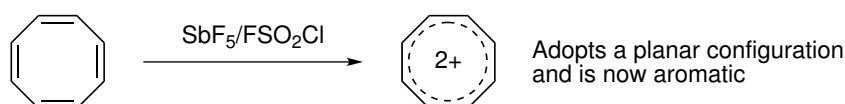
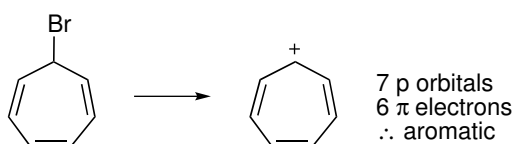
1 Aromaticity

Benzene is very stable and therefore it does not behave like alkenes. Rather than undergoing addition reactions, it undergoes substitution reactions.

Hückels rule: A planar, fully conjugated cyclic compound with $4n+2$ electrons is aromatic. However we can also have 3, 5, 7 and 8 carbon aromatic compounds.

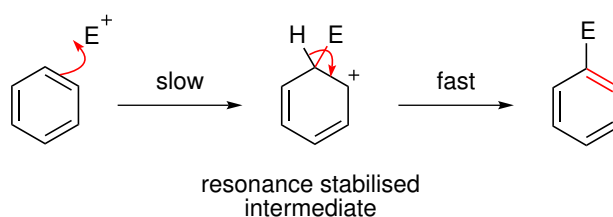


Similarly:



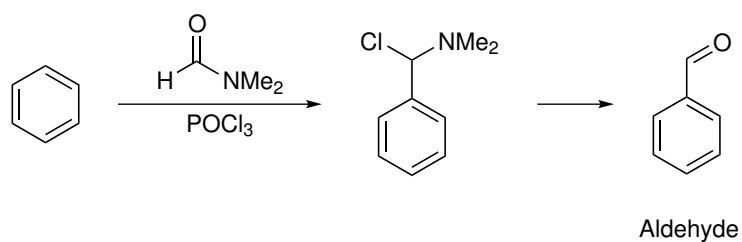
1.1 Reactions of Benzene

The typical reaction of benzene is electrophilic substitution, one of the H's is replaced by an electrophile:

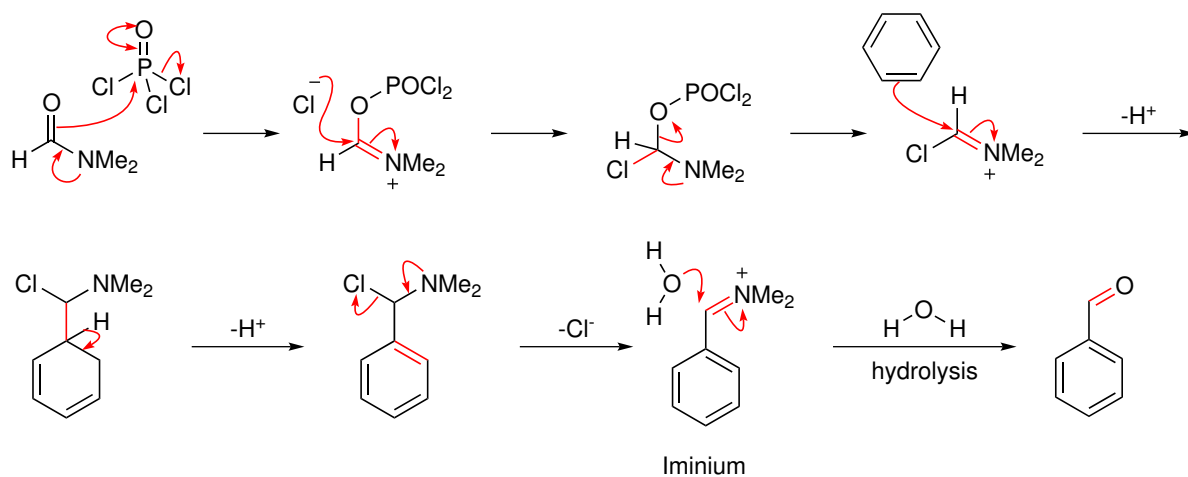


Because of the stabilised intermediate, the 1°C is no good for Friedel-Crafts acylation or alkylation therefore the reaction is different, using DMF and phosphorus oxychloride.

a) Vilsmeier-Haack Formylation

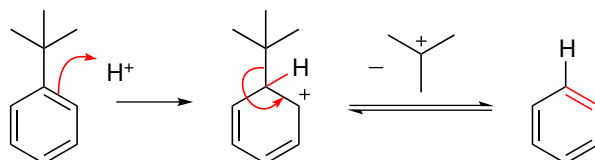


Mechanism:



b) Dealkylation

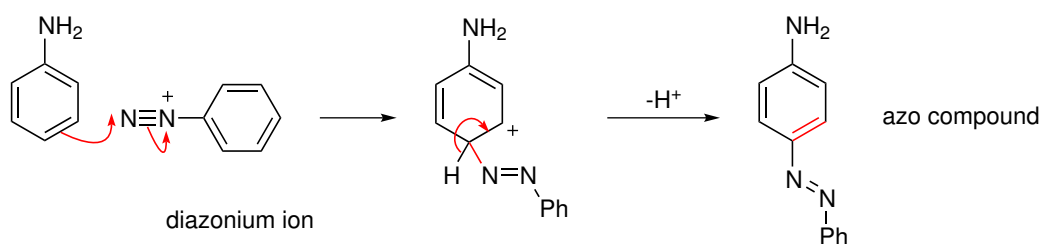
E.g. Removal of tertiary alkyl group with protic acid. Reverse of Friedel crafts alkylation.



Position of equilibrium depends on reaction conditions

c) Diazo coupling

React aromatic diazonium ion with phenol or aniline (e.g. Electron rich aromatic) to get azo compounds.



Azo compounds have 2 aromatic groups either side of $-(N=N)-$

1.2 Directing Effects in Electrophilic Aromatic Substitution

Substituents will influence rate and position:

a) Activating - Ortho/Para directing

- Alkyl Groups
- Oxygen substituents
- Nitrogen substituents (NH_2 , NR_2 , NHCOR) I.e. Electron donating hence activating, either inductively or resonance.

b) Deactivating - Meta directing

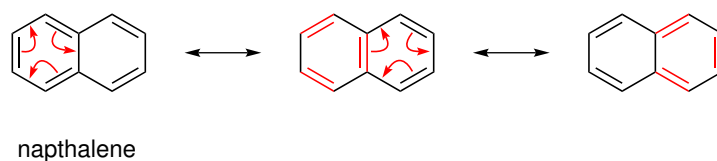
- Nitro groups and nitriles
- Carbonyl groups (COR , CO_2R)
- Positively charged substituents (NR_3^+) I.e. Electron withdrawing and therefore deactivating.

c) Deactivating - Ortho/Para directing

- Halogen atoms - inductively electron withdrawing but donating through resonance.

2 Polycyclic Aromatic Hydrocarbons

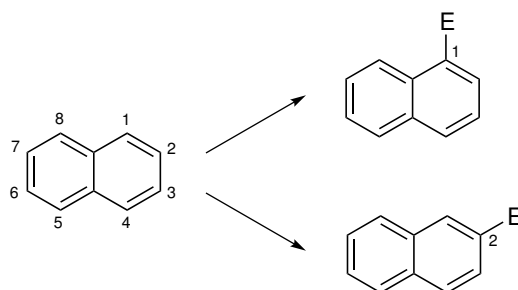
2.1 Naphthalene



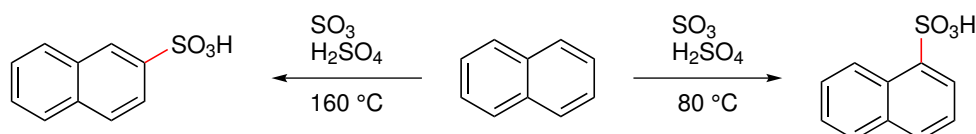
Hückels rule applies here with $n=2$

The aromatic stability of naphthalene is higher than benzene but less than twice as large. For this reason it is easier to disrupt aromatically and so naphthalene is more reactive than benzene in electrophilic substitutions. E.g. It will react with Cl_2 without a catalyst.

There are 2 points of electrophilic attack, C-1 or C-2:



The lowest resonance forms retain aromaticity in the left hand ring. C-1 attack has two such forms, C-2 has only one. Therefore, the energy of the intermediate from attack at C-1 is lower than C2 so substitution is more rapid at C-1. In general, in polycyclic aromatic hydrocarbons, electrophilic substitution occurs most readily to a ring junction. However, the major product in the sulfonation of naphthalene depends on the conditions under which the reaction is carried out.

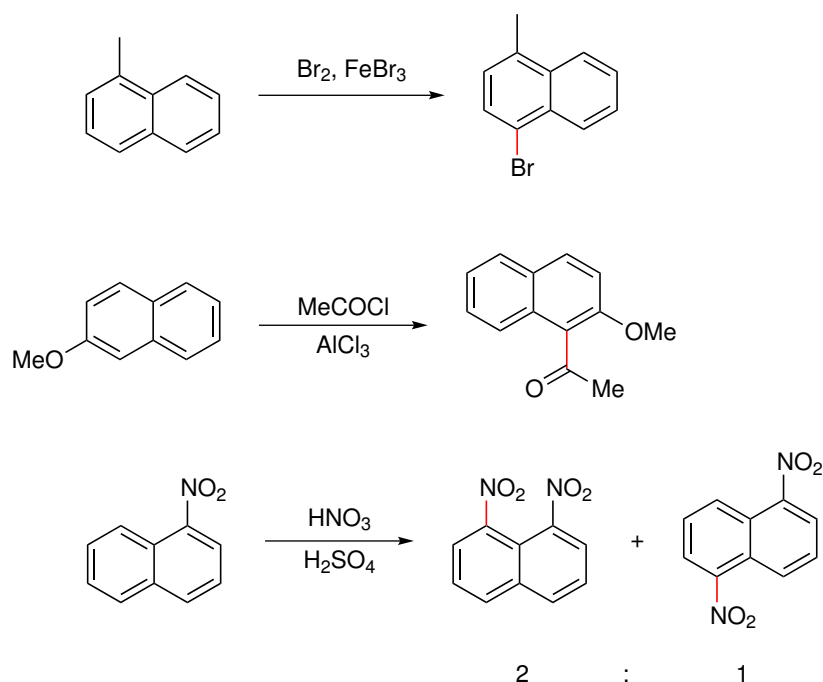


This is because at 80 °C the reaction is irreversible and therefore the product obtained is fastest formed (kinetic product). At 160 °C the reaction is reversible therefore the product formed is the most stable (thermodynamic production).

If we carry out electrophilic substitutions on substituted naphthalene:

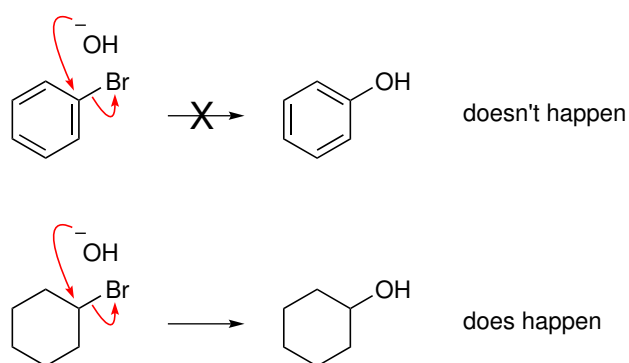
- Substitution will occur in the more electron rich ring
- Substitution will occur adjacent to the ring junction
- Normal directing effects apply

E.g.



2.2 Nucleophilic Substitution in Aromatic Compounds

Nucleophilic substitution in aromatic compounds is rare as the $\text{S}_{\text{N}}2$ mechanism is impossible at the sp^2 hybridised carbons of benzene.

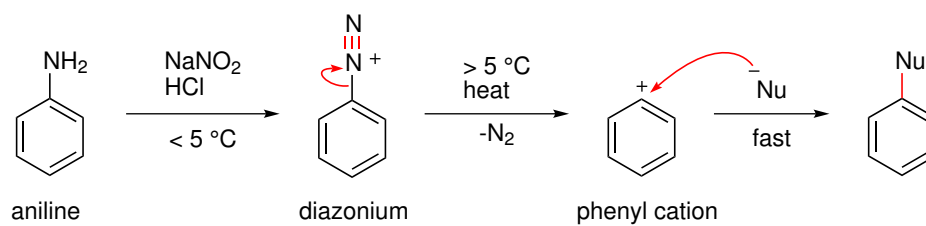


It only occurs under 3 sets of circumstances:

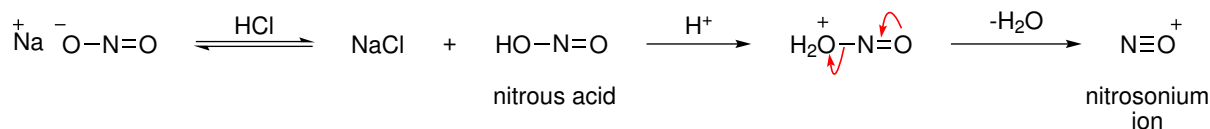
1. There is a very good leaving group e.g. N_2 (g)
2. The nucleophile is also a strong base e.g. NH_2^-
3. There are strongly electron withdrawing substituents ortho and/or para to the leaving group.

Each of these has a different mechanism.

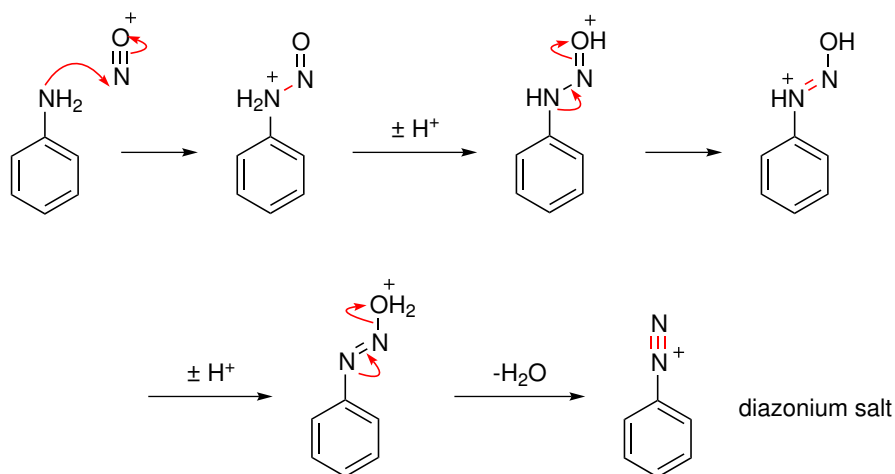
a) $\text{S}_{\text{N}}1$ Mechanism



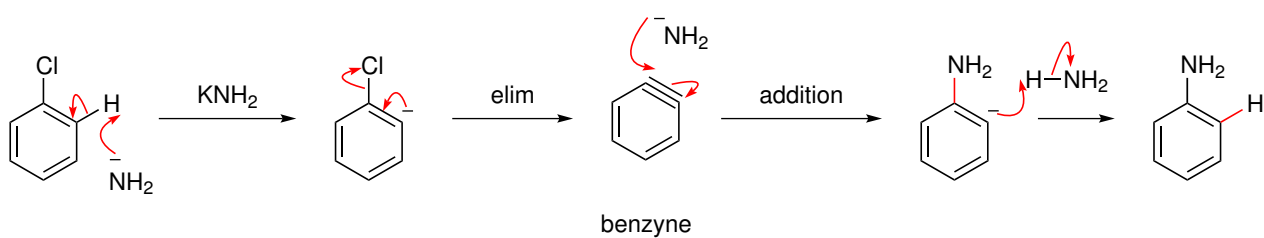
Diazonium formation



Mechanism

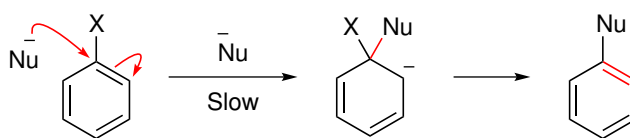


b) Benzyne Mechanism



The nucleophile must be a strong base, HO^- or NH_2^- are most commonly used.

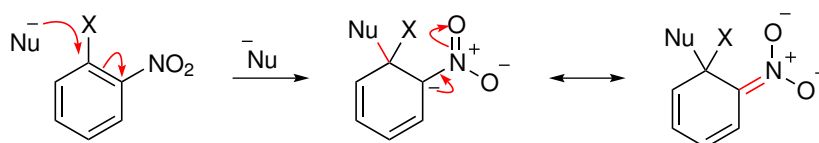
c) $\text{S}_{\text{N}}\text{Ar}$ Mechanism



Addition of Nu is the rate determining step therefore leaving group ability of X is not important but electronegativity of X is important ($F > Cl > Br$)

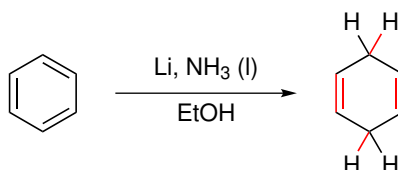
This mechanism requires strongly electron withdrawing groups ortho and/or para to the leaving group.

NO_2 is best for this purpose followed by carbonyl groups.

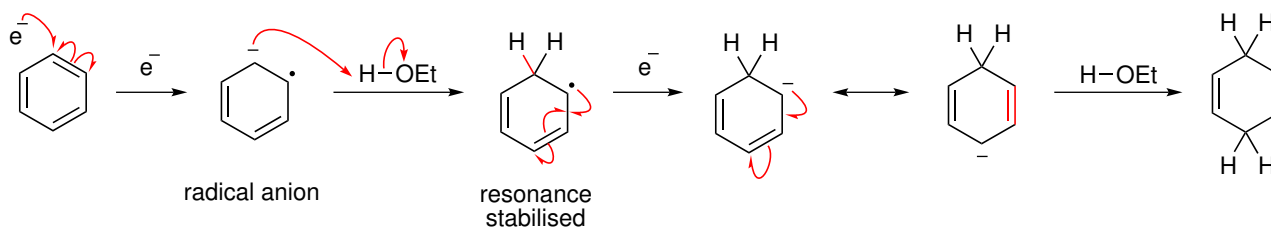


2.3 Birch Reduction

This is the partial reduction of aromatic rings.

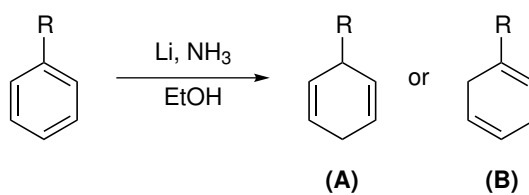


Mechanism:



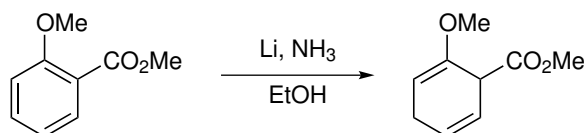
The product formed depends on which resonance ion is protonated first

If the Birch reduction is carried out with monosubstituted benzene then there are 2 possible products.



The isomer obtained depends on the nature of the substituent:

- If R is e^- withdrawing (e.g. carbonyl group) isomer A is obtained.
- If R is e^- donating (e.g. alkyl or OR), isomer B is obtained.
- If there is more than one substituent, it occurs as much as possible to put e^- donating substituents on the double bond and e^- withdrawing ones off them.



Birch reduction followed by ozonolysis is useful for generating 1,6 dicarbonyl compounds.

