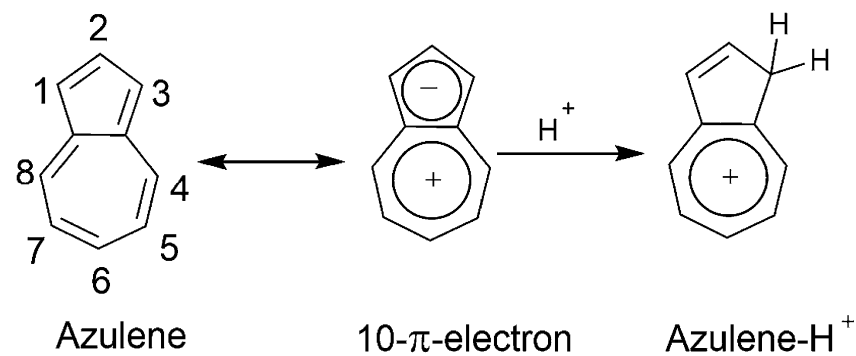


# Azulene, Chrysene



- **Azulene** is an organic compound and an isomer of naphthalene.

- Whereas naphthalene is colourless, azulene is dark blue.

- Less stable than naphthalene

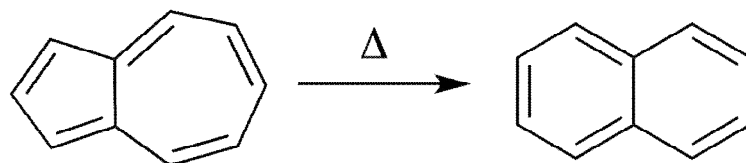
- Resonance energy of naphthalene is 77 Kcal/mole

- Resonance energy of azulene is 49 Kcal/mole

- On heating above 350 0C, isomerizes to naphthalene

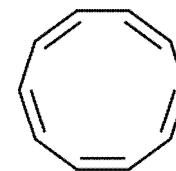
- Azulene has a dipole moment of 1.0 D, while isomeric naphthalene is zero

- Absorbs in the range of 230-345 nm indicating the presence of highly conjugated system



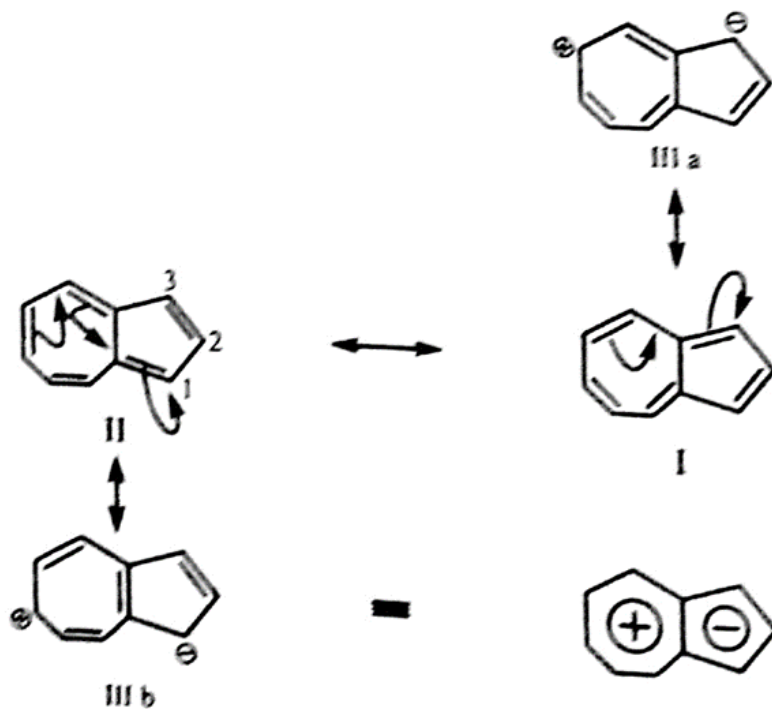
- Azulene is usually viewed as resulting from fusion of cyclopentadiene and cycloheptatriene rings.

- Like naphthalene and cyclodecapentaene, it is a 10 pi electron system.

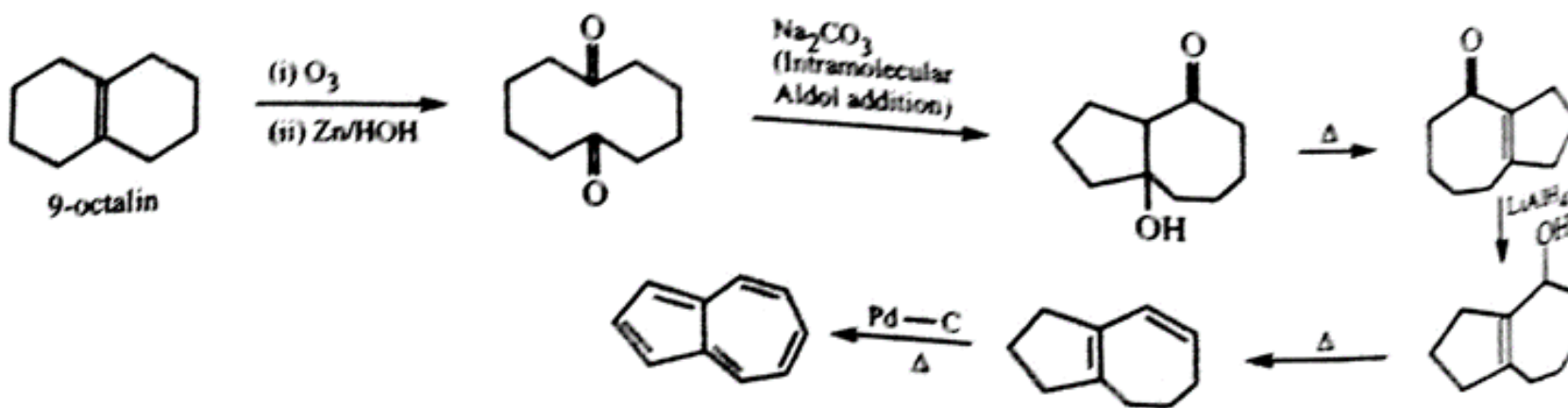


- It exhibits aromatic properties: (i) the peripheral bonds have similar lengths and (ii) it undergoes Friedel-Crafts-like substitutions.
- The stability gain from aromaticity is estimated to be half that of naphthalene.
- This polarity can be explained by regarding azulene as the fusion of a 6  $\pi$ -electron cyclopentadienyl anion and a 6  $\pi$ -electron tropylium cation: one electron from the seven-membered ring is transferred to the five-membered ring to give each ring aromatic stability by Hückel's rule.
- Reactivity studies confirm that seven-membered ring is electrophilic and the five-membered ring is nucleophilic.

- The ionic structure of azulene (a non benzenoid aromatic compound) is an important contributor to the resonance hybrid



The synthesis of azulene is outlined as follows:

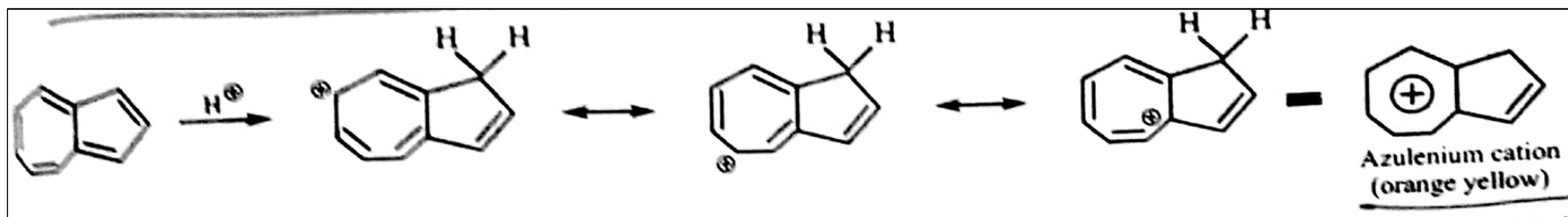


It can also be prepared from fulvene. Thermolysis of fulvene in the presence of base gives azulene

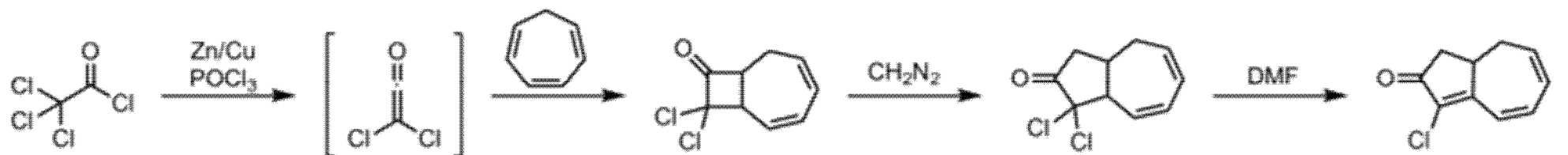
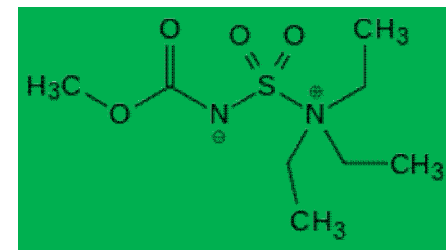
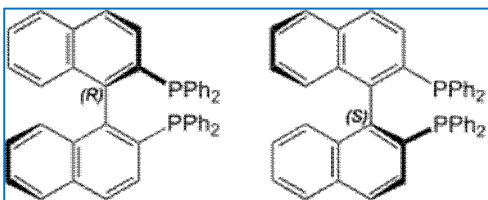


It is a non benzenoid aromatic compound. Aromatic characteristics of azulene are

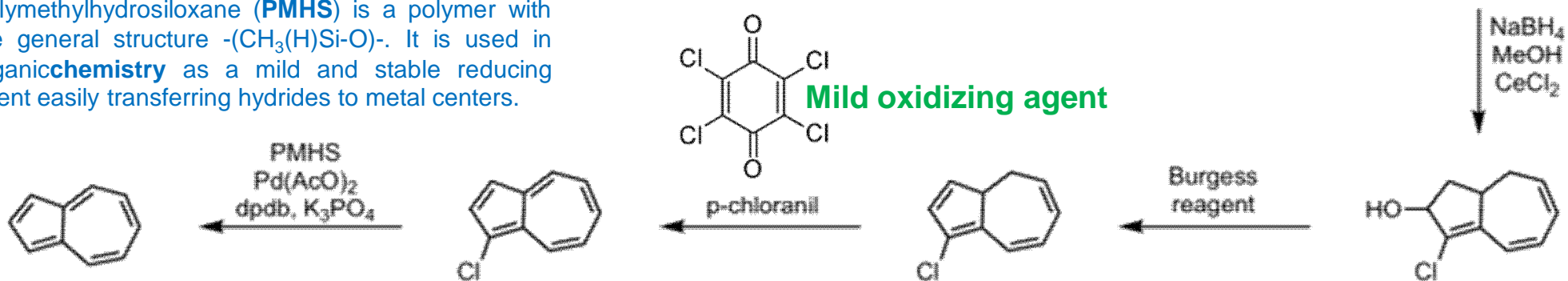
- It does not undergo autoxidation
- It does not get polymerized
- Under normal conditions it does not act as a diene in Diels Alder reaction
- It is capable of undergoing electrophilic substitution reactions in five membered ring. The first substituent enters at position 1 and the second at position-3.
- These positions are electron rich in dipolar structures of azulene
- Azulene is sensitive to strong acids. It forms azulonium cation with strong acid.



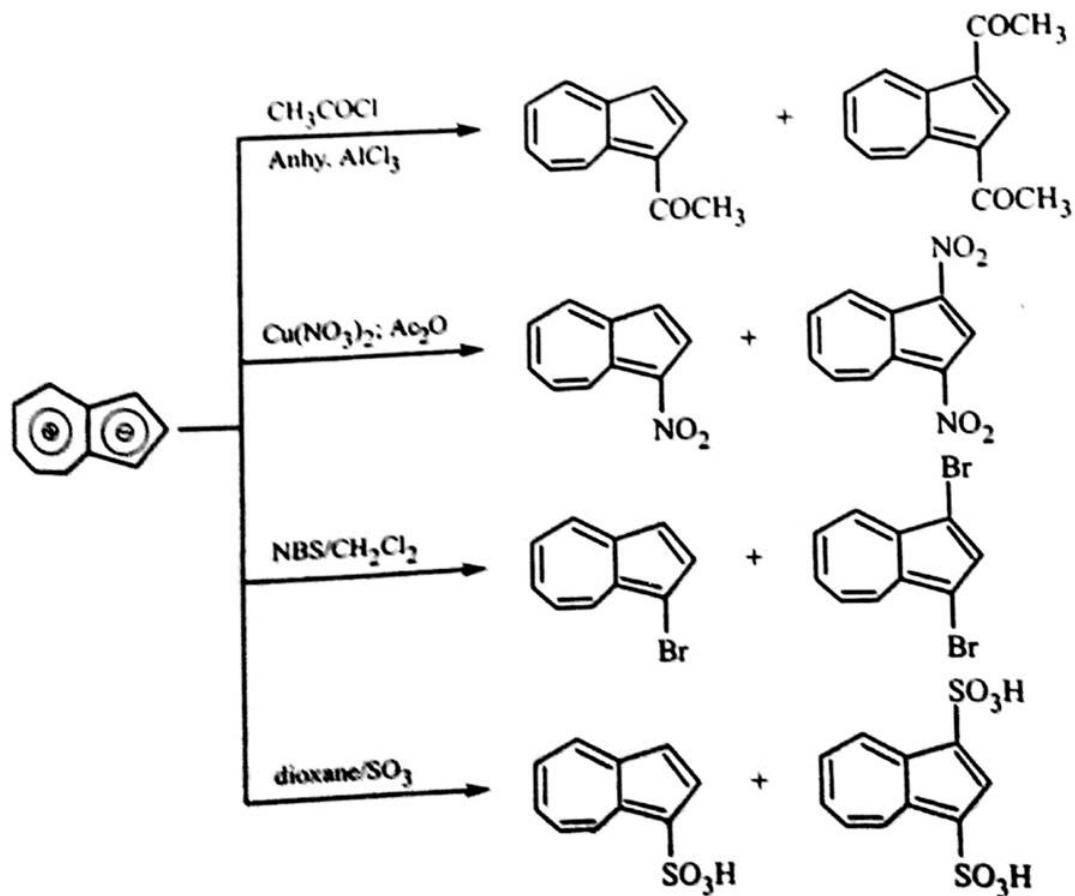
Procedure: step 1: cycloheptatriene 2+2 cycloaddition with dichloro ketene step 2: diazomethane insertion reaction step 3: dehydrohalogenation reaction with DMF step 4: Lucho reduction to alcohol with sodium borohydride step 5: elimination reaction with Burgess reagent step 6: oxidation with p-chloranil step 7: dehalogenation with polymethylhydrosiloxane, palladium(II) acetate, potassium phosphate and the DPDB ligand



Polymethylhydrosiloxane (**PMHS**) is a polymer with the general structure  $-(\text{CH}_3(\text{H})\text{Si}-\text{O})-$ . It is used in organic chemistry as a mild and stable reducing agent easily transferring hydrides to metal centers.



Therefore special reagents have to be used for nitration [**tetranitromethane pyridine, Copper acetate in Ac<sub>2</sub>O or HNO<sub>3</sub> in AcOH**], halogenation (**N-halosuccinamide**) and sulphonation (**dioxane-SO<sub>3</sub>**)

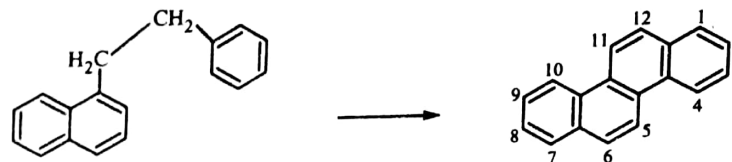




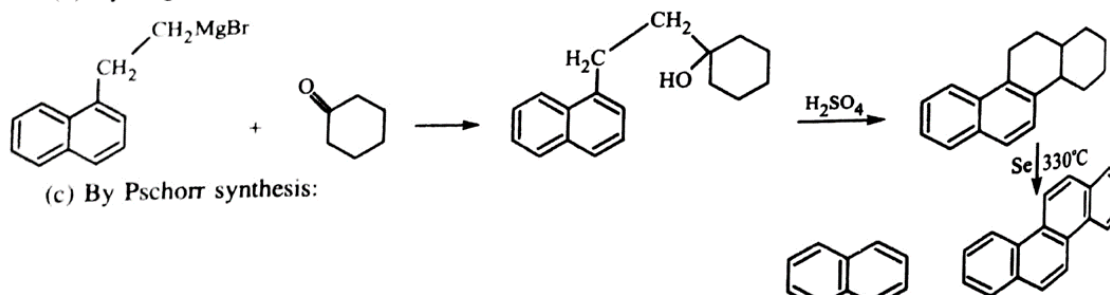
- **Chrysene** is a polycyclic aromatic hydrocarbon (PAH) that consists of four fused benzene rings.
- It is a natural constituent of coal tar, from which it was first isolated and characterized.
- A colourless solid
- M.pt. 251 0C

# Synthesis of Chrysene

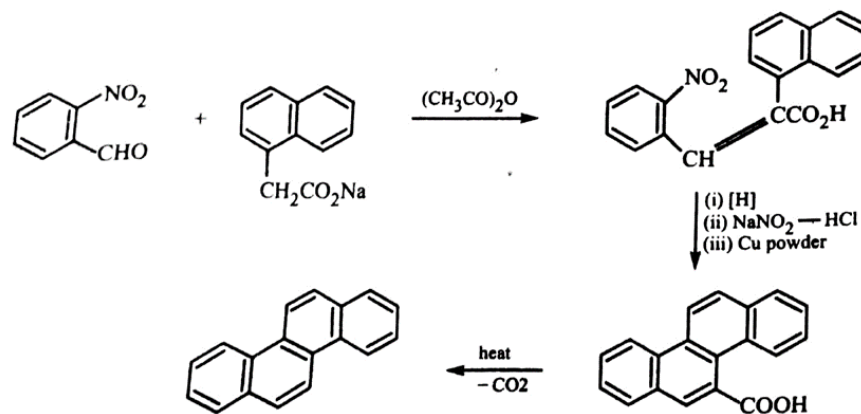
1. By strongly heating 2-(1-naphthyl)-1-phenylethane

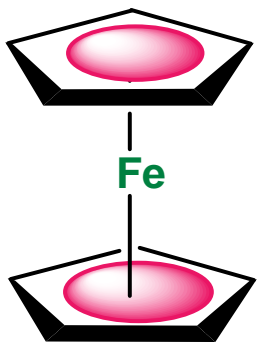


2. By Bogert-Cook Synthesis



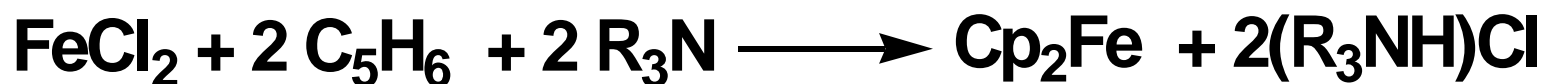
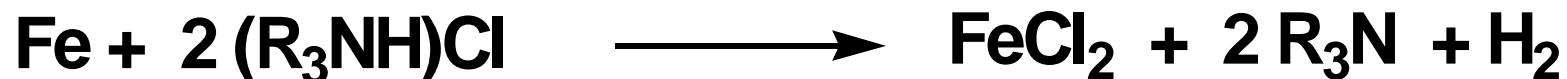
3. By Pschorr synthesis





## Ferrocene: synthesis

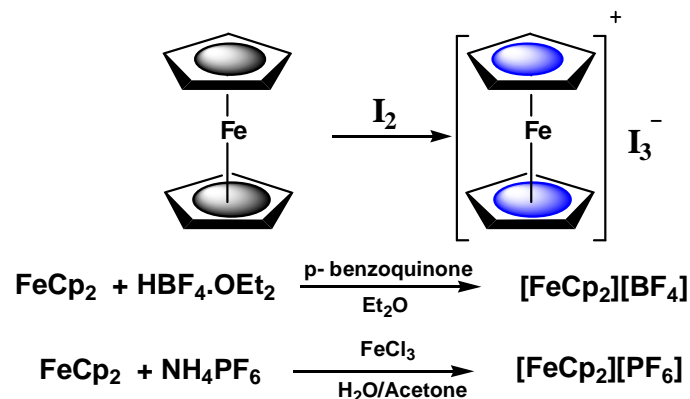
Lab Synthesis



- Most stable member in metallocene series
- It sublimes readily and not attacked by air or water but can be oxidized reversibly, electrochemically or by oxidizing agents such as iodine to give the blue ferrocenium cation  $[\text{Cp}_2\text{Fe}]^+$ .

# Reactions of Ferrocene

Ferrocene undergoes electrophilic substitution reactions. Many of its reactions are faster than similar reactions of benzene **Necessary requirement:** The electrophile should not be oxidizing in nature



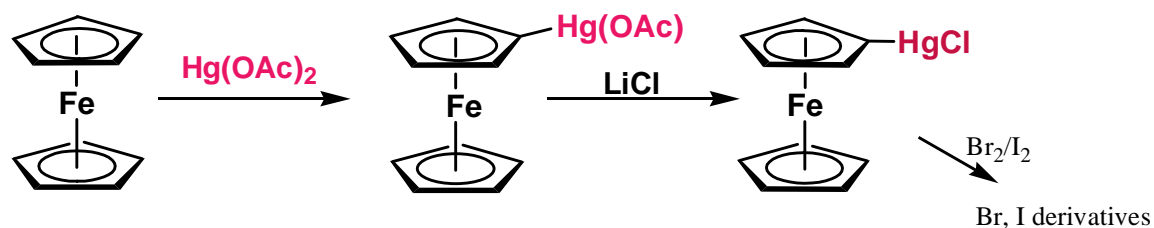
The oxidized Cp<sub>2</sub>Fe<sup>+</sup>, ferrocenium cation, will repel the electrophile away. Therefore direct nitration, halogenation and similar reactions cannot be carried out on ferrocene.

## Acetylation



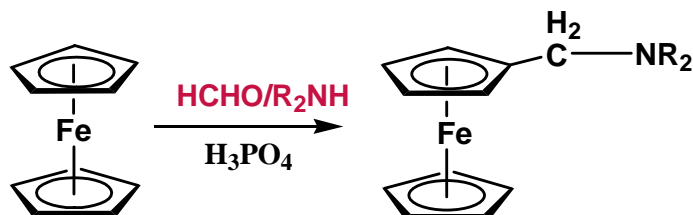
**3.3 x 10<sup>6</sup> times faster than benzene**

## Chloromercuration (*hazardous*)



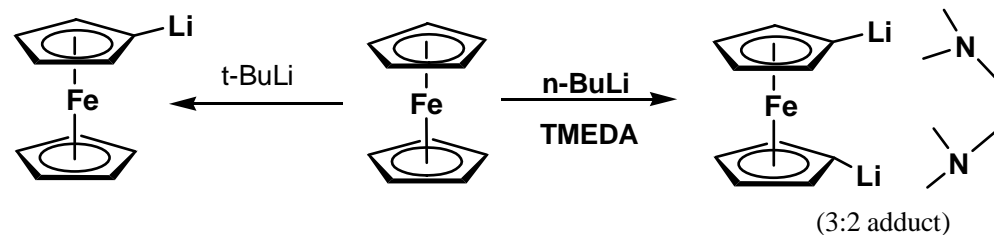
109 times faster than benzene

## Mannich reaction



Does not happen with benzene;  
only with phenols/anilines

## Lithiation reaction



Does not happen with benzene;  
only with bromobenzene

## Lithiation and 1,1'-di-lithiation – access to range of new derivatives

