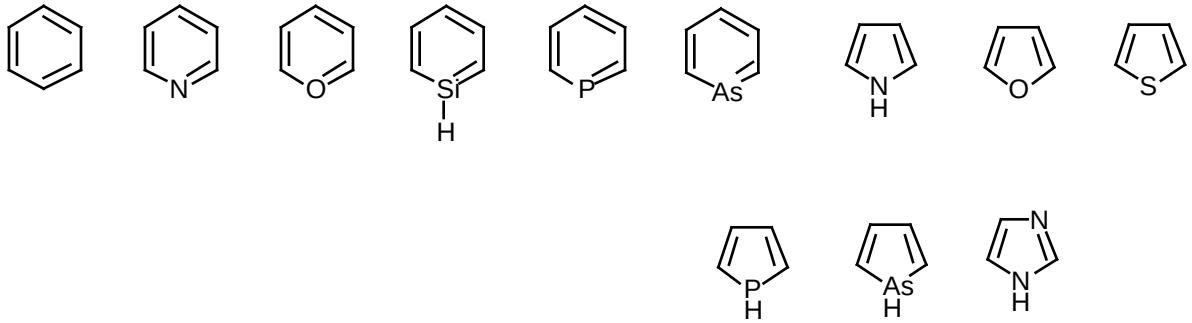
Chemistry 304B, Spring 1999 Lecture Notes 10

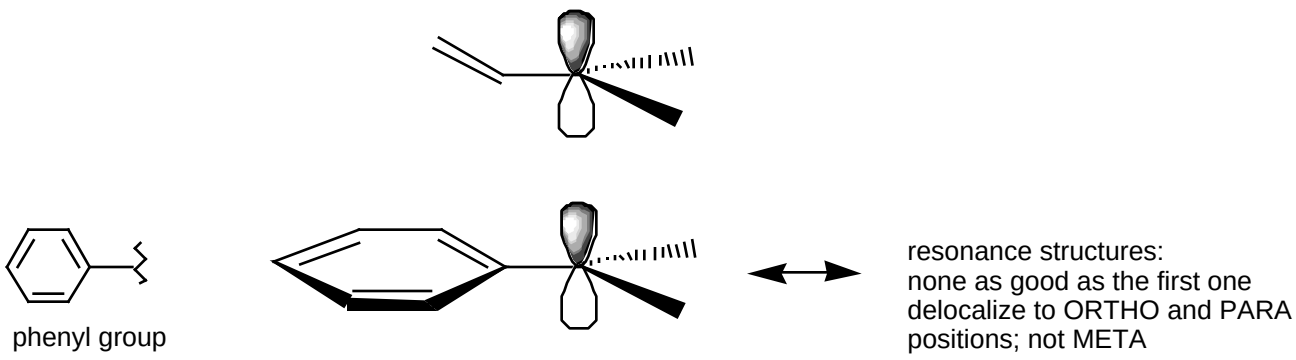
Derivatives of Benzene:
- Polycyclic aromatics
- Paracyclophanes
- Graphite
- Bucky ball and Bucky tubes

Hetero Benzenes:



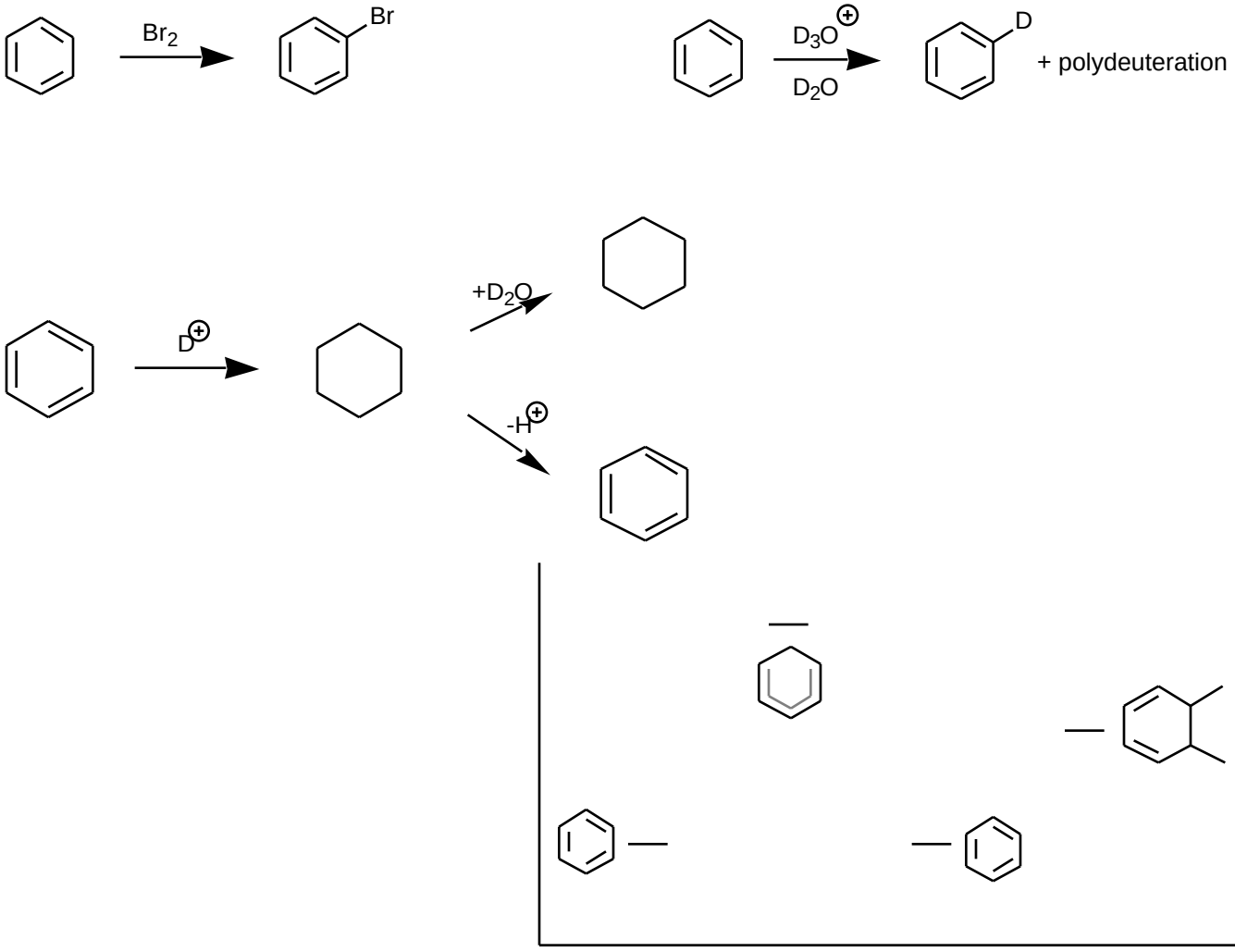
Reactions of Aromatic Compounds:

Read Section 13.12--The Benzyl System: Obvious extension from our discussion of allyl stabilization and reactions. The effect of a phenyl group

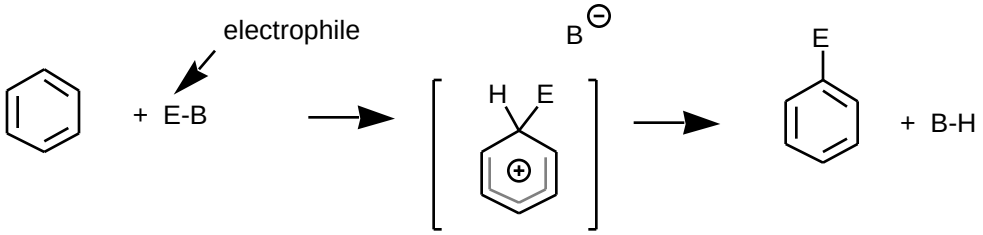


REACTIONS AT THE BENZENE RING:

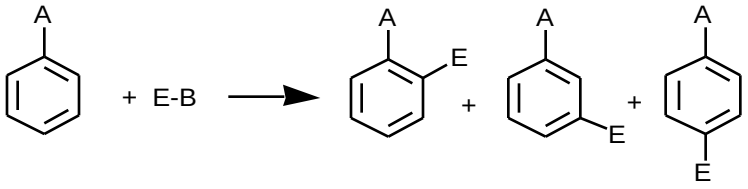
General point: Thermodynamically and Kinetically stabilized, deep valley and high mountains
Disturbing one pi bond removes "aromaticity"



Generic Electrophilic Aromatic Substitution: S_EAr (i.e., benzene is a weak nucleophile)



Questions: Which electrophiles?
What happens in substituted cases, such as:

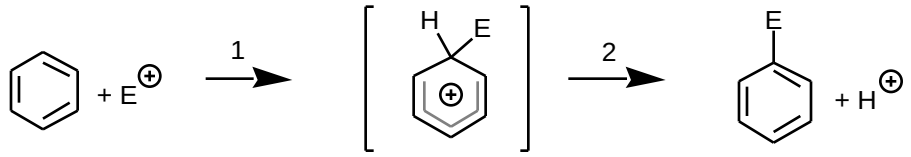


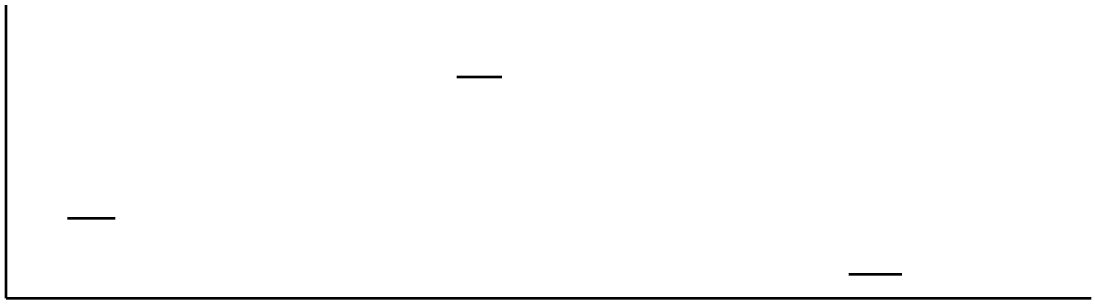
How does the nature of **A** influence the rate and selectivity in the substitution?

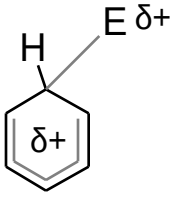
Resonance, Inductive, Steric

Always ask: Which is the rate-determining-step?

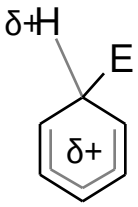
General facts: (a) rate correlates with reactivity of E^+.
(b) faster if **A** = electron donor; slower if **A** = electron withdrawing group.







TS1



TS1

If step 1 is RDS, electron withdrawing group (EWG) should RETARD, destabilize TS (like product cation)
no special effect on reactant

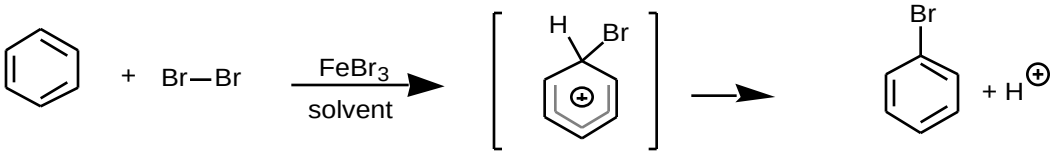
If step 2 is RDS, EWD should ACCELERATE Destabilize intermediate cation (more localized charge)
more than TS (more delocalized charge)

Useful Electrophiles: Think about adding:

carbon nitrogen oxygen sulfur halide

Easy ones:

A. Bromine: Br_2 is electrophilic. Further activate with a Lewis acid

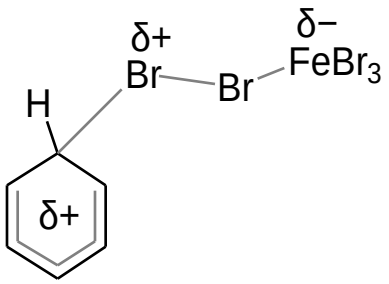


Solvent effects: polar or non-polar?

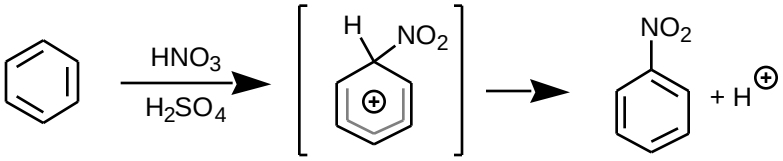
donating or non-donating? (coordinating)

protic or aprotic?

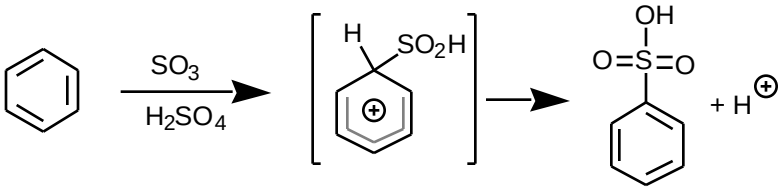
what is the rate-determining TS like?



B. Nitration: $HNO_3 + H^+ \rightarrow [H_2O\text{-}NO_2]^+ \rightarrow H_2O + [NO_2]^+$ **nitronium ion**



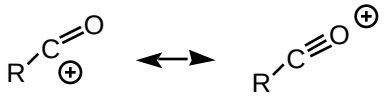
C. Sulfonation: $SO_3 + H_2SO_4 \rightarrow HSO_3^+ + HSO_4^-$



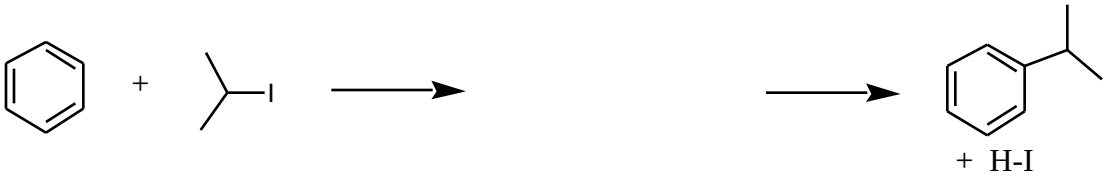
D. Oxygen?????

E. Carbon Electrophiles: Friedel-Crafts Reaction

alkyl cation $R^{\oplus}$ acyl cation



Alkylation:



Catalyst?
Benzene is a (weak) nucleophile: S_N1 or S_N2-like?