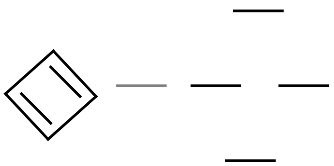
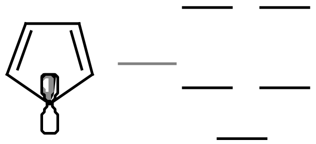
Chemistry 304B, Spring 1999 Lecture Notes 9

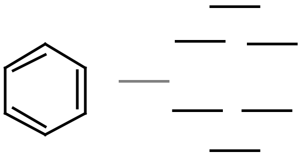
Review sessions: Sunday, 2/21 at NOON in rm 324 Frick
Wednesday, 2/24 at 8 pm in rm 324 Frick

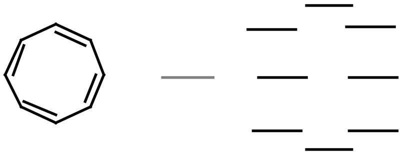
Memorize the nomenclature on p 592 and the ortho/meta/para terms on p 594. If you really want to imagine yourself to be an organic chemist, memorize the names on p 595. I will not test you these things, but I will use common names and systematic names, and you will move through problems faster if you know some basics.

From last time:

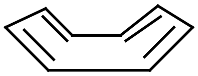


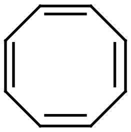


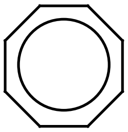


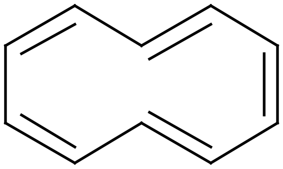


Hueckel: 4n+2 pi electron rule--final criterion for aromaticity. The cyclic planar continuous set of p orbitals will be more stable with a total of 4n+2 pi electrons.

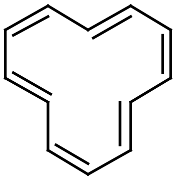




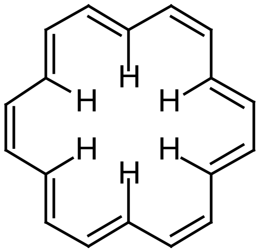




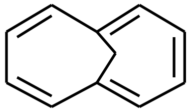
[10]annulene

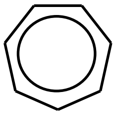


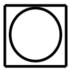
[12]annulene

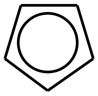


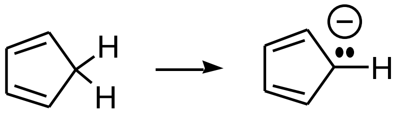
[18]annulene

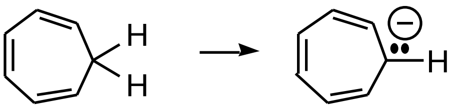




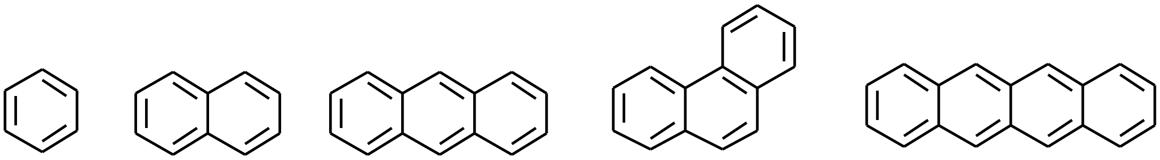




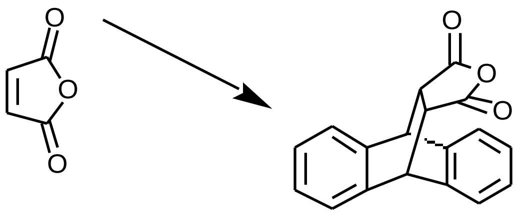


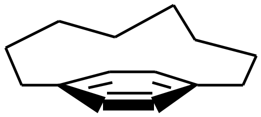


Polycyclic Aromatics:



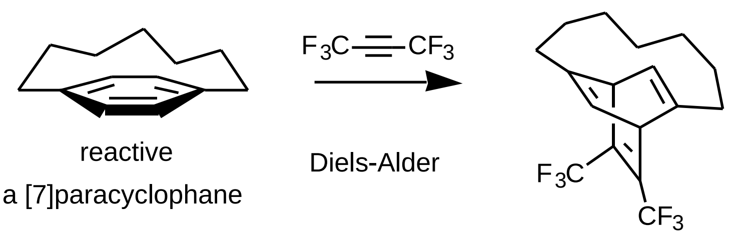
		naphthalene	anthracene	phenanthrene	naphthacene
stabilization energy (calc)	36	66.24 (72)	95.58 (108)	97.92 (108)	124.74 (144)



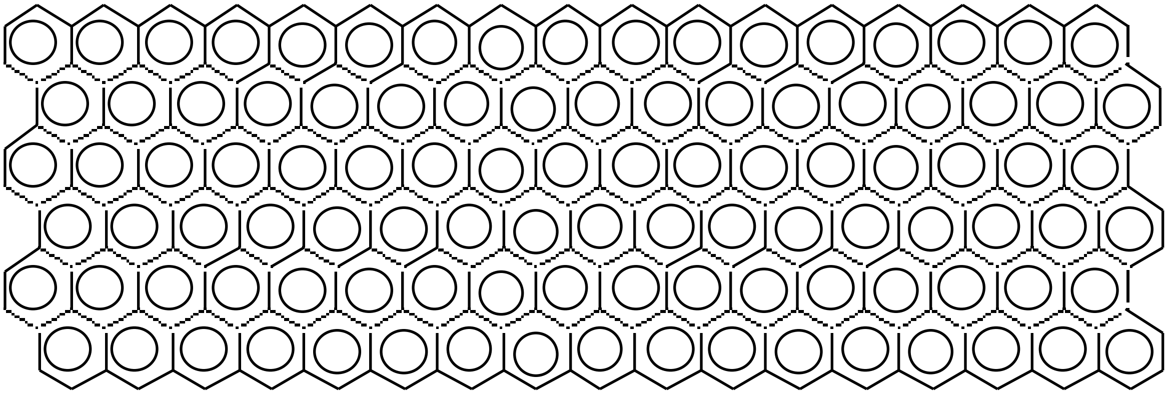


"normal"

an [8]paracyclophane



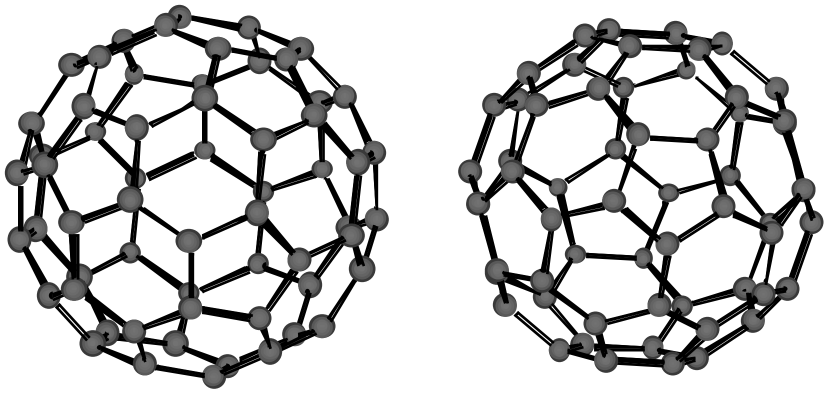
Graphite:



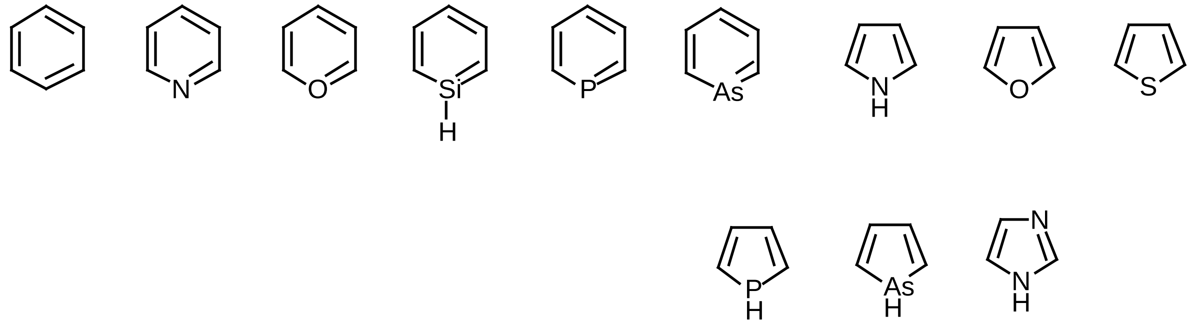
Buckminsterfullerene (Bucky Ball):

(cross-eyed stereo view)

Bucky ball framework:

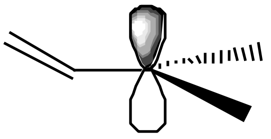


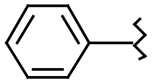
Hetero Benzenes:



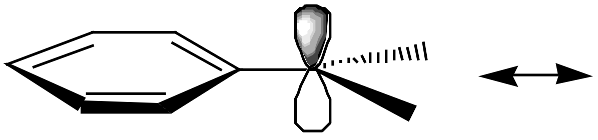
Reactions of Aromatic Compounds:

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





phenyl group

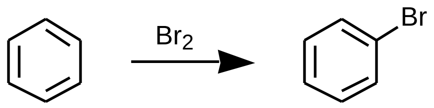


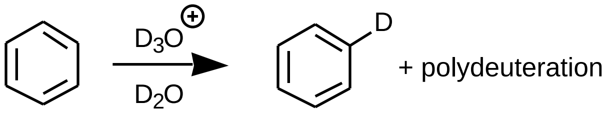
resonance structures:
none as good as the first one
delocalize to ORTHO and PARA
positions; not META

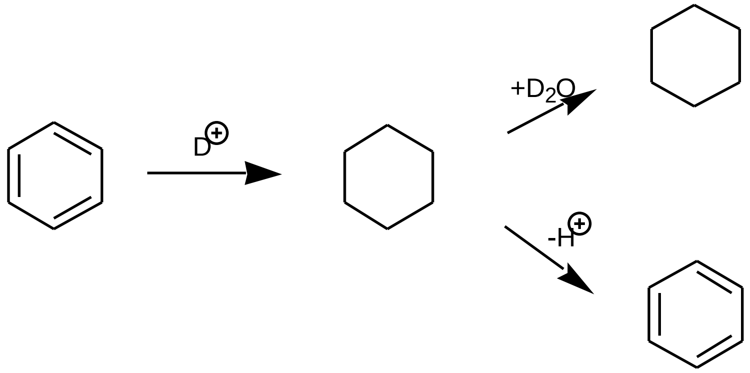
REACTIONS AT THE BENZENE RING:

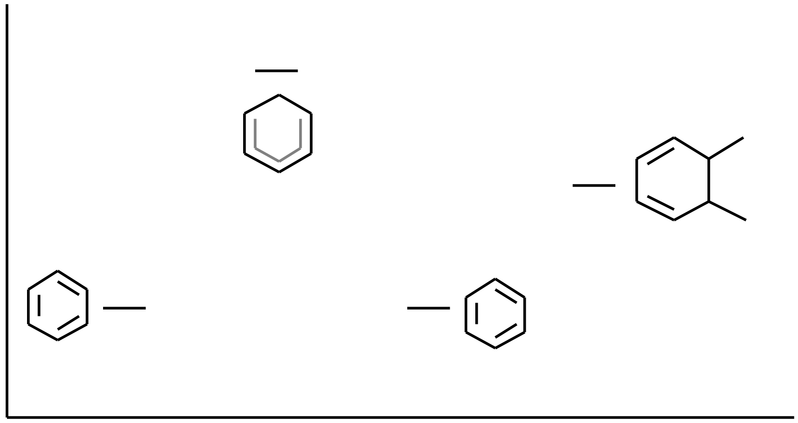
General point: Thermodynamically and Kinetically stabilized, deep valley and high mountains

Disturbing one pi bond removes "aromaticity"

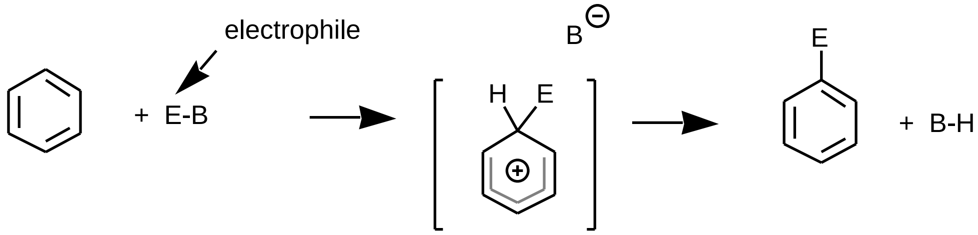




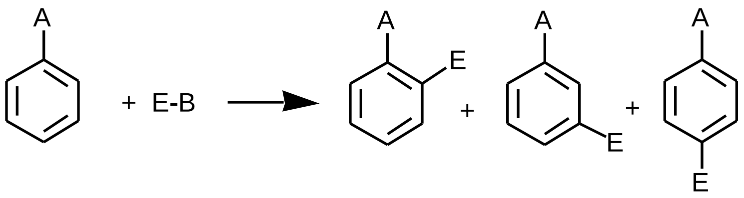




Generic Electrophilic Aromatic Substitution: S_EAr (i.e., benzene is a weak nucleophile)



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



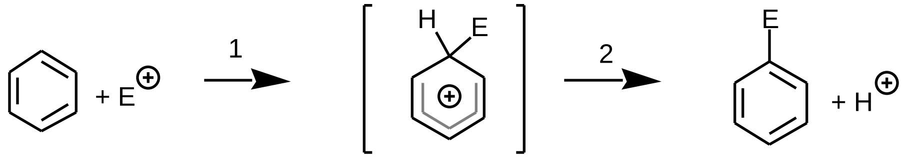
How does the nature of **A** influence the rate and selectivity in the substitution?

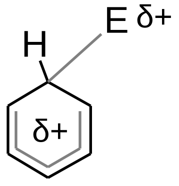
Resonance, Inductive, Steric

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

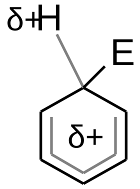
General facts: (a) rate correlates with reactivity of E^+.

(b) faster if **A** = electron donor; slower if **A** = electron withdrawing group.





TS1

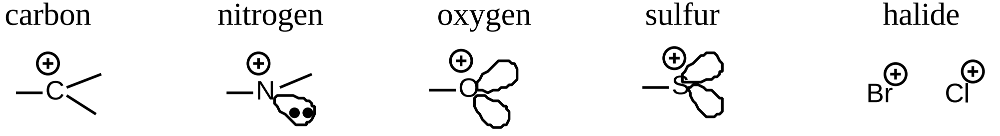


TS1

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

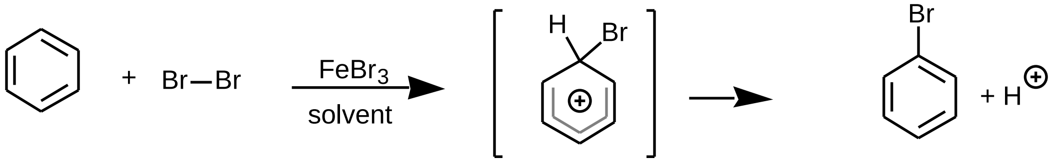
If step 2 is RDS, EWD should ACCELERATE Destabilize intermediate cation (more localized charge)
more than TS (more delocalized charge)

Useful Electrophiles: Think about adding:



Easy ones:

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

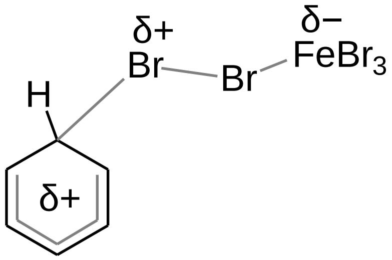


Solvent effects: polar or non-polar?

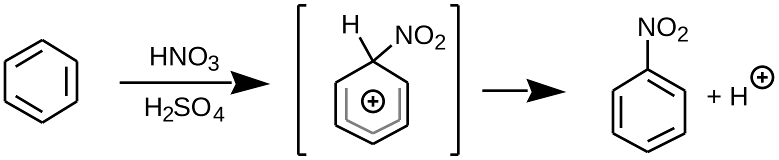
donating or non-donating? (coordinating)

protic or aprotic?

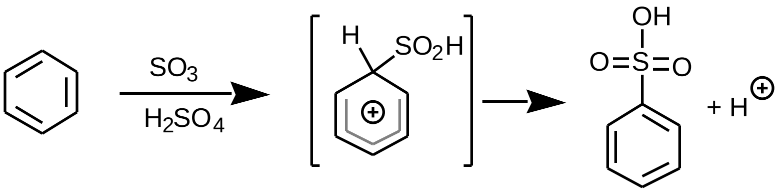
what is the rate-determining TS like?



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



C. Sulfonation: $SO_3 + H_2SO_4$



D. Oxygen?????

E. Carbon Electrophiles?