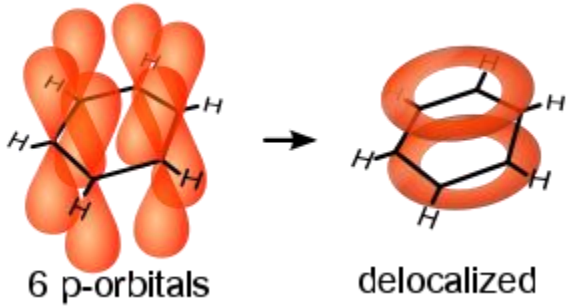
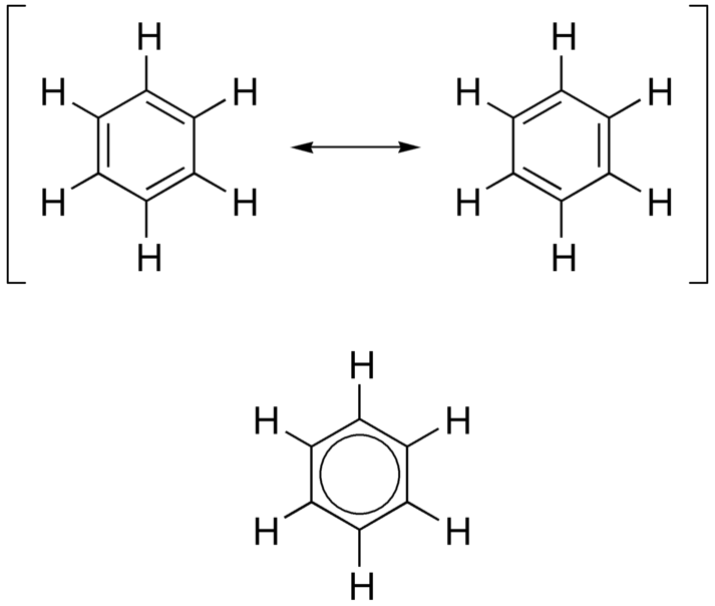
QO 427
Química Orgânica I

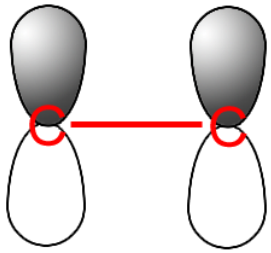
(Engenharia Química)

MARCOS N. EBERLIN

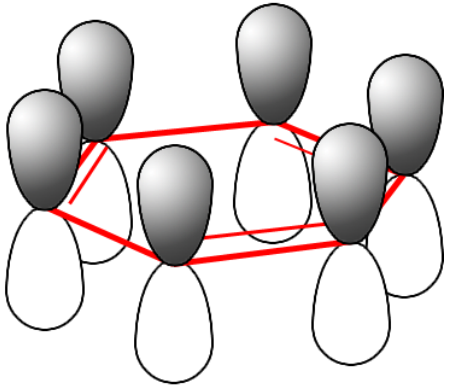
Aromaticidade



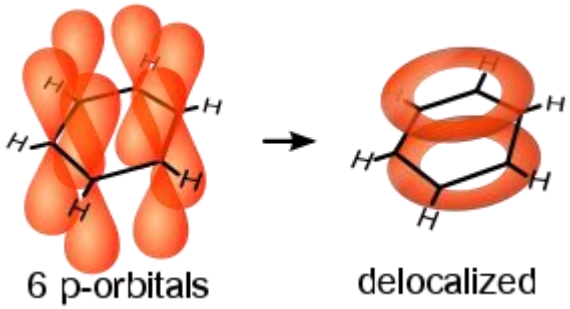




Side view



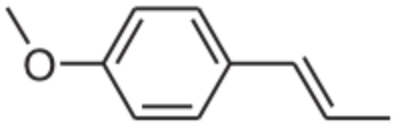
Projection



6 p-orbitals

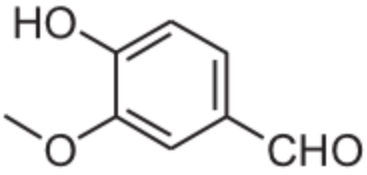
delocalized

Muito mais estável e menos reativo que alcenos



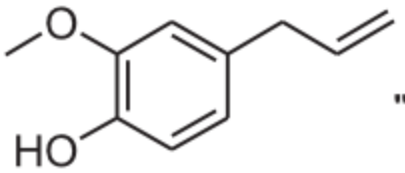
Anetol

"Extrato de Erva Doce"
Pimpinella anisum L.



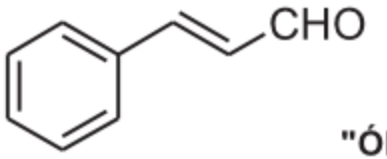
Vanilina

"Extrato de Gluco-Vanilina"
Vanilla planifolia



Eugenol

"Óleo de Cravo da Índia"
Eugenia caryophyllata



Cinamaldeído

"Óleo de Canela da Índia"
Cinamomum zeylanecum

COMPOSTO DE FORTE ODOR, QUE TÊM PROPRIEDADES SINGULARES, DESCOBERTO NO COMEÇO DO DESENVOLVIMENTO DA QUÍMICA.

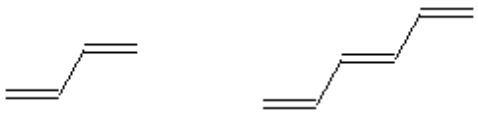
O Benzeno foi descoberto em 1825 por Michael Faraday (1791 - 1867) no gás de iluminação usado em Londres na época. Faraday isolou o benzeno pela compressão do gás de iluminação, obtido pela pirólise do óleo de baleia. À partir de uma mancha oleosa que havia sido depositada como resultado da queima de gás usado por uma lamparina.

Faraday fez vários testes com o novo composto, e descobriu que ele tinha o mesmo número de átomos de carbono quanto de hidrogênio, e portanto, o chamou de "hidrogênio carburetado", numa tradução meio liberal da terminologia inglesa do passado.

Faraday viria a ficar famoso, inclusive recebendo o Prêmio Nobel, pelos trabalhos em conjunto com Maxwell na unificação das teorias da Eletricidade e do Magnetismo.

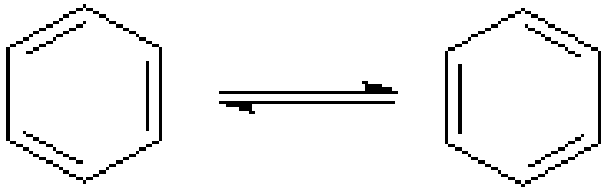
O Grande Enigma: quem se liga a quem?

O fato de o benzeno possuir o mesmo número de átomos de carbono e de hidrogênio colocava uma questão intrigante aos cientistas do Século 19: qual a estrutura do composto? Suspeitava-se que ele possuía a estrutura de um poli*eno*, ou seja, um composto com as duplas ligações conjugadas, como no butadieno ou no hexatrieno, por exemplo:

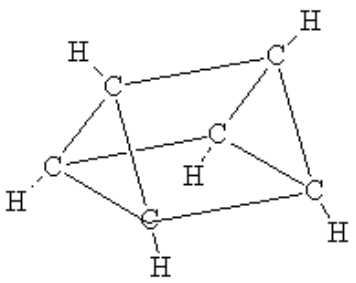


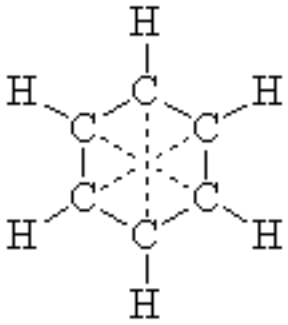
Foi então que Friedrich August Kekulé von Stradonitz, mais conhecido por apenas **Kekulé** (1829 - 1896), teve um sonho enquanto pegava no sono diante da sua lareira. Ele mesmo descreve: *"meu olho mental... podia agora distinguir grandes estruturas com as mais variadas conformações; longas filas, algumas vezes comprimida umas com as outras, todas girando e se enrolando como cobras. Mas olhe! O quê é aquilo? Uma das cobras mordeu o seu próprio rabo!"* Com esse sonho, Kekulé sugeriu a estrutura de ciclohexatrieno para o benzeno que era um anel hexagonal.

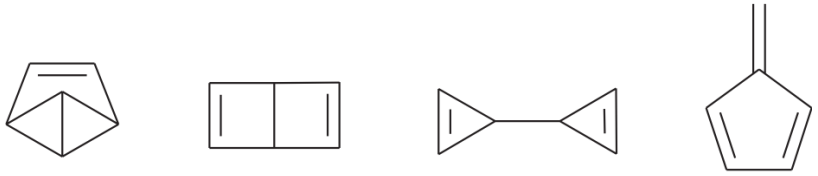
Logo depois,no ano seguinte, Kekulé propôs a hipótese da existência de um par de estruturas em equilíbrio, com a alternância de ligações duplas:

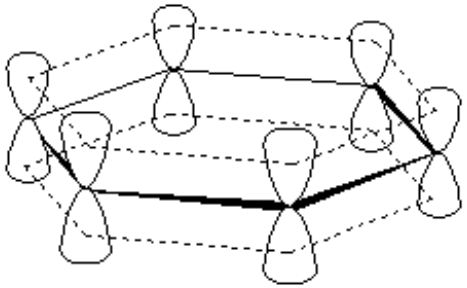


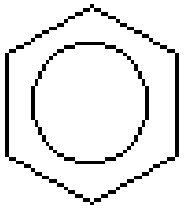
Mas tal (ou tais) estrutura(s) deveria (m) ser altamente reativa (s). Outros químicos sugeriram então estruturas como o centróide (Armstrong) ou o prismano (Ladenburg):

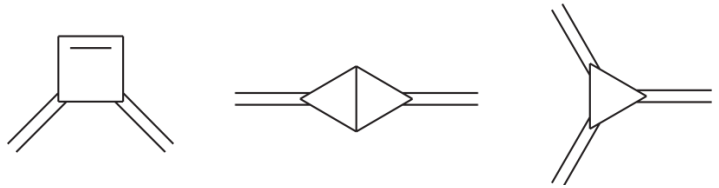




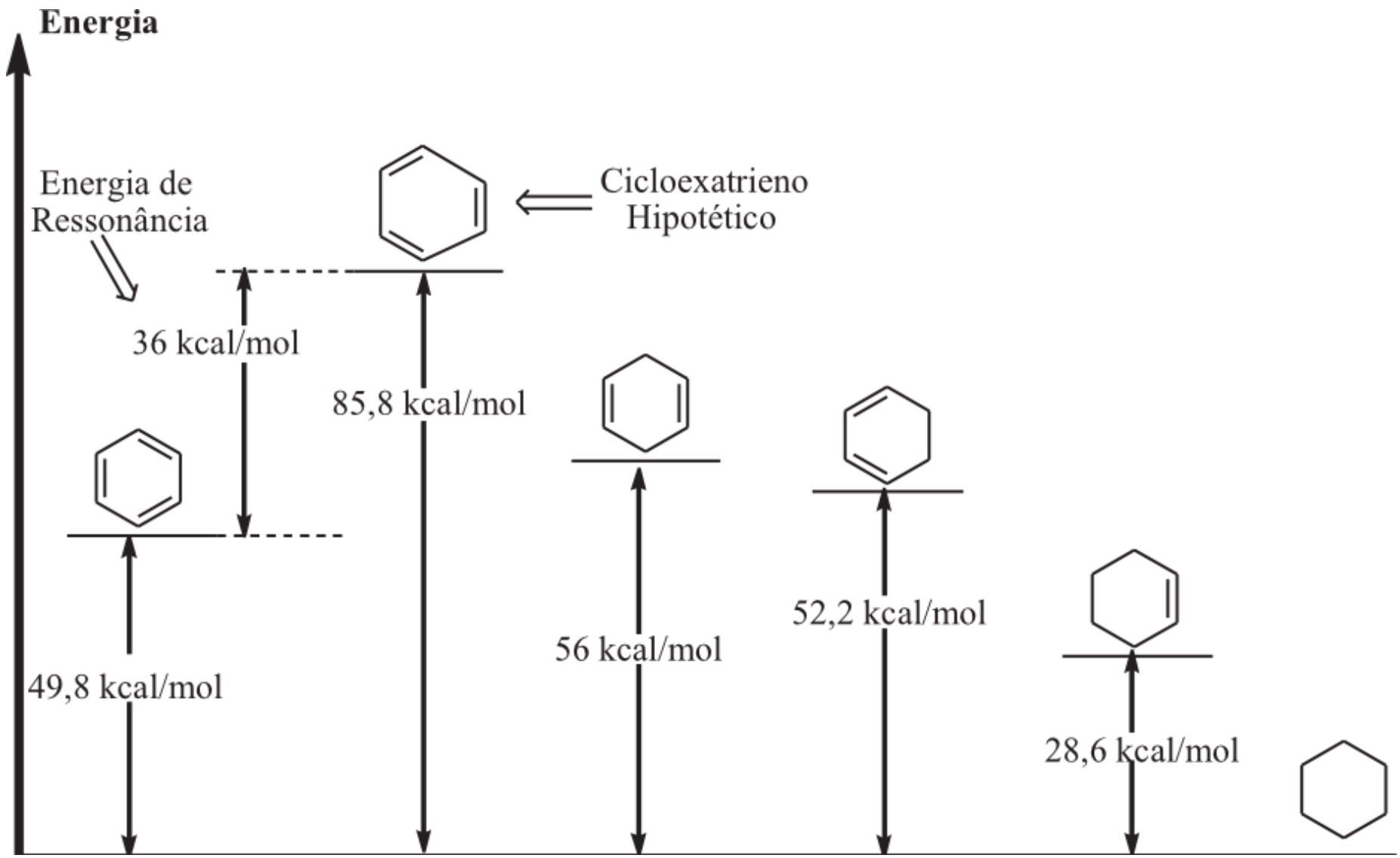






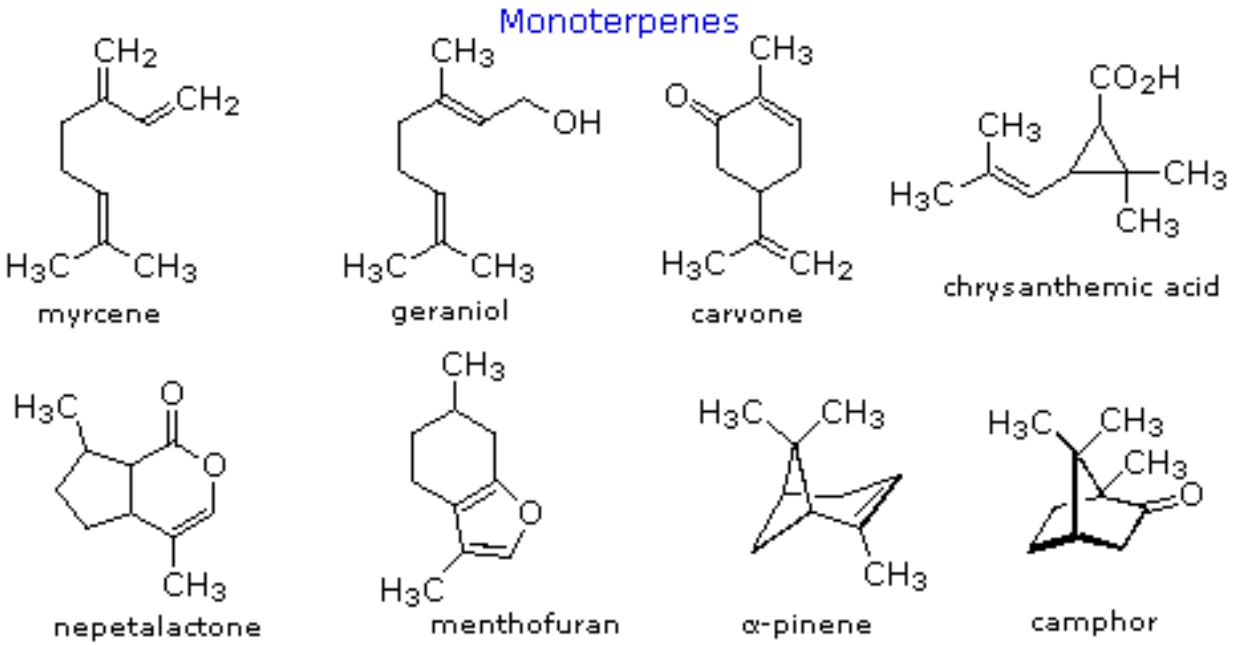


De fato, os isômeros de valência do benzeno, ou seja, os outros C_6H_6 que conhecemos, são todos menos estáveis, e se transformam no benzeno quando aquecidos. São eles o benvaleno, o prismano, o biciclopropenilo e o fulveno:


Energia
Energia de Ressonância
Cicloexatrieno Hipotético
36 kcal/mol
85,8 kcal/mol
49,8 kcal/mol
56 kcal/mol
52,2 kcal/mol
28,6 kcal/mol

1. Termo “Aromático" August Wilhelm Hofmann in 1855.

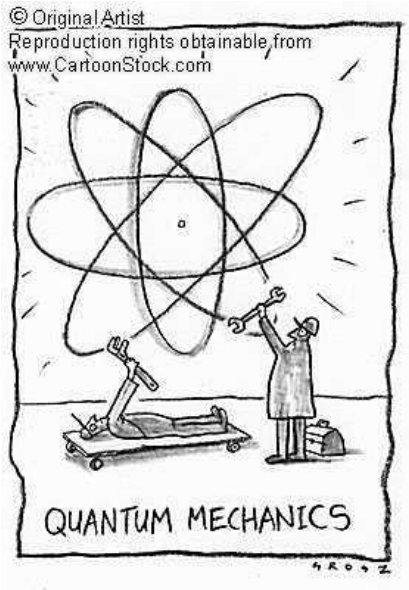
2. Nem todos os aromáticos tem aromas fortes . Terpenos são mais “aromáticos” que os aromáticos = alto grau de insaturação

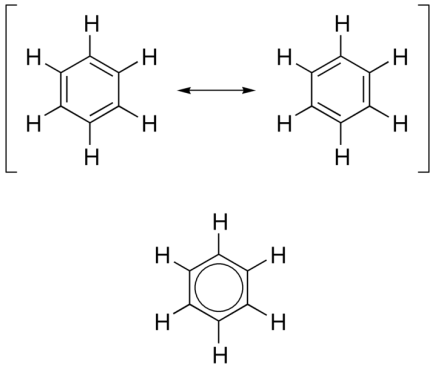


3. A estrutura ciclohexatrieno do benzeno foi proposta por August Kekulé em 1865.

4. Foi sempre um mistério o porque de moléculas tão insaturadas serem tão estáveis = pouco reativas.

5. Explicação vem da mecânica quântica.





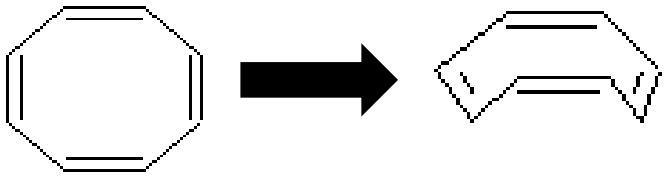
Um composto aromático (arila) contém um conjunto de átomos ligados covalentemente com características específicas:

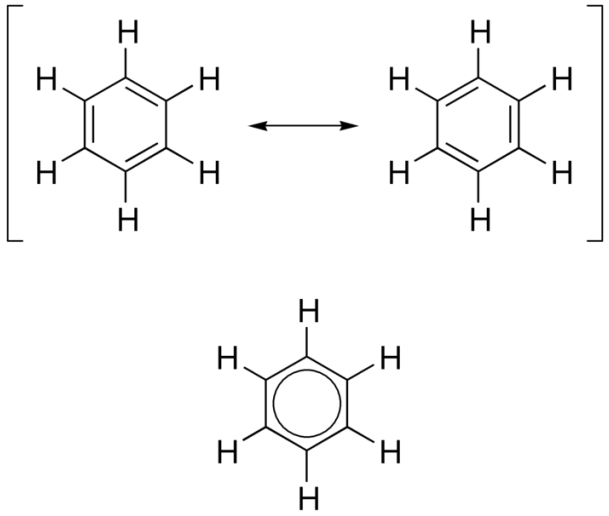
1.Um sistema conjugados de elétrons π deslocalizados, alternância de ligações simples e duplas.

2.Estrutura coplanar, com todos os átomos contribuintes no mesmo plano.

3.Átomos dispostos em um ou mais anéis.

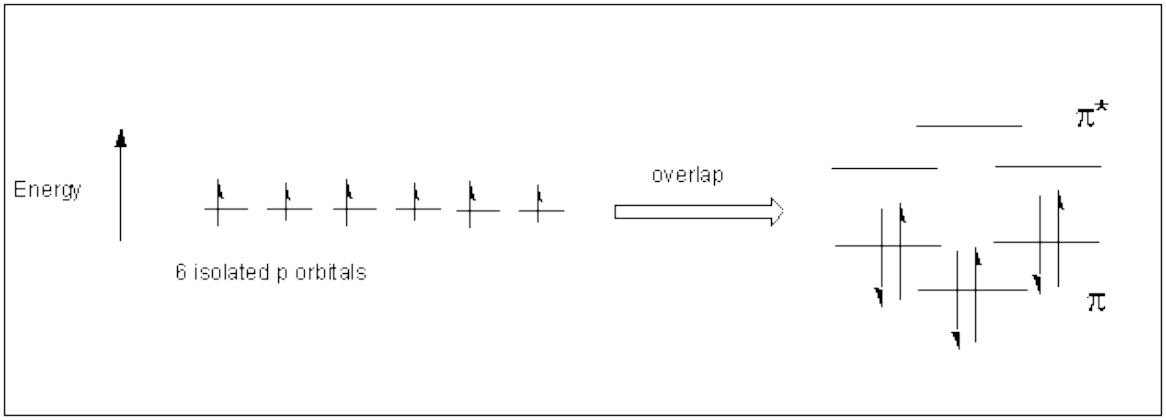
4. Número de elétrons π deslocalizados dados pela equação 4n + 2 elétrons π, onde n = 0, 1, 2, 3, ... Regra de Hückel

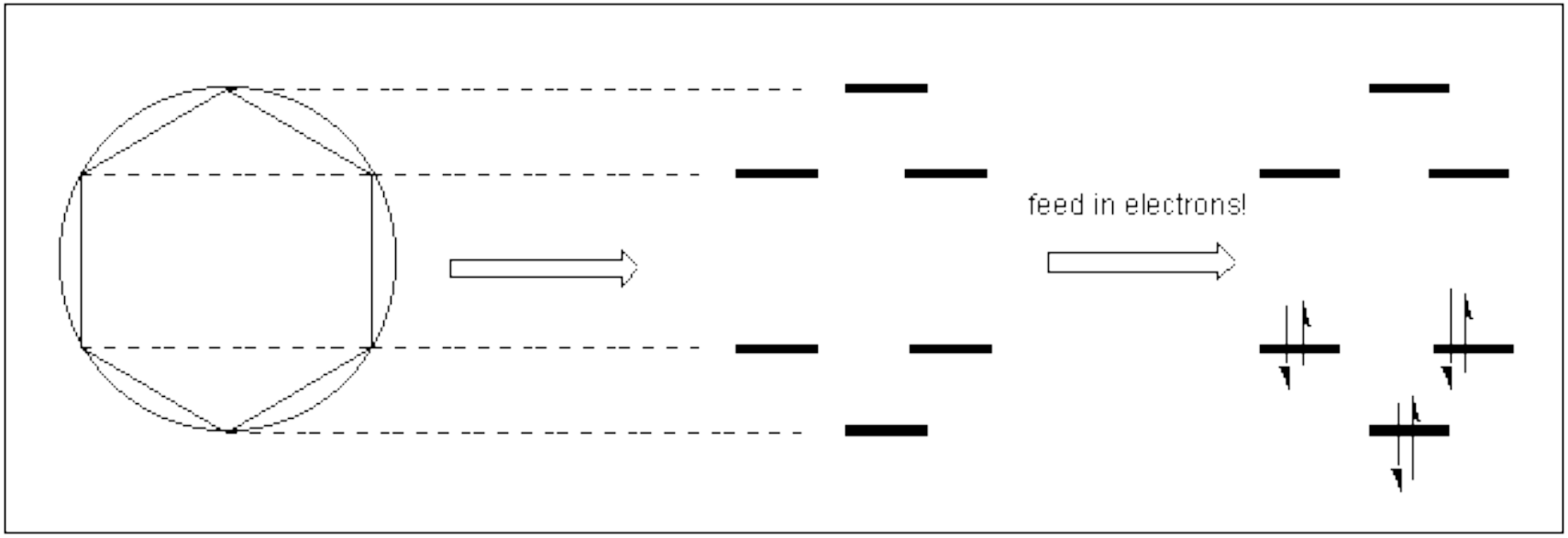


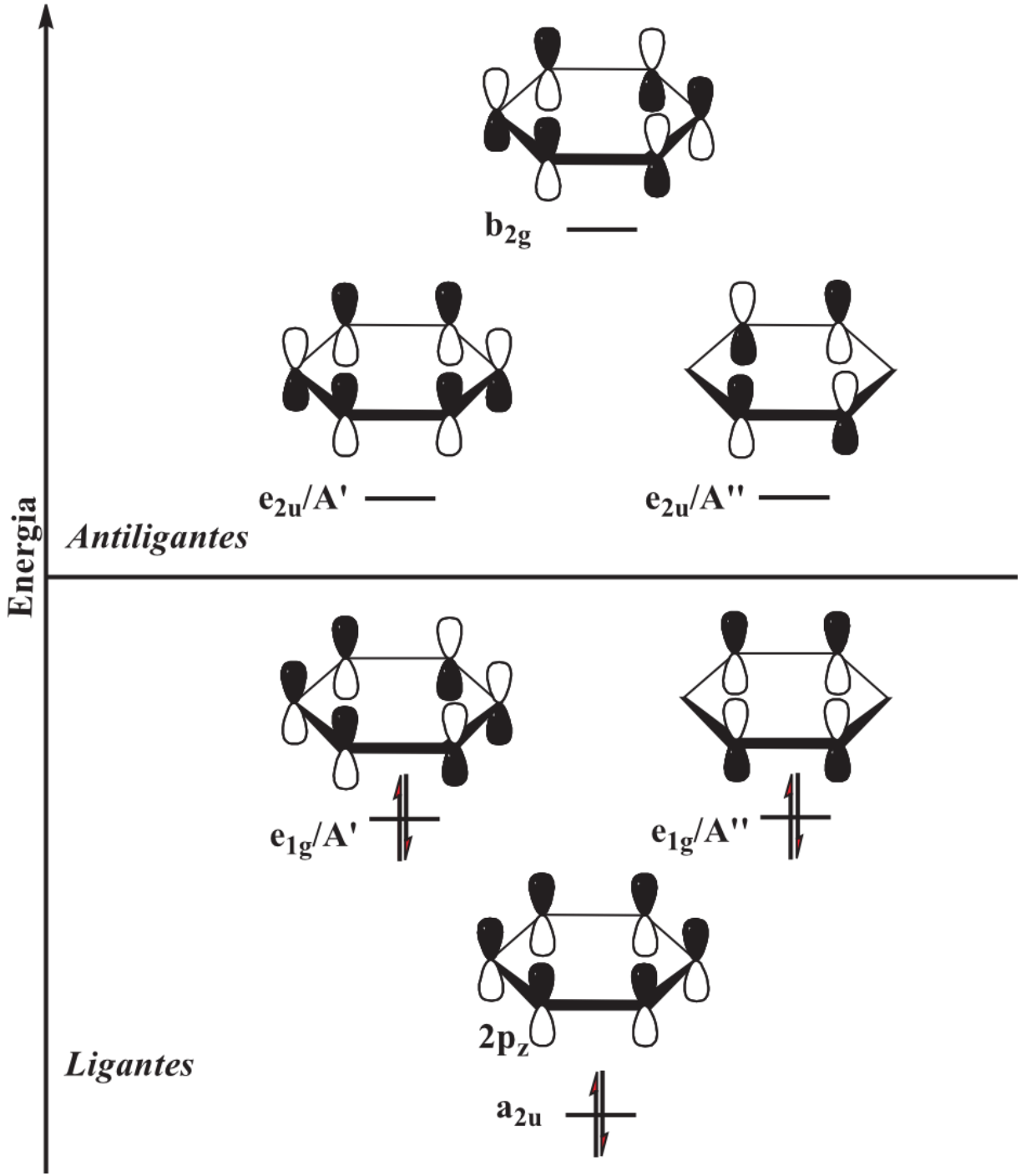


4. Número de elétrons π deslocalizados dados pela equação 4n + 2 elétrons π, onde n = 0, 1, 2, 3, ... Regra de Hückel

Hückel mostrou que hidrocarbonetos cíclicos com (4*n*+2) elétrons π (sendo *n* um número inteiro) possuíam uma estabilidade *extra* de energia, isto porque seriam compostos de camada de valência fechada (sem elétrons desemparelhados) – aromáticos.

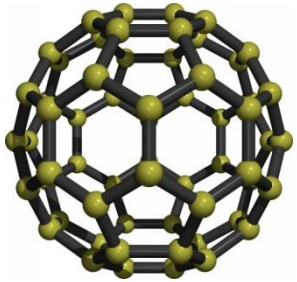


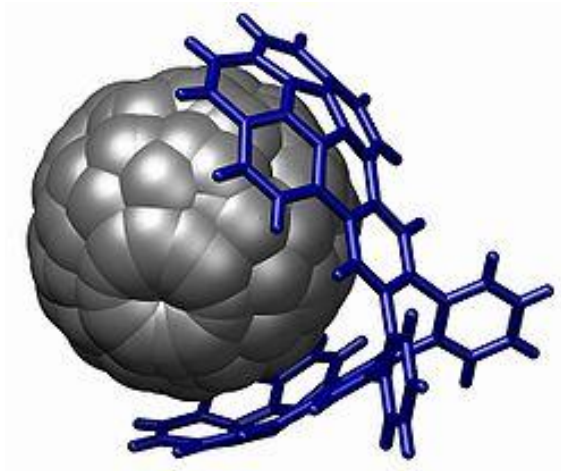


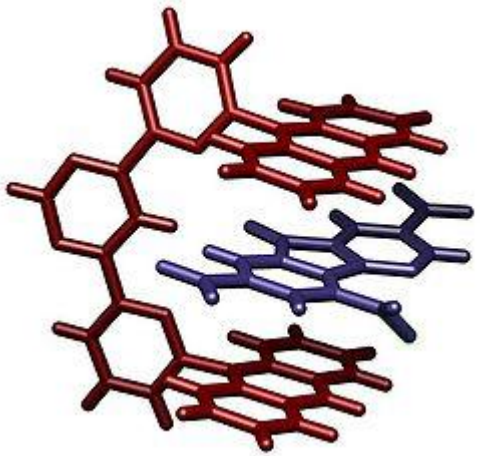

Energia
b2g
e2u/A'
e2u/A''
Antiligantes
e1g/A'
e1g/A''
2pz
Ligantes
a2u

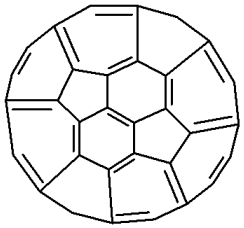
1. Moléculas aromáticas são capazes de interagir por empilhamento π-π.

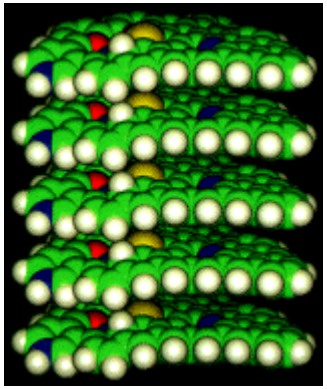
2. Muitos dos primeiros exemplos conhecidos de compostos aromáticos, como benzeno e tolueno, tem cheiro agradável distintivo.



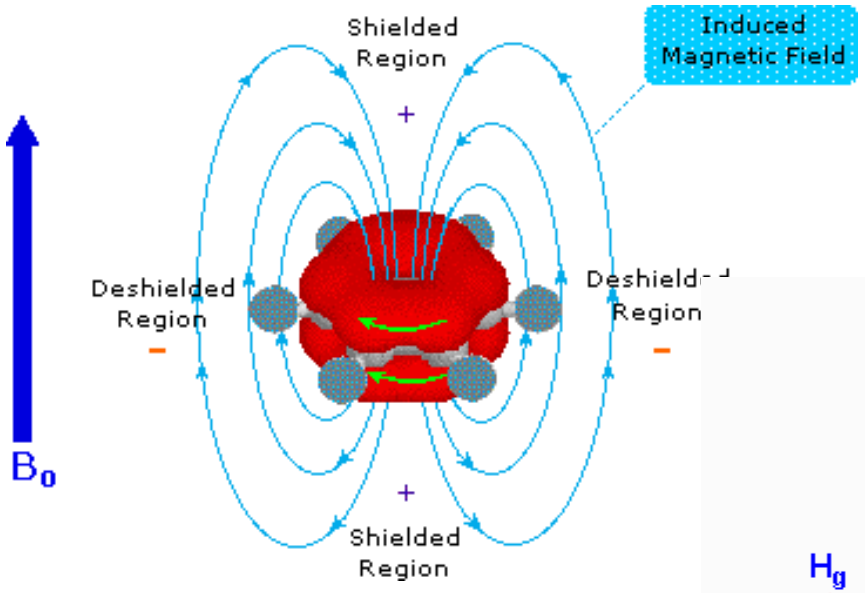








3. Os elétrons π que circulam em uma molécula aromática produzem correntes e campos magnéticos que se opõem ao campo magnético aplicado em RMN.



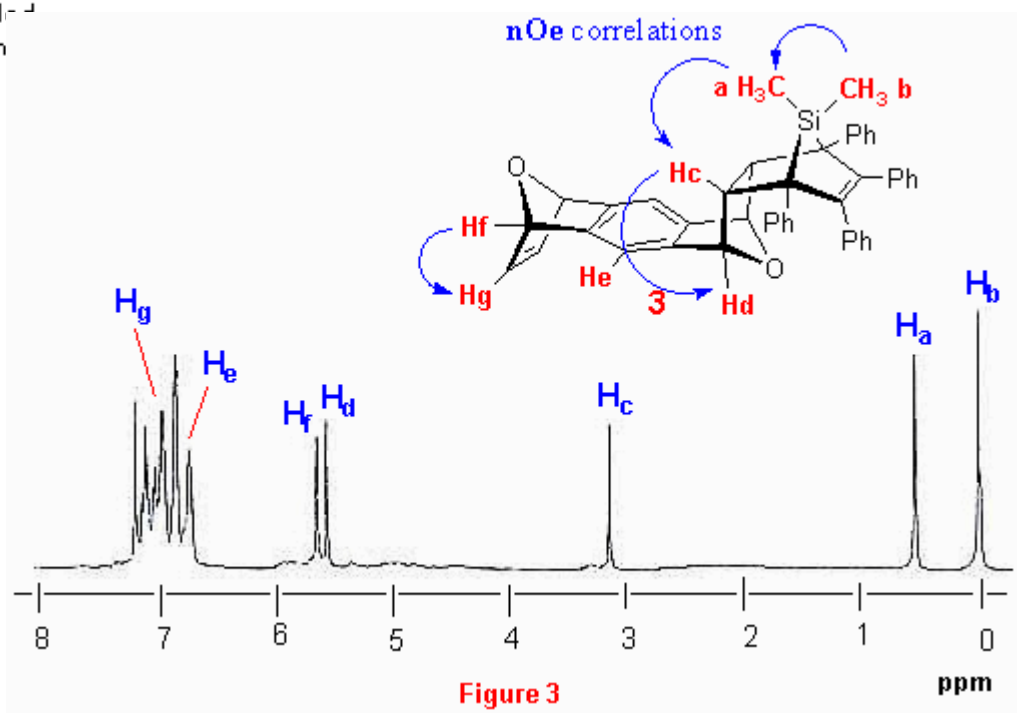
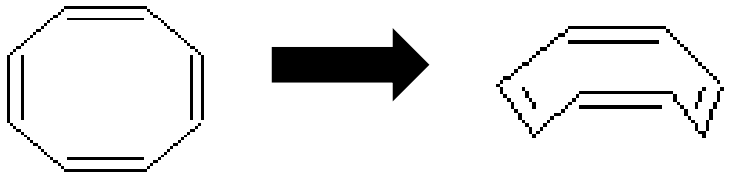
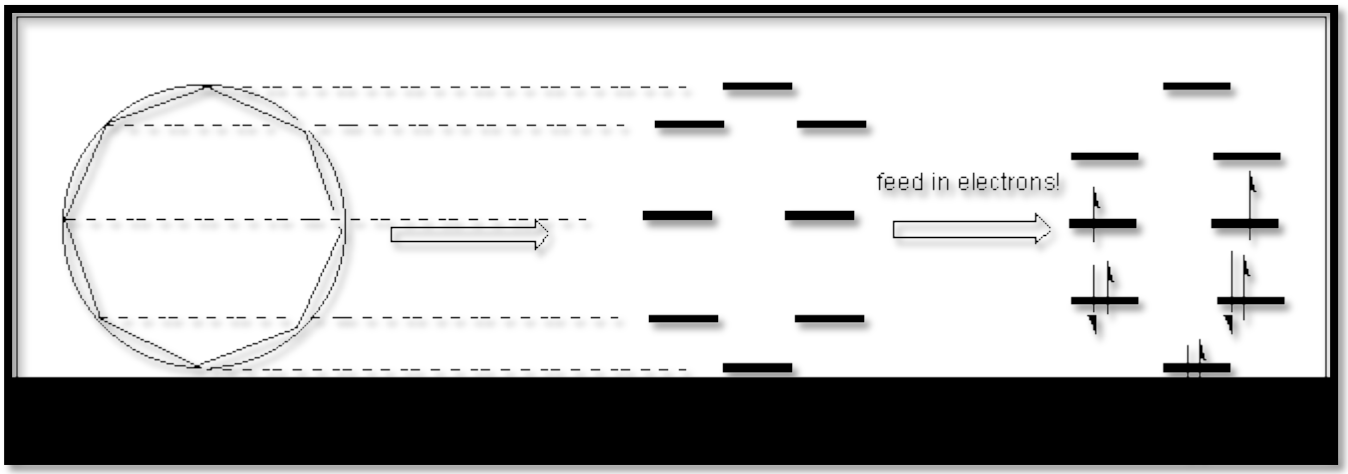
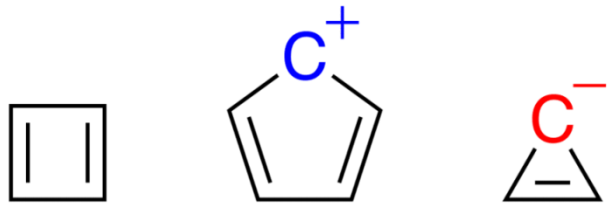


Figure 3

4. Moléculas monocíclicas contendo 4n elétrons π planares são anti-aromáticas ou não-aromáticas.

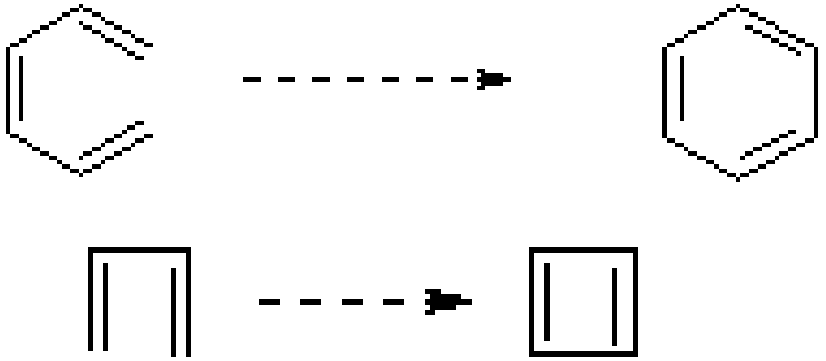




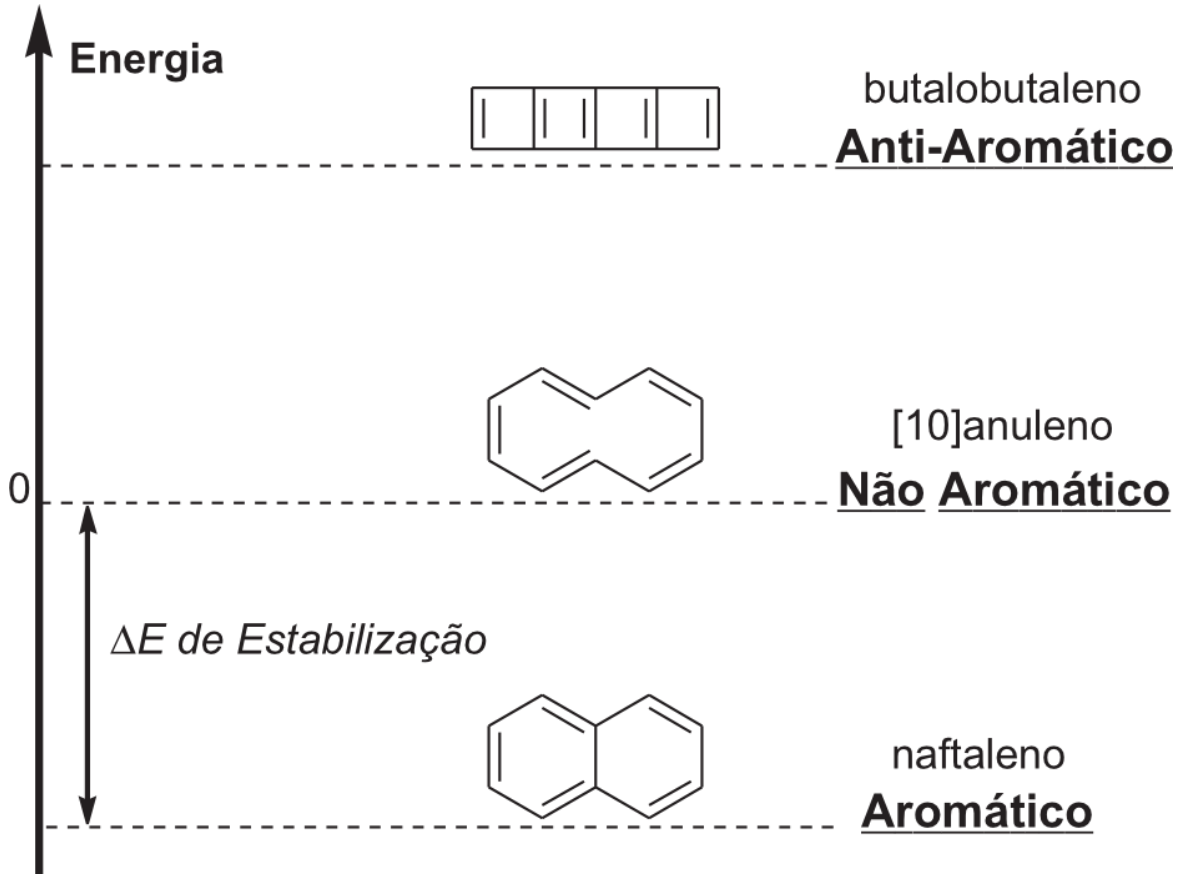


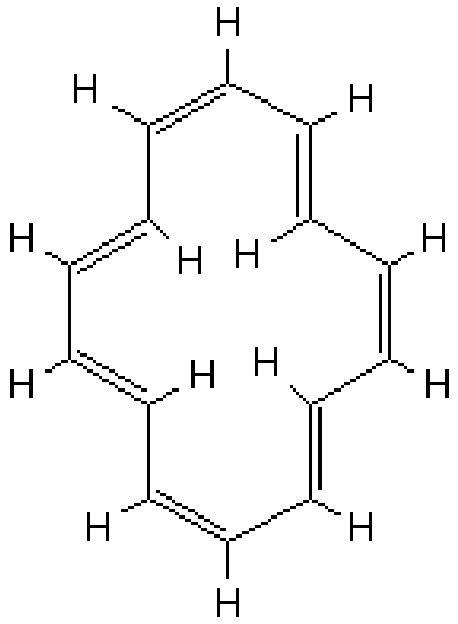
A **B** **C**

Aromático
Anti-aromático
Não-aromático



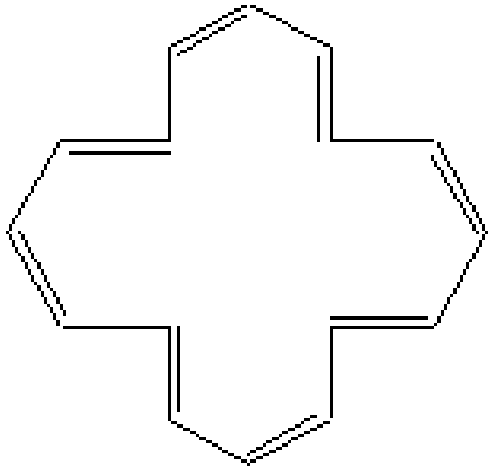
Uma molécula antiaromática é um sistema cíclico contendo ligações simples e duplas alternadas, onde a energia de elétrons pi de compostos antiaromáticos é maior do que a sua congênere de cadeia aberta.





(4n+2)electrons
n = 3
aromatic

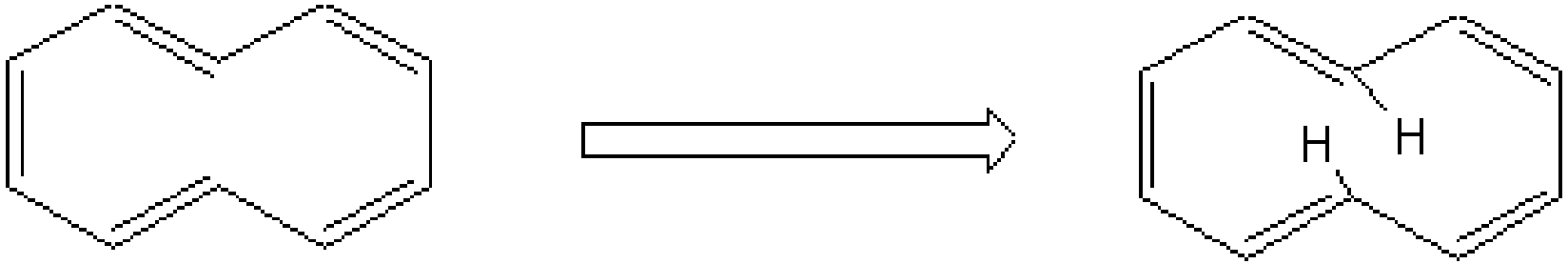
[14] anuleno

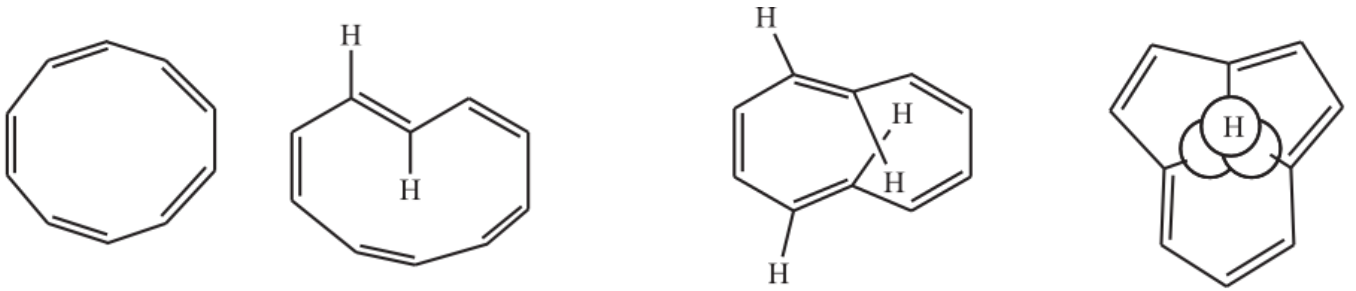


(4n)electrons
NOT aromatic

[16] anuleno

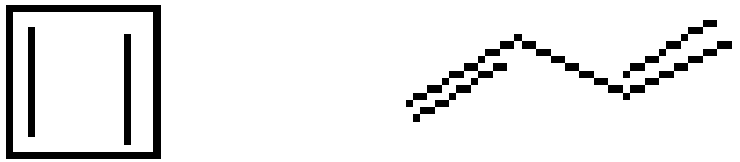
[10] anuleno? **aromático por teoria mas não aromático na prática**

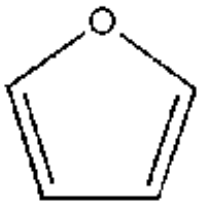




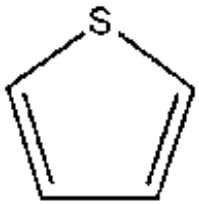
cis-[10]anuleno *mono-trans*-[10]anuleno *di-trans*-[10]anuleno *tri-trans*-[10]anuleno

[4] anuleno? Ciclobutadieno? Síntese em 1965 mas como um tempo de vida muito curto, mais instável que butadieno – anti-aromático

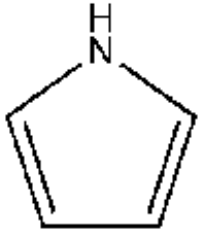




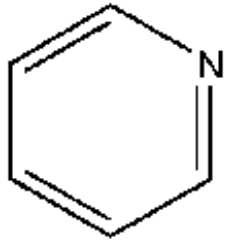
furan



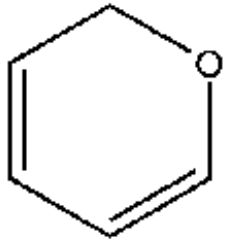
thiophene



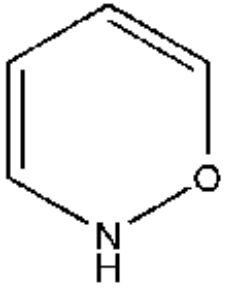
pyrrole



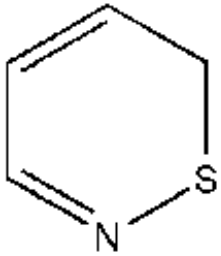
pyridine



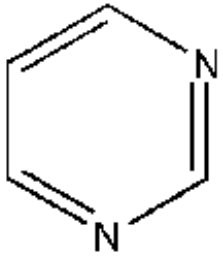
pyran



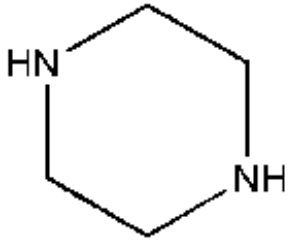
oxazine



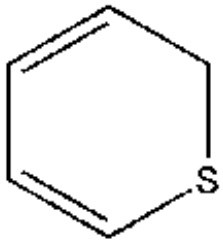
thiazine



pyrimidine

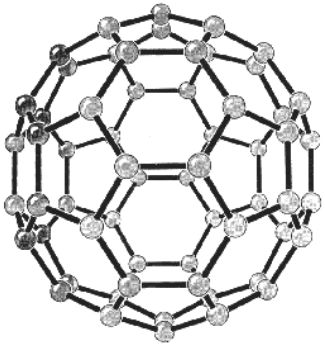


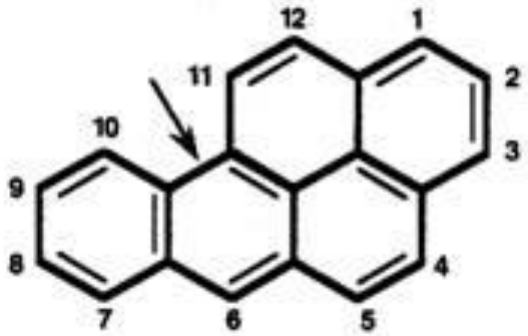
piperazine



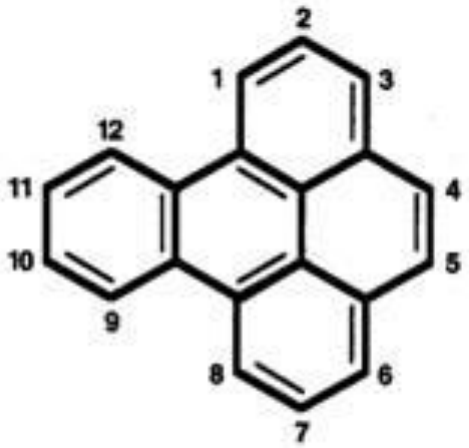
thiine

12
C
O VERSÁTIL CARBONO
6

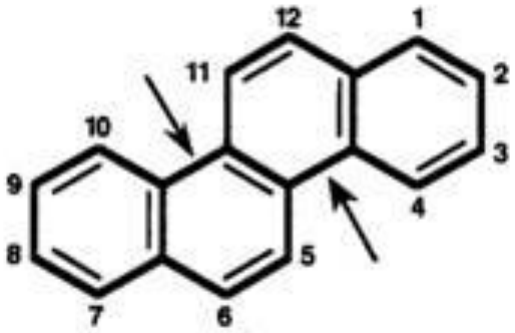




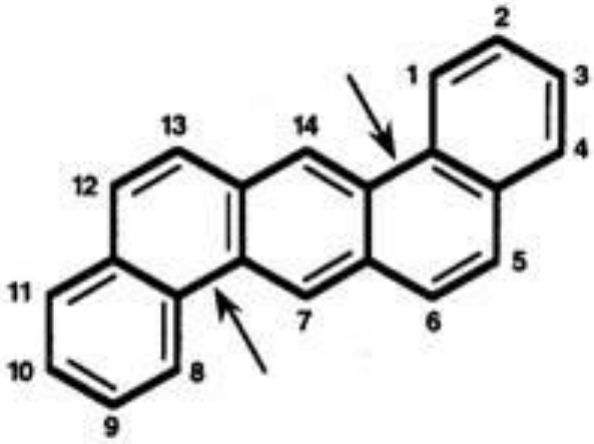
Benzo[*a*]pyrene



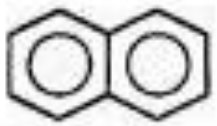
Benzo[*e*]pyrene



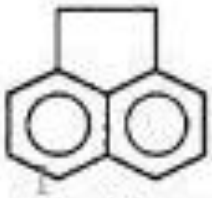
Chrysene



Dibenz[*a*,*h*]anthracene



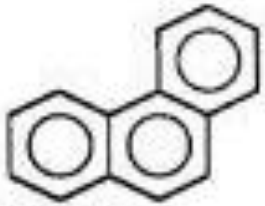
Naphthalene
($C_{10}H_8$) *



Acenaphthene
($C_{12}H_{10}$) *

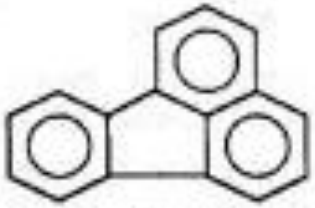
Acenaphthylene
($C_{12}H_8$) *

Fluorene
($C_{13}H_{10}$) *



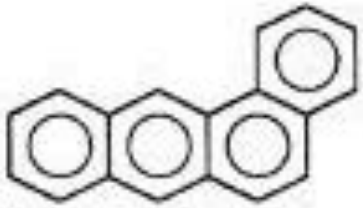
Phenanthrene
($C_{14}H_{10}$) *

Anthracene ($C_{14}H_{10}$) *

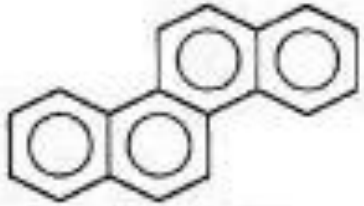


Fluoranthene ($C_{16}H_{10}$) *

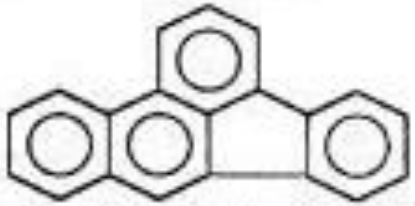
Pyrene
($C_{16}H_{10}$) *



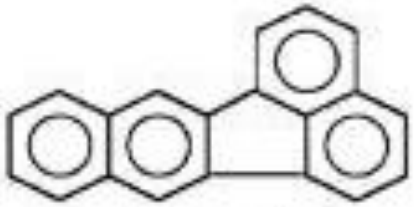
Benz[a]anthracene
($C_{18}H_{12}$) *



Chrysene ($C_{18}H_{12}$) *

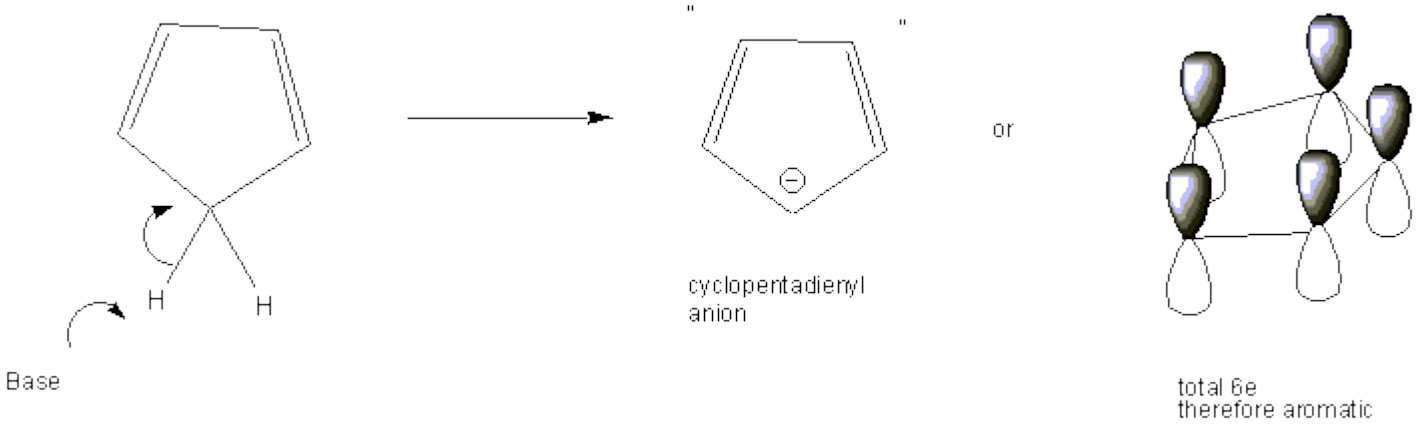


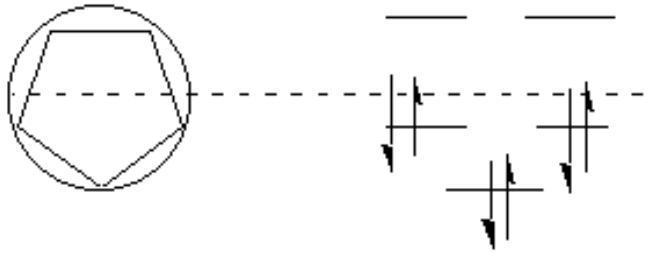
Benzo[*b*]fluoranthene ($C_{20}H_{12}$) *



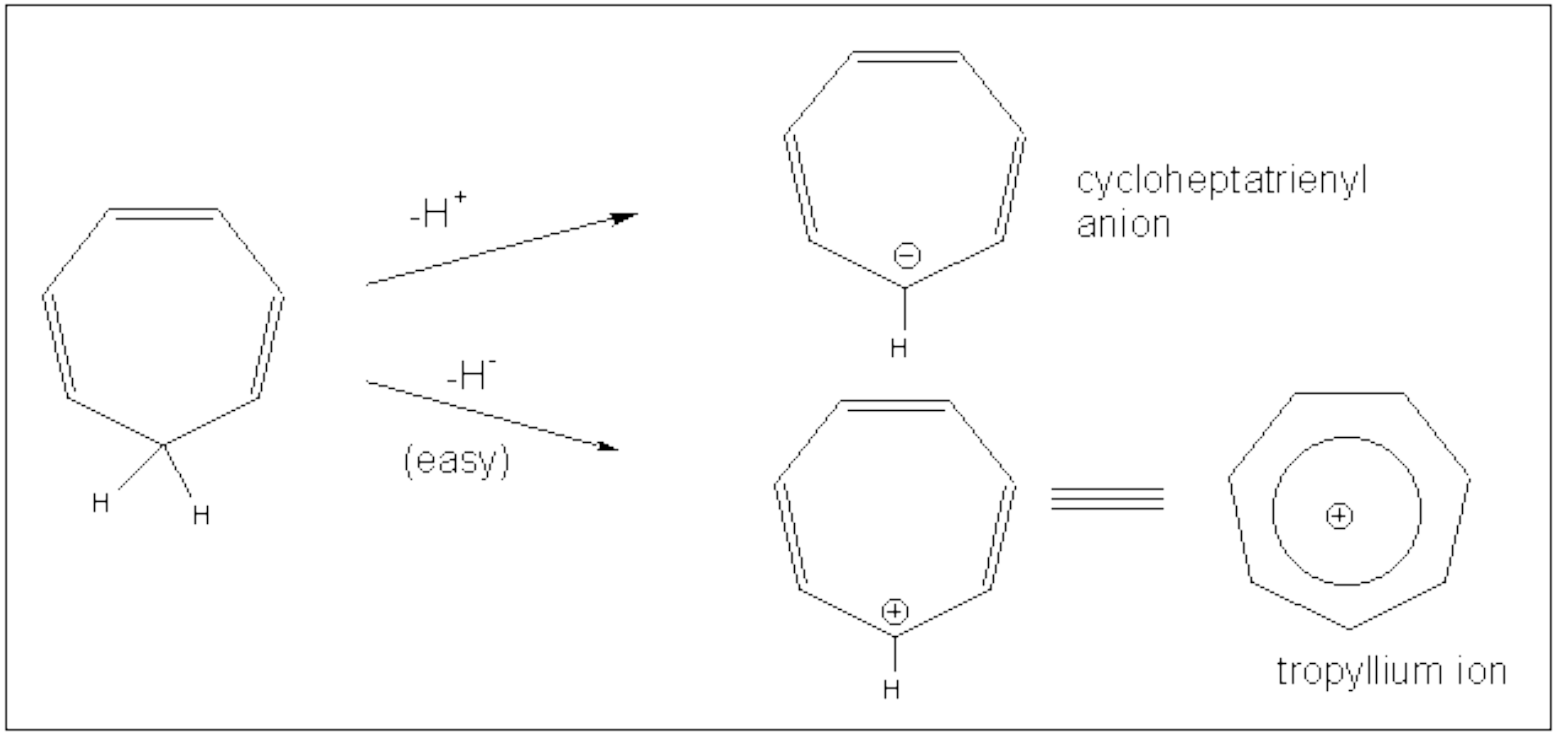
Benzo[*k*]fluoranthene ($C_{20}H_{12}$) *

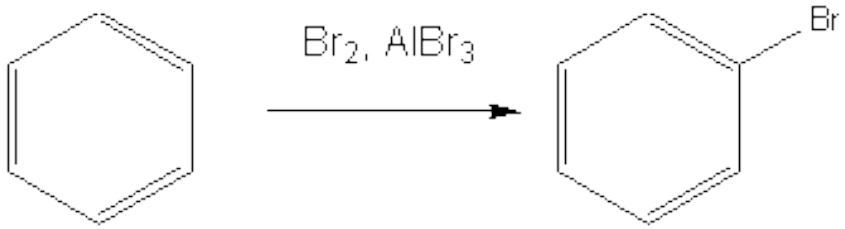
Ciclopentadiene é relativamente ácido pKa = 16





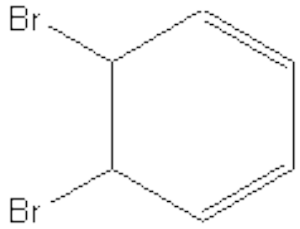
Cicloheptadriene pKa = 36. Perda de hidreto é favorecido – cátion tropílio



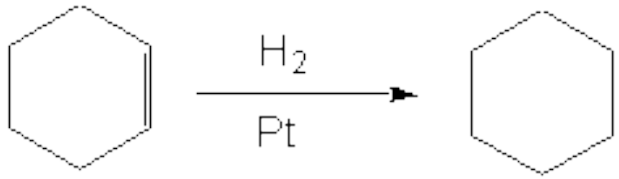


electrophilic substitution (S_EAr)

NOT

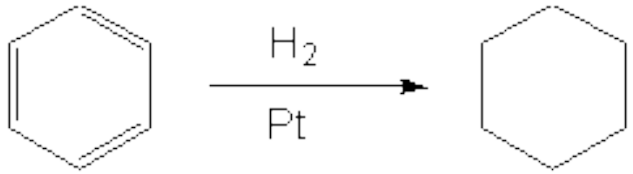


addition (normal for alkenes)



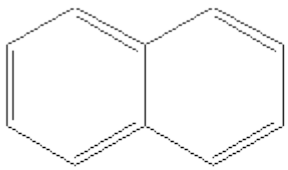
$\Delta H = -119 kJ/mol$

BUT



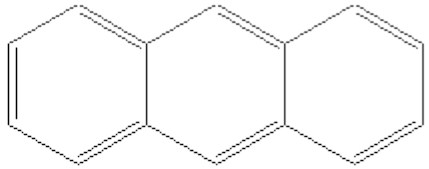
$\Delta H = -207 kJ/mol$

(Expect 3x-119=357kJ/mol)



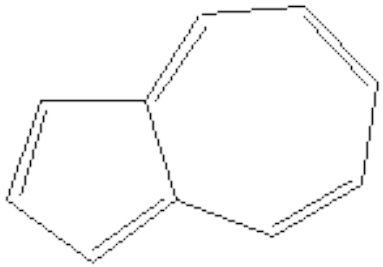
naphthalene

RE 254kJ/mol

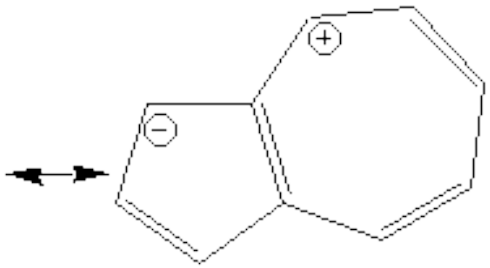


anthracene

RE 350kJ/mol

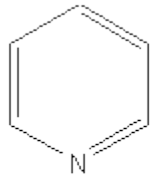


azulene

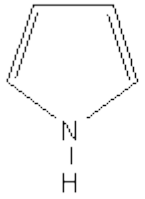


etc

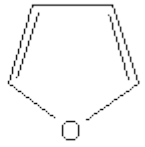
RE 204kJ/mol



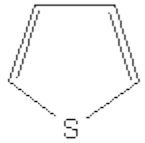
pyridine



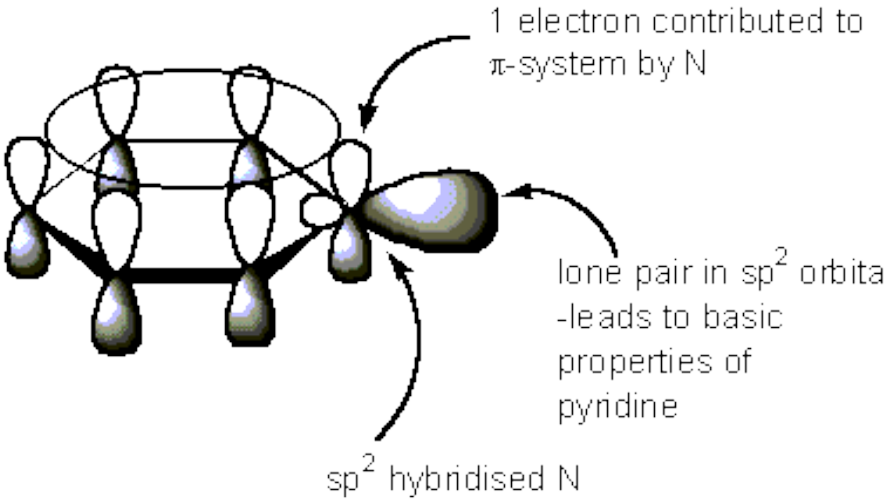
pyrrole

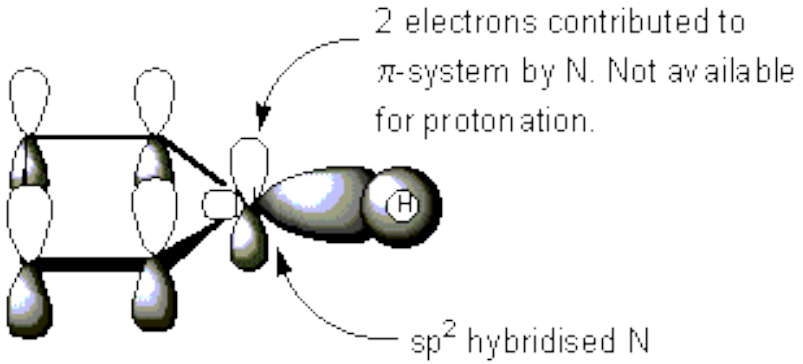


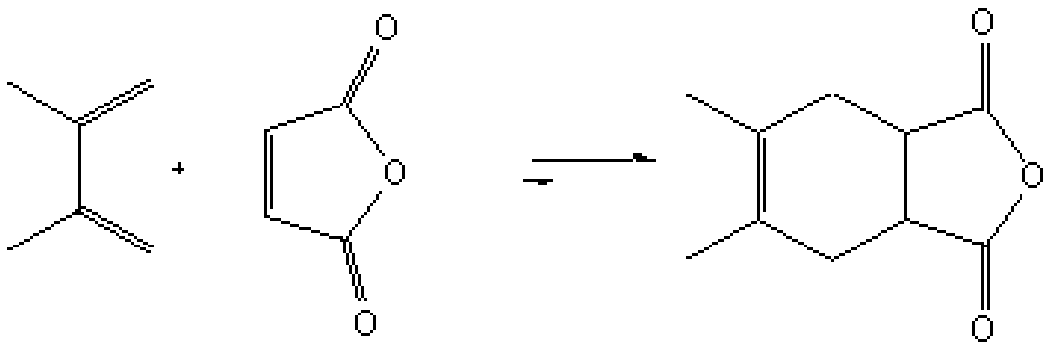
furan



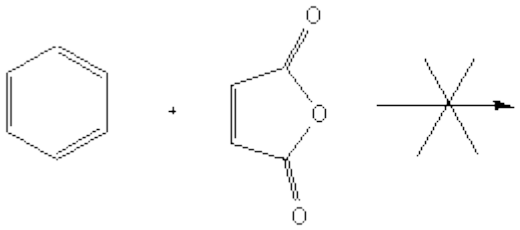
thiophene



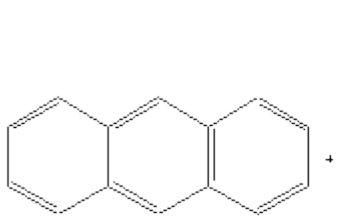


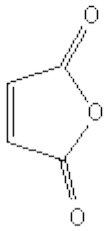


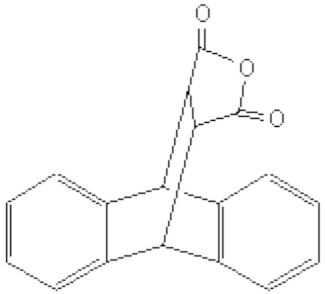
maleic anhydride



NO REACTION

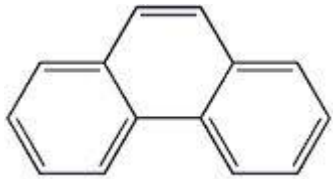






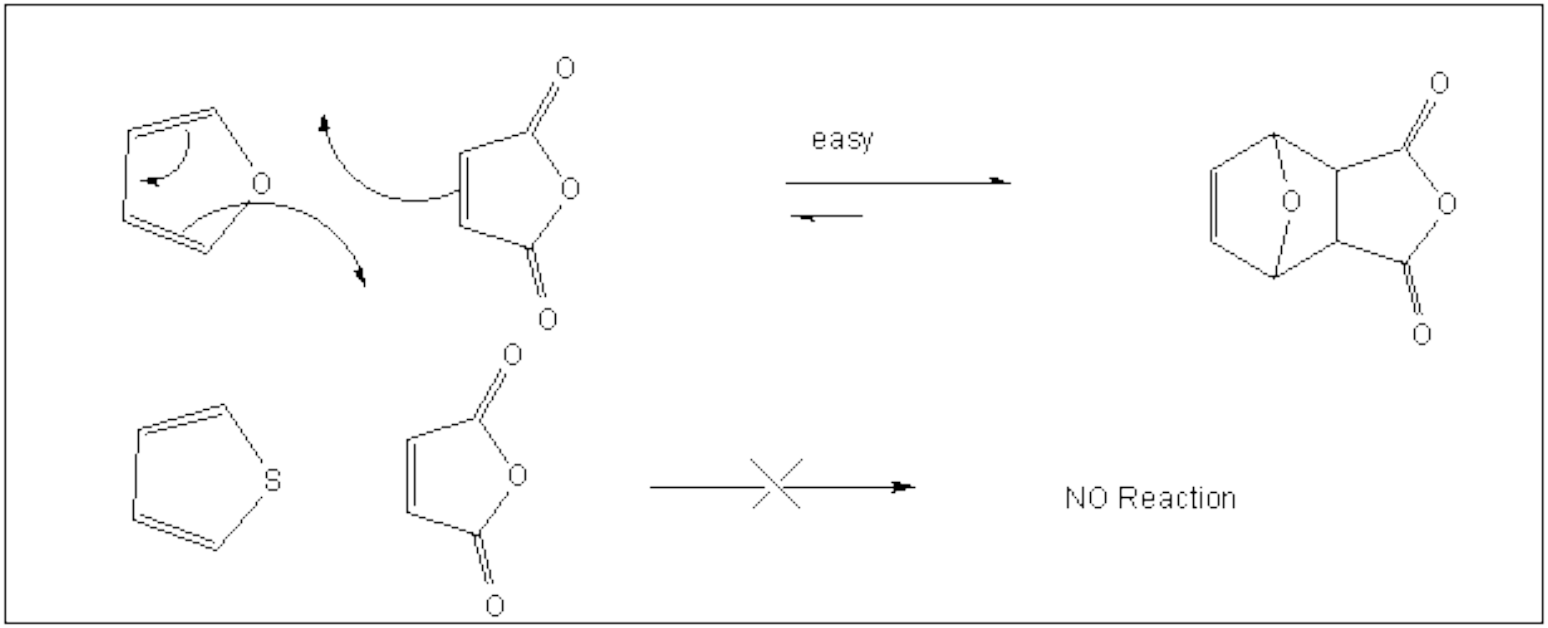
RE = 350kJ/mol

RE = 2x150 = 300kJ/mol

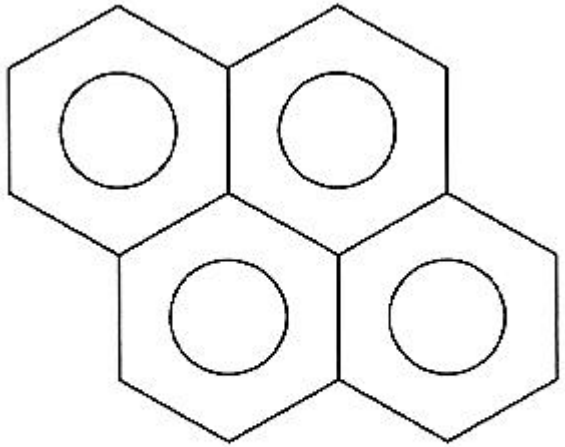


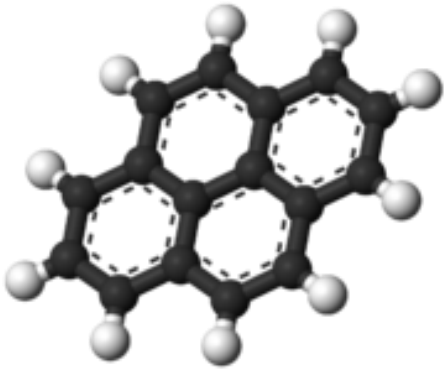
Phenanthrene

Therefore loss of RE = 50kJ/mol



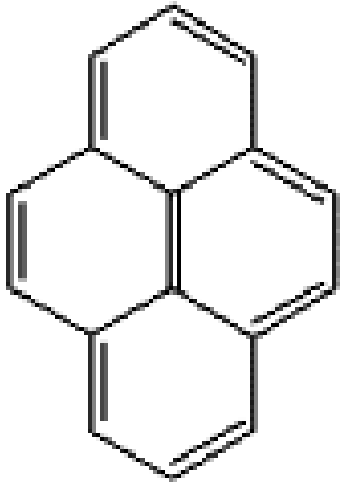
Tiofeno é mais aromático do que furano!

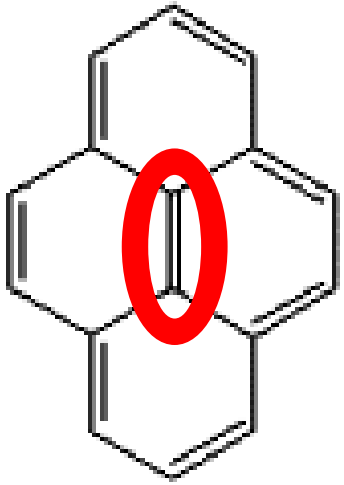


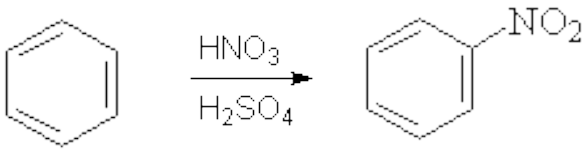


Pyrene

$C_{16}H_{10}$



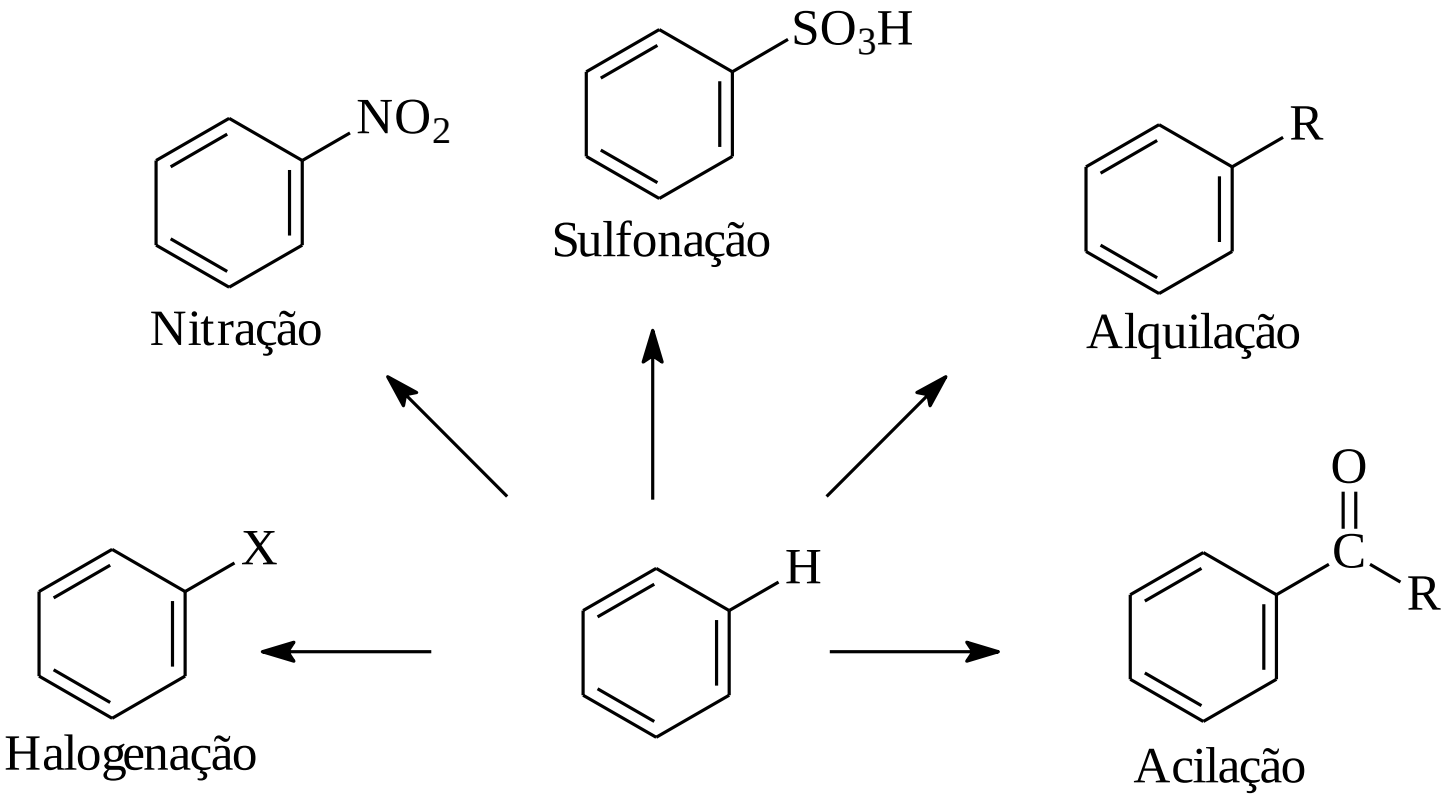


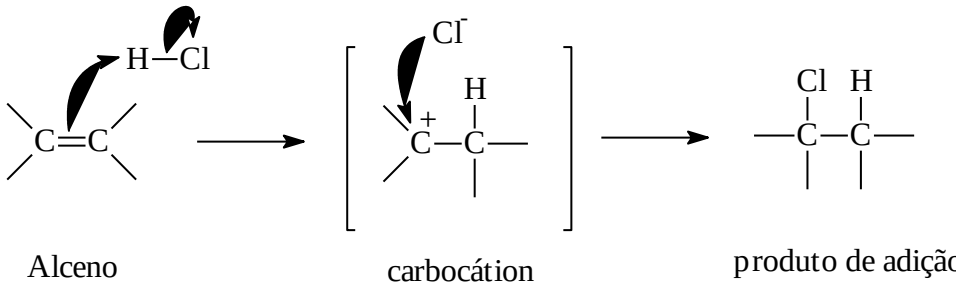


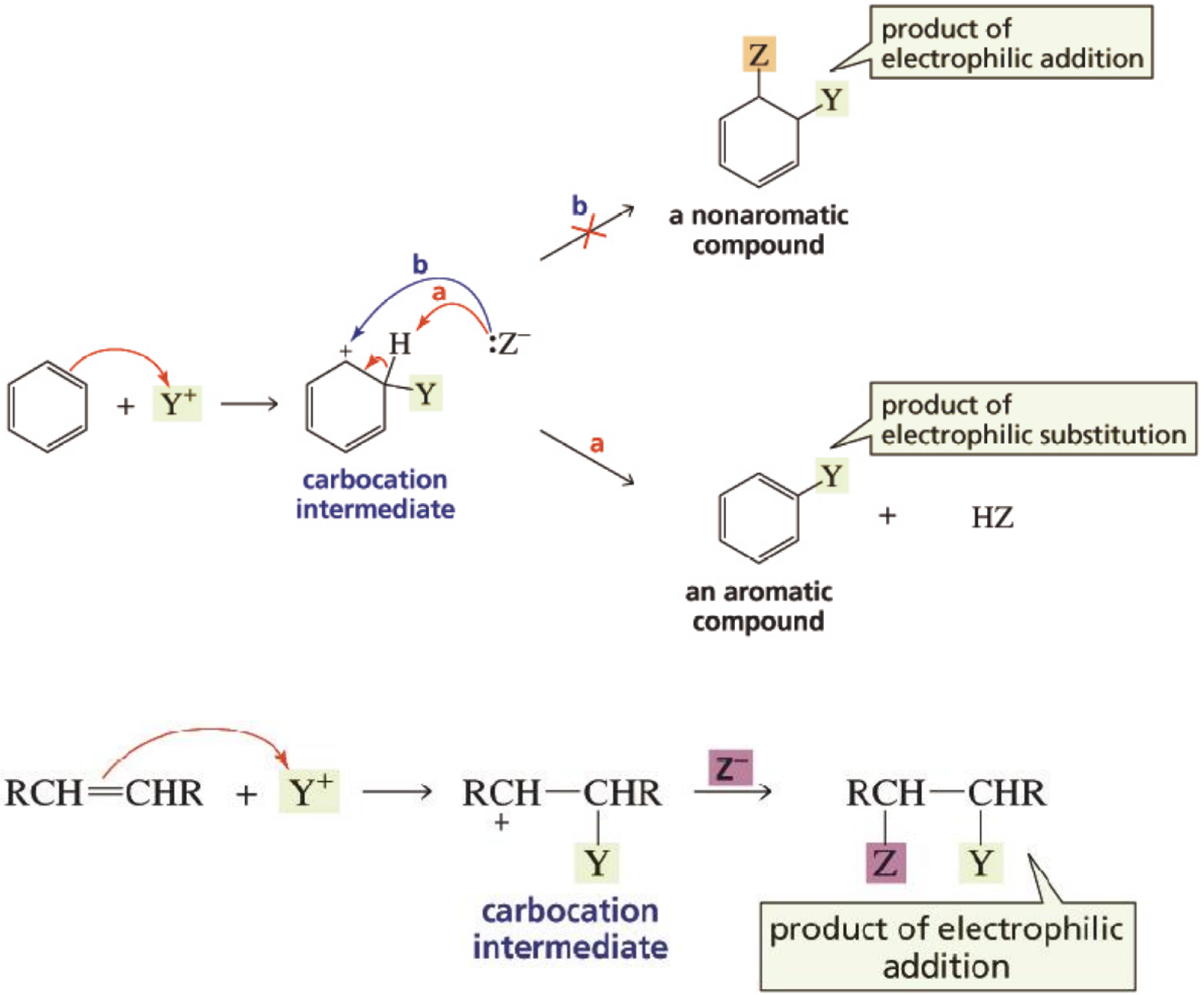
Reação de Substituição Eletrofílica

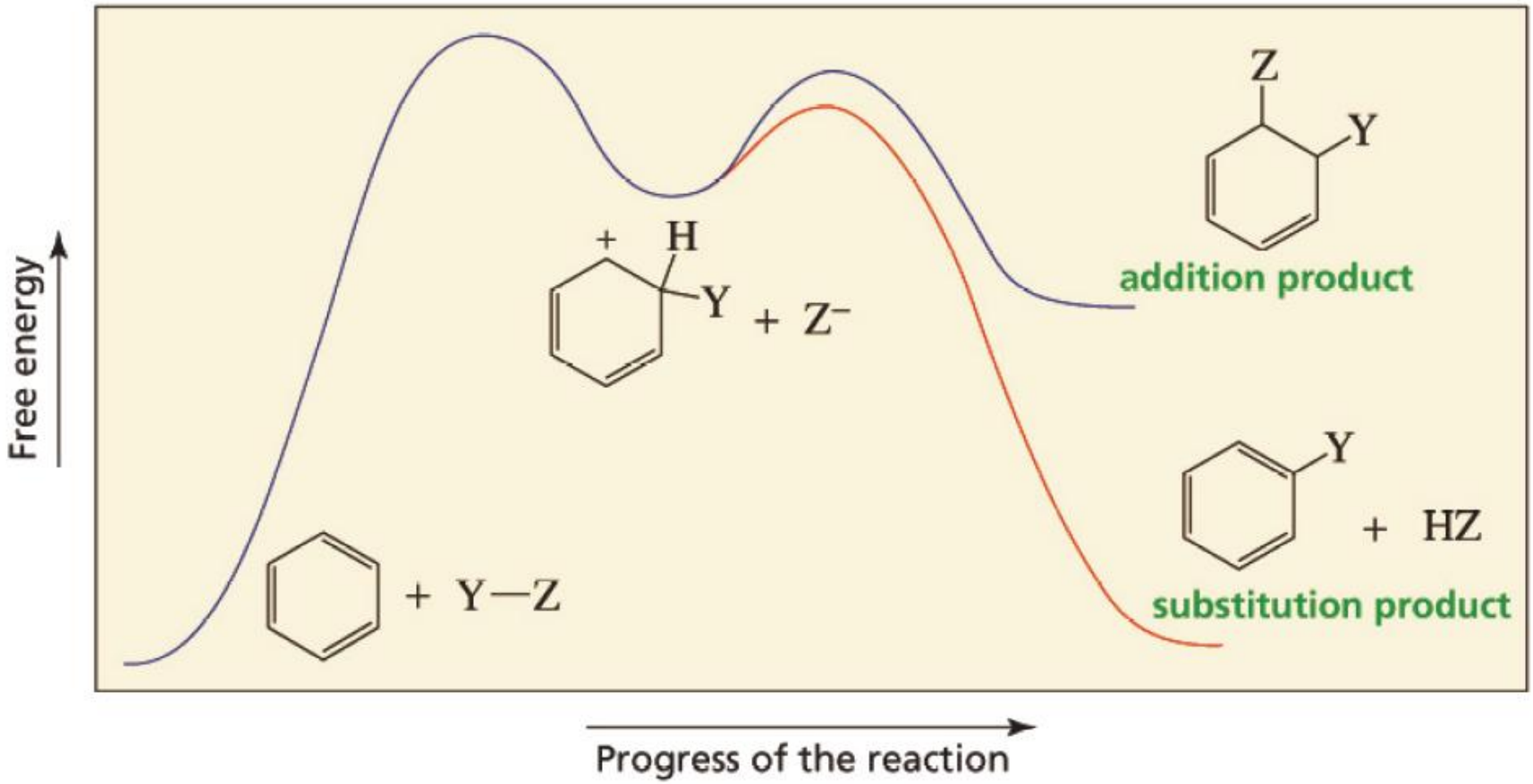
Ordem de reatividade de benzeno substituído

Substituent	Position of Reaction	log(rate relative to H)
NR_2	o, p	1.3
OH, OR	o, p	0.9
R	o, p	0.3
Ar	o, p	0.2
F	o, p	0.1
H	"o, p"	0
NHCOR	o, p	-0.1
Cl, Br, I	o, p	-0.1
CO_2H	m	-0.4
COR, CO_2R	m	-0.5
CX_3	m	-0.5
SO_3H	m	-0.6
CN	m	-0.7
NO_2	m	-0.8
NR_3^+	m	-0.9

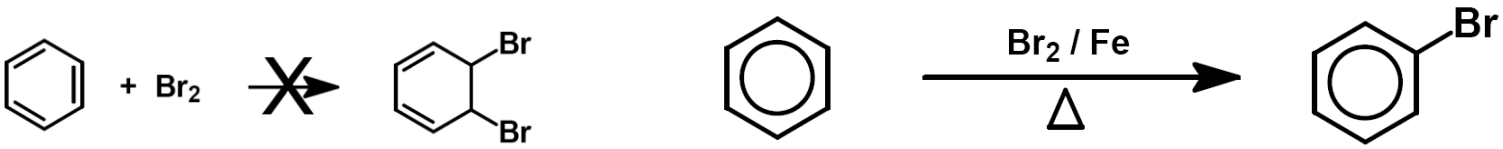

SO3H
NO2
R
Sulfonação
Nitração
Alquilação
O
C
R
X
H
Halogenação
Acilação


H—Cl
Cl⁻
H
C=C
C—C
Cl H
C—C
Alceno
carbocátion
produto de adiçã

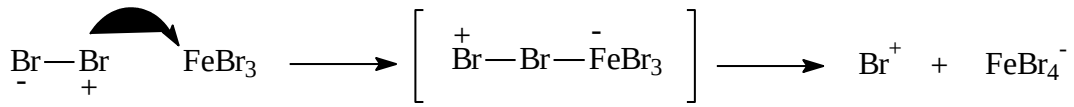

product of electrophilic addition
Z
Y
a nonaromatic compound
b
b
a
H
:Z⁻
+
Y⁺
Y
carbocation intermediate
a
product of electrophilic substitution
Y
+
HZ
an aromatic compound
RCH=CHR + Y⁺
RCH—CHR
+
Y
carbocation intermediate
Z⁻
RCH—CHR
Z
Y
product of electrophilic addition


Free energy
+ H
Y
+ Z⁻
Z
Y
addition product
Y
+ HZ
substitution product
+ Y—Z
Progress of the reaction

Halogenação

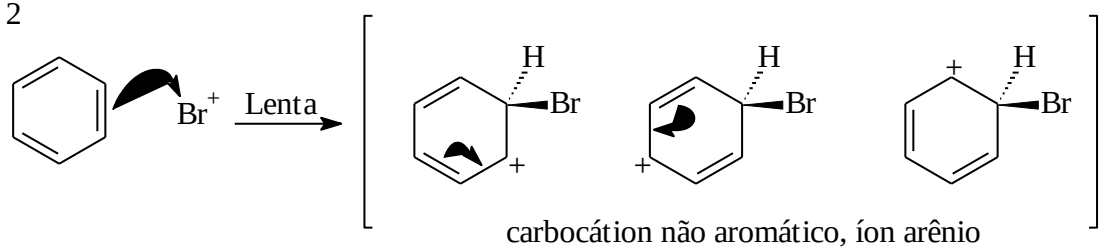


Etapa 1



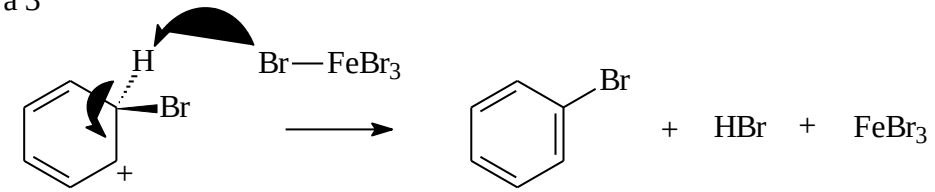
O bromo de combina com FeBr3 para formar um complexo que se dissocia para formar um íon bromo positivo e FeBr4-

Etapa 2



O íon bromo positivo ataca o benzeno para formar um íon arênio

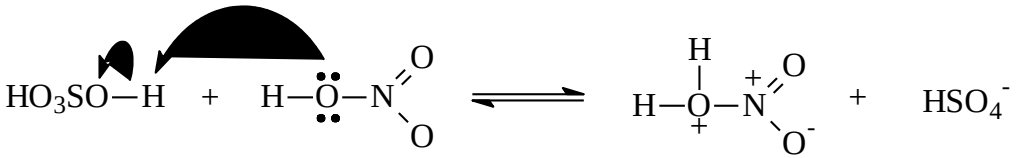
Etapa 3



Um próton é removido do íon arênio para torna-se bromobenzeno

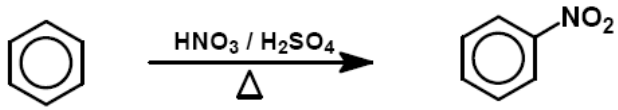
Etapa 1

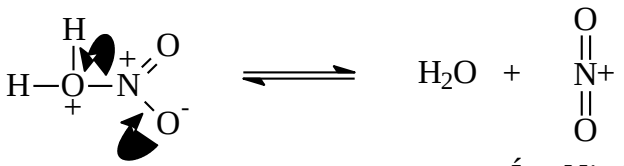
Nitração



Nessa etapa, o ácido nítrico aceita um próton do ácido mais forte, o ácido sulfúrico

Etapa 2

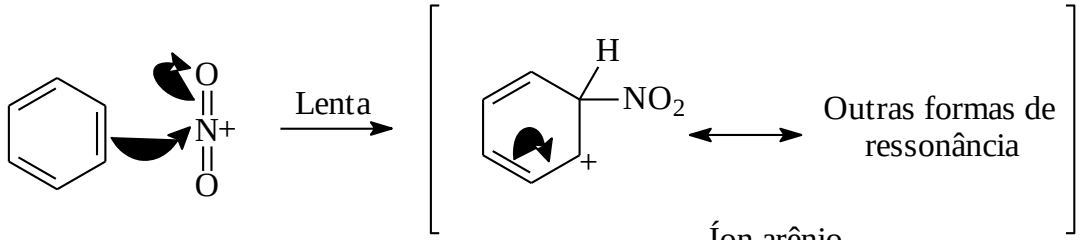




Íon Nitrônio

Agora que está protonado, ácido nítrico pode se dissociar para formar um íon nitrônio

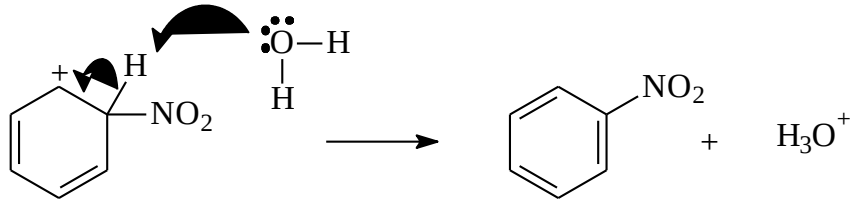
Etapa3



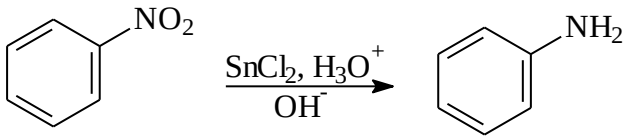
Íon arênio

O íon nitrônio é o eletrófilo real na nitração, ele reage com o benzeno para formar um íon arênio estabili por ressonância.

Etapa 4

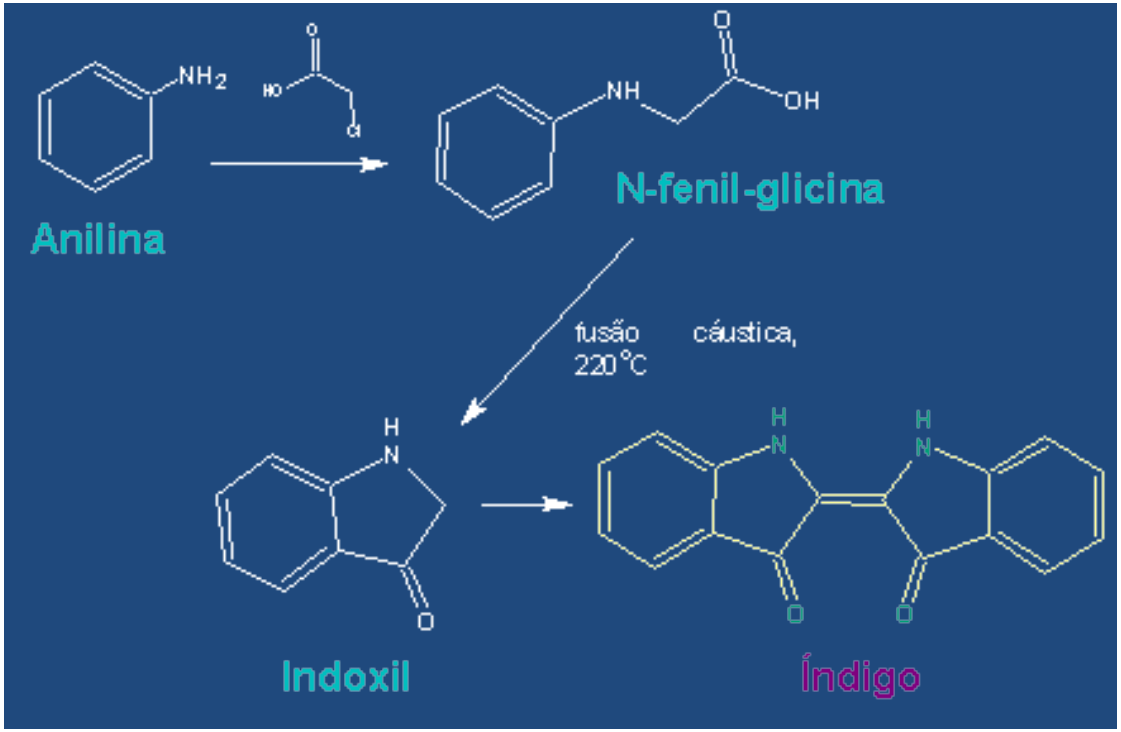


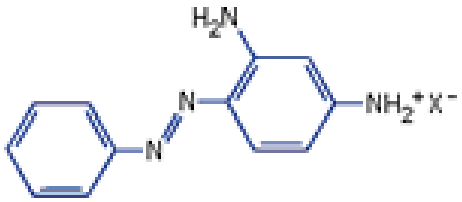
O íon arênio então perde um próton para uma base de lewis (nucleófilo) e torna-se nitrobenzeno.



Nitrobenzeno

Anilina



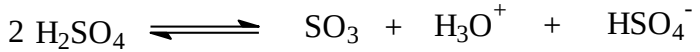


crisoidina
(um azobenzeno)

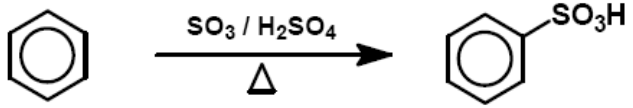
pararosanilina
(um trifenilmetano)

Sulfonação

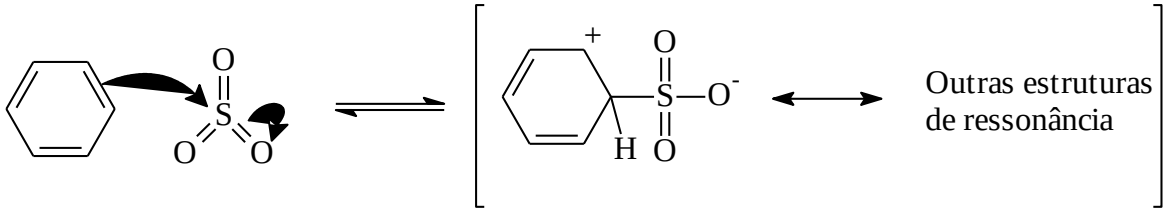
Etapa 1



Este equilíbrio produz SO_3 em H_2SO_4 concentrado

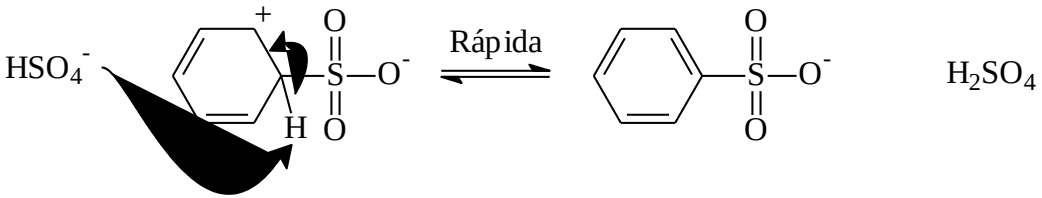


Etapa 2



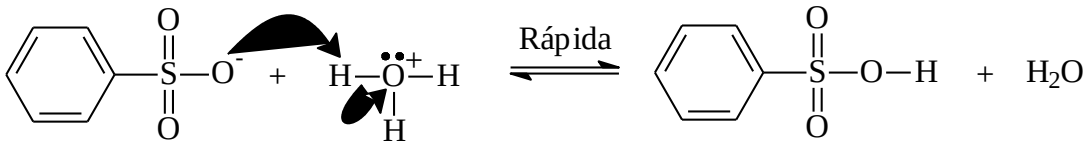
SO_3 é o eletrófilo real que reage com benzeno para formar o íon arênio

Etapa3



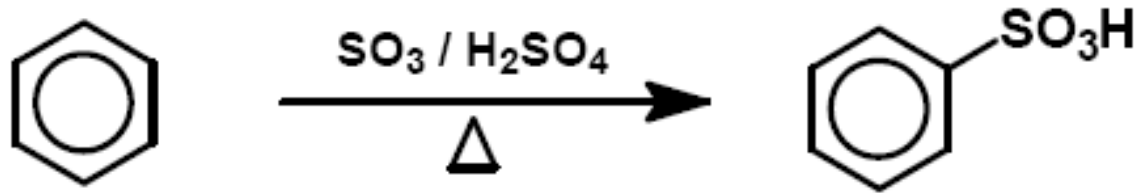
Um próton é removido do íon arênio para formar o íon benzenossulfonato

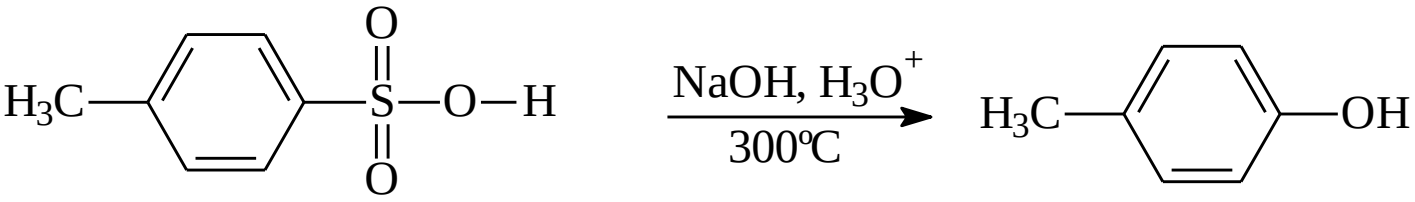
Etapa 4



O íon benzenossulfonato aceita um próton para tornar-se ácido benzenossulfônico.

Sulfonação

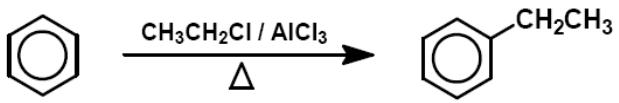




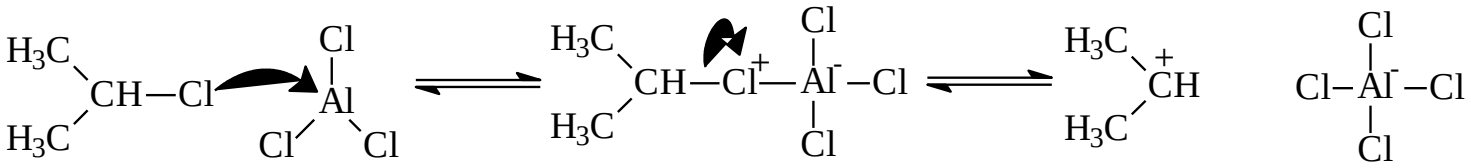
Ácido p-toluenossulfônico

p-cresol (fenol)

Alquilação de Friedel-Crafts



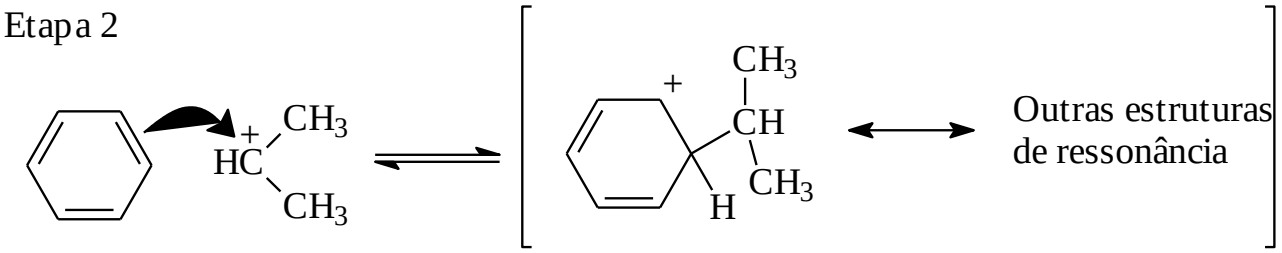
Etapa 1



Está é uma reação de ácido e base de Lewis

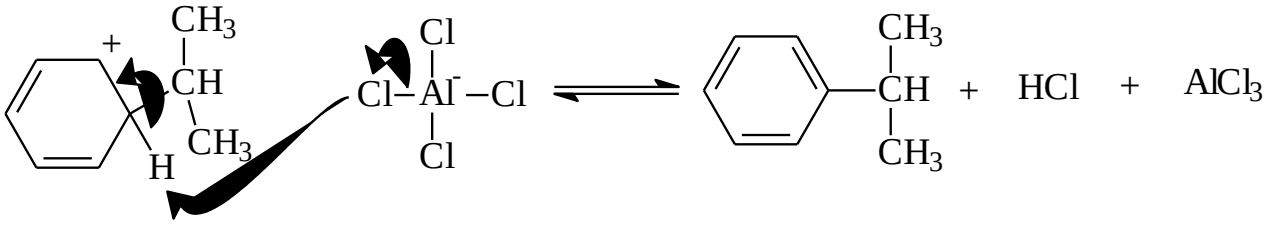
O composto se dissocia para formar um carboncátion e $AlCl_4^-$.

Etapa 2



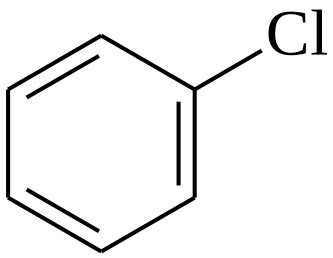
O carbocátion, atuando como um eletrófilo, reage com benzeno para produzir um íon arênio.

Etapa 3

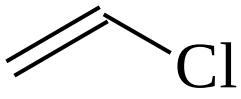


Limitações da alquilação de Friedel-Crafts

1) Somente podem ser usados haletos de alquila. Haletos de arila e vinila não reagem.



Haleto de arila



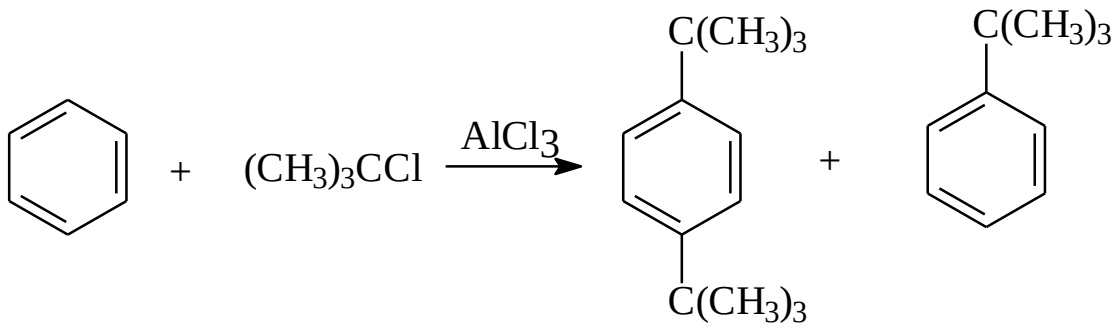
Haleto de vinil

Limitações da alquilação de Friedel-Crafts

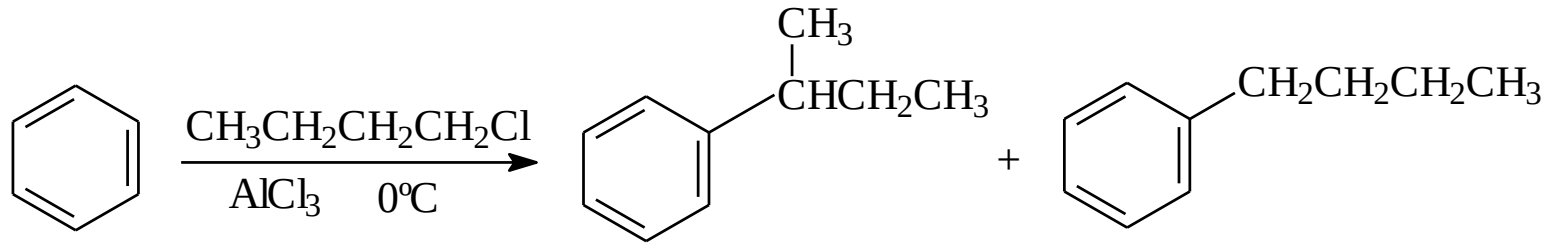
2) A reação não ocorre quando o anel aromático é substituído por:

a. **Grupo amino**
b. **Grupos retiradores de elétrons fortes (NO_2, CN, SO_3H, CHO, CO_2H, CO_2CH_3).**

3) A dificuldade de cessar a reação após ter ocorrido uma única substituição.

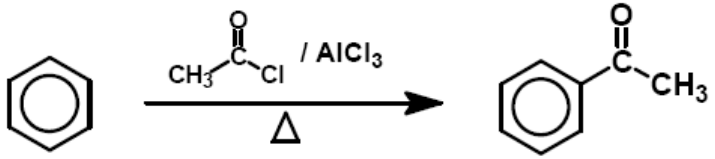


4) Freqüentemente ocorre um rearranjo do grupo alquila durante a reação, principalmente quando é empregado um haleto de alquila primário.

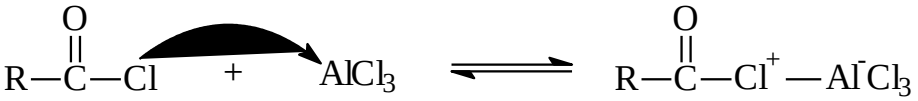


Benzeno sec-butilbenzeno butilbenzeno

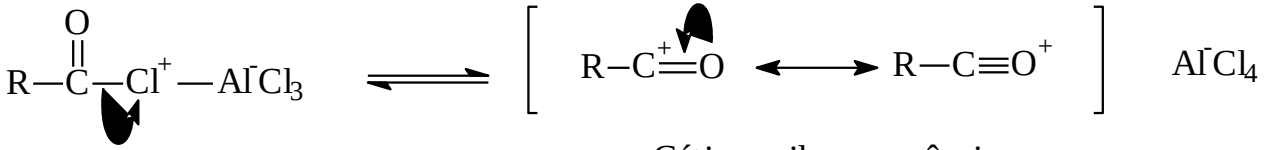
Acilação de Friedel-Crafts



Etapa 1

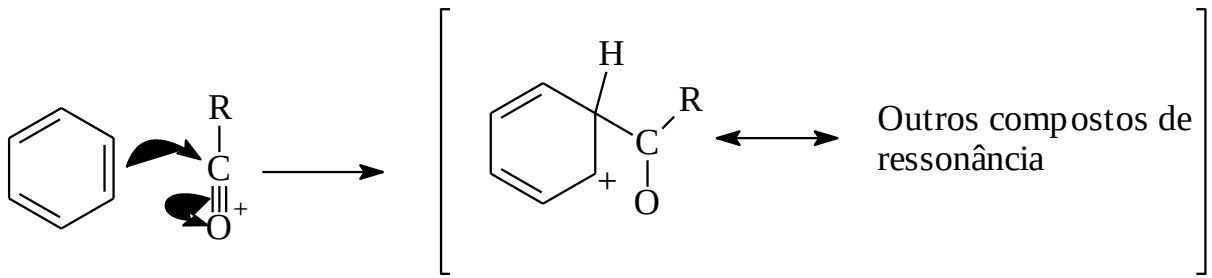


Etapa 2

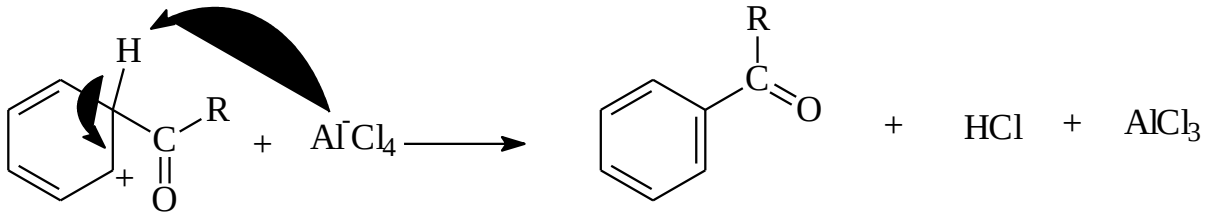


Cátion acila ressonância

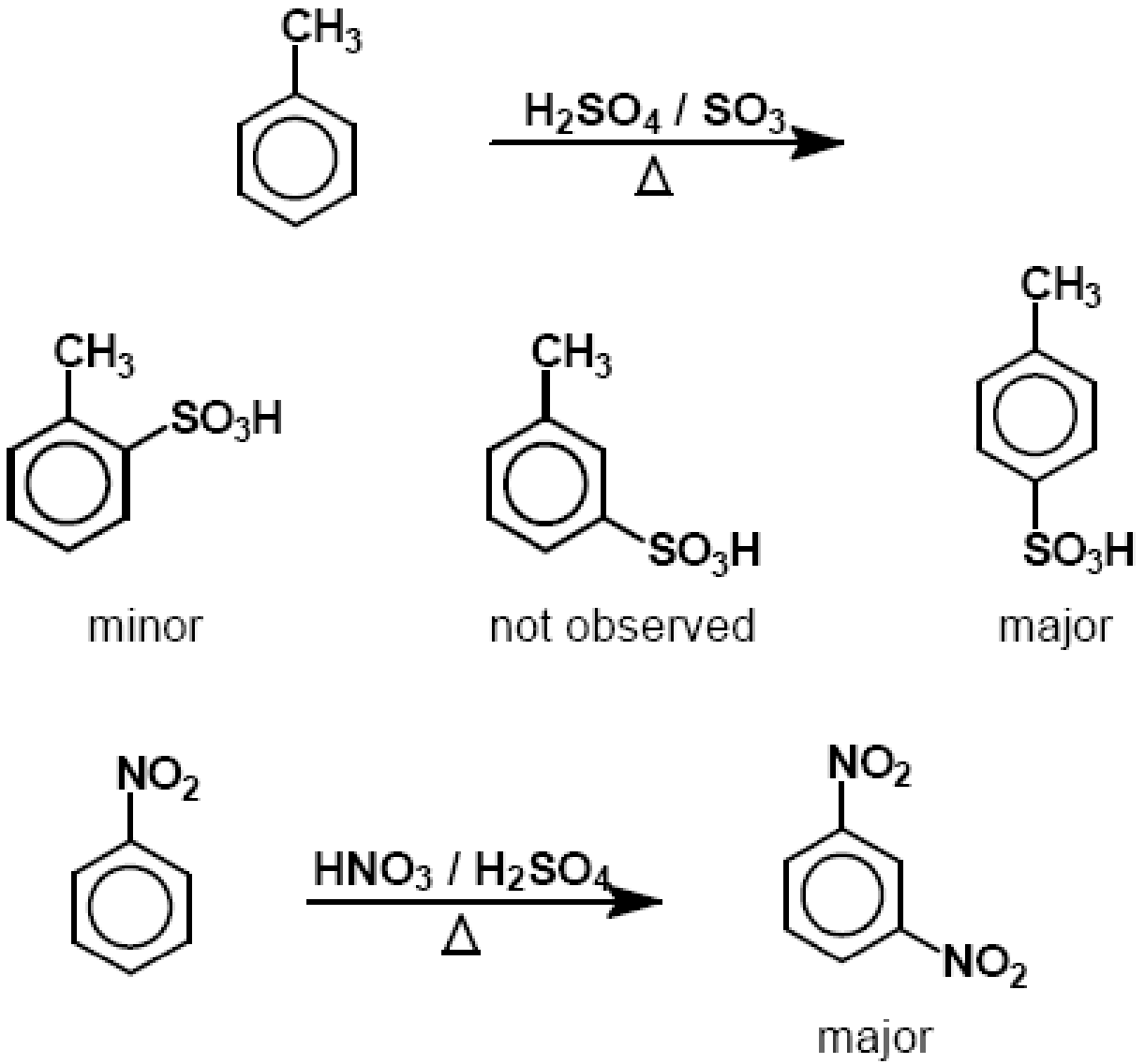
Etapa 3



Etapa 4



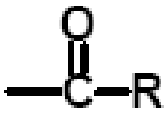
Efeito do Substituinte



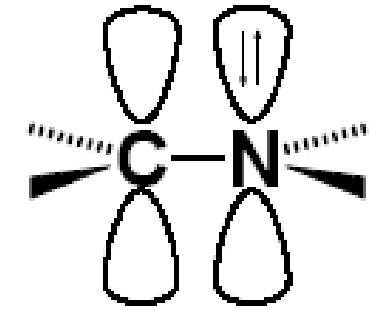
ortho/para directors

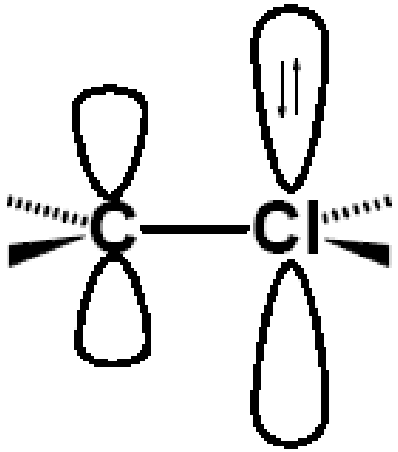
Activate				Deactivate		
$-NH_2$	-OH	-OR	-Alkyl	-Cl	-Br	-I

meta directors---all deactivate

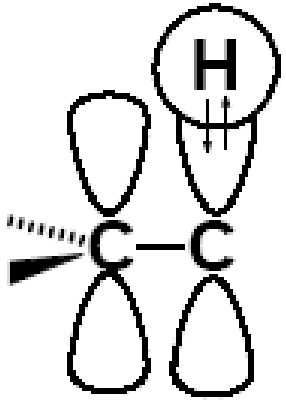
$-NO_2$	$-SO_3H$		

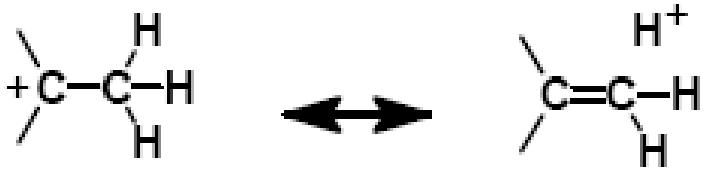
Electron-Donating Substituents (*ortho/para* directors)
---Lone pairs available (conjugation)



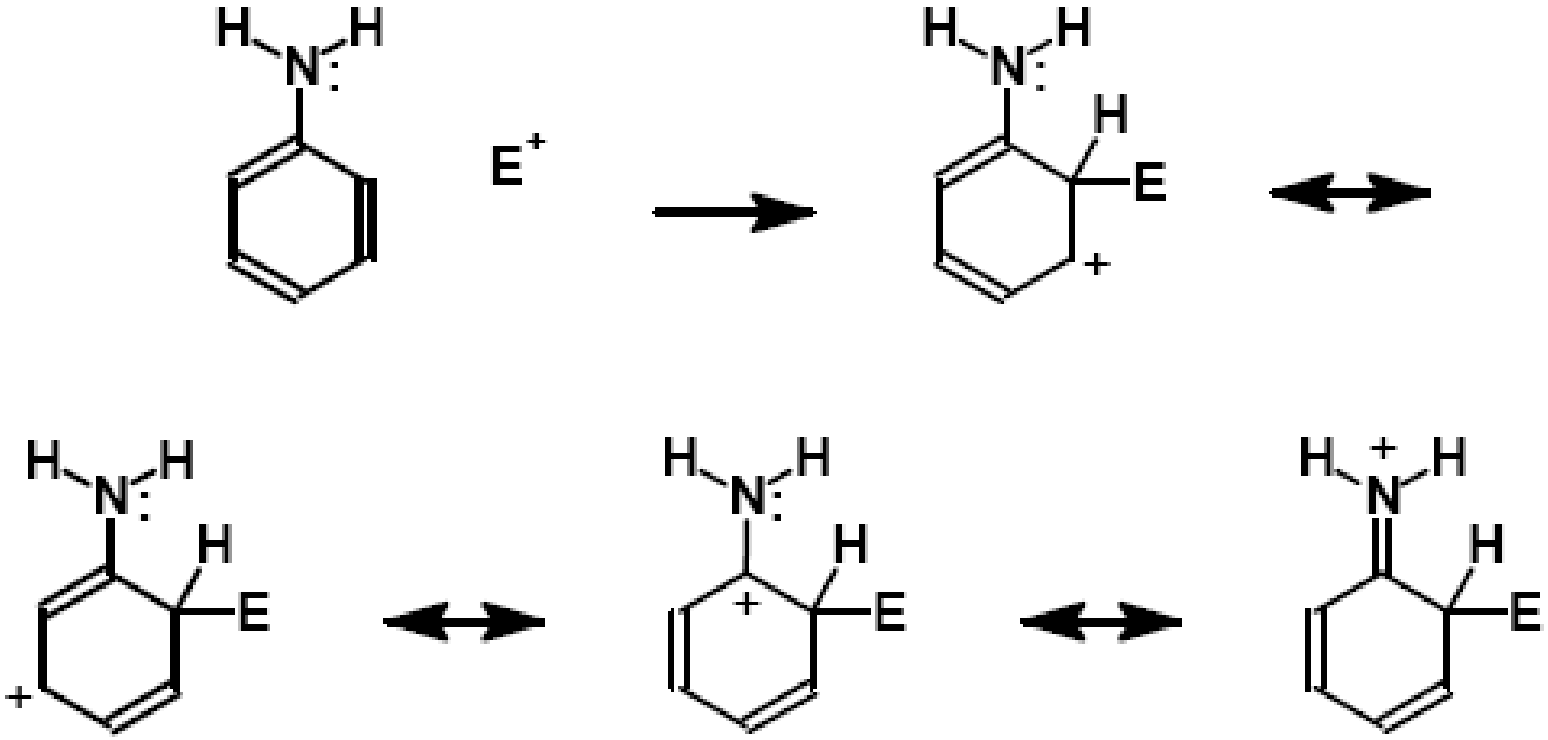


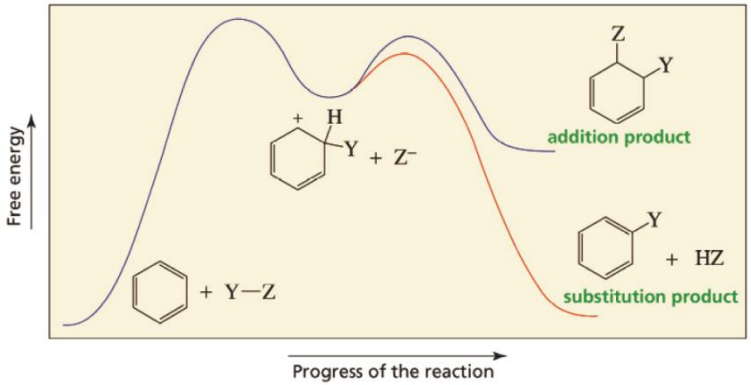
---Alkyl groups (hyperconjugation)



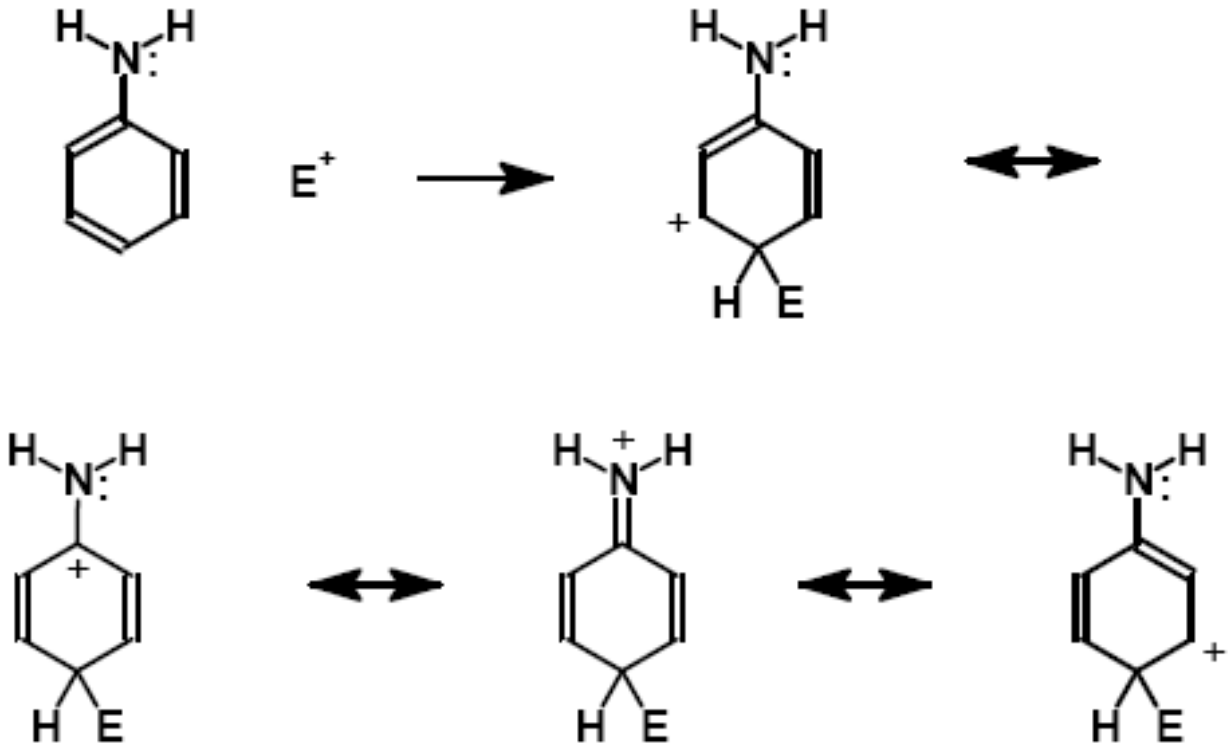


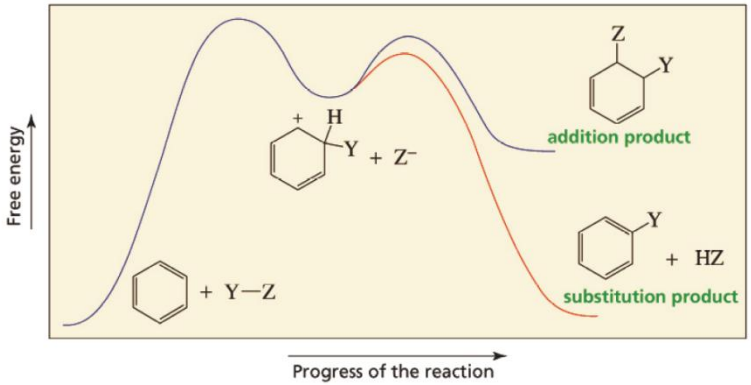
Look at intermediates (*ortho* attack):



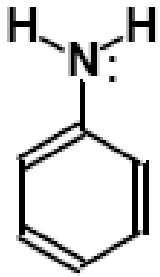


para attack:

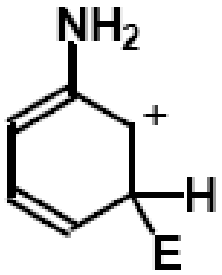

H
N
H
E+
+
H
E

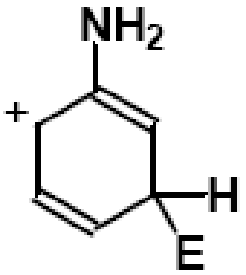

Free energy
Progress of the reaction
+ Y—Z
+ Z⁻
addition product
+ HZ
substitution product

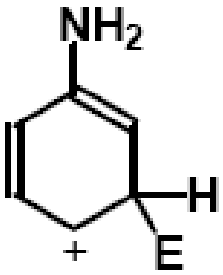
But, *meta* attack:

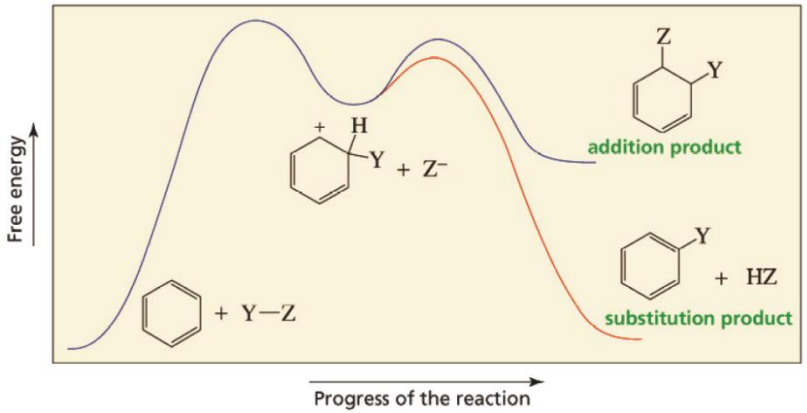


E^+

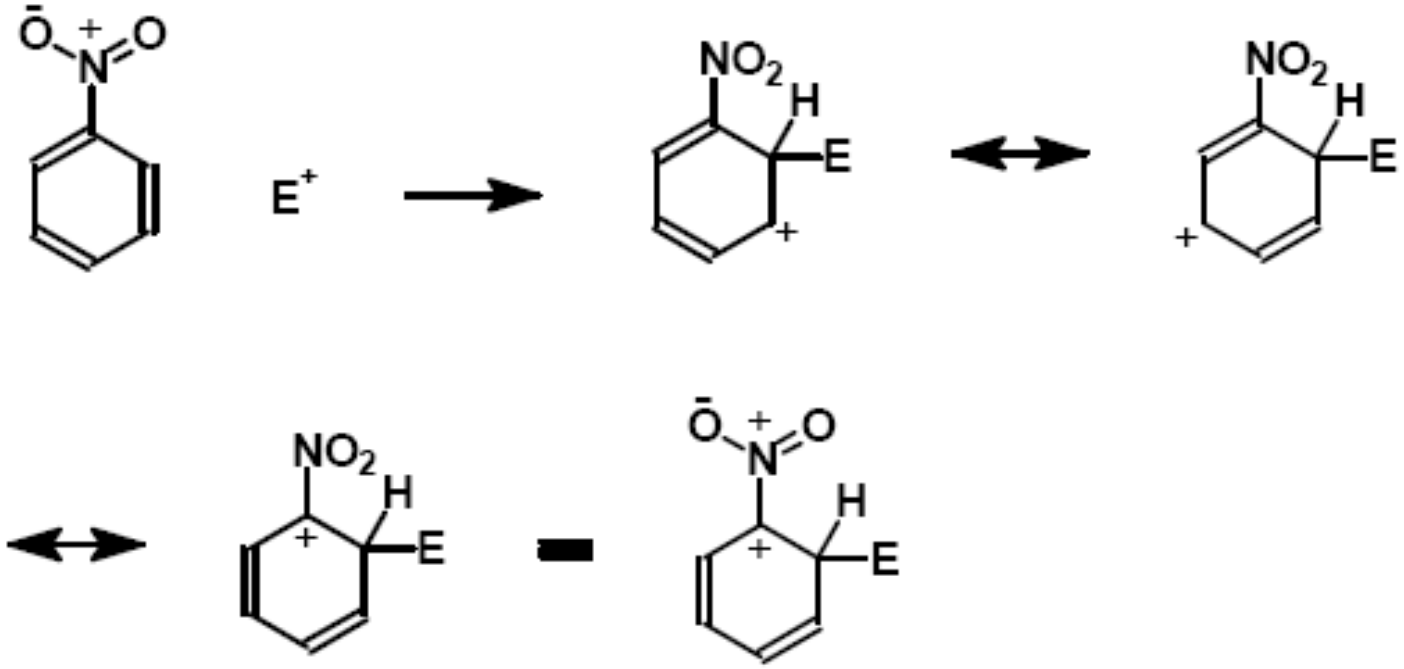




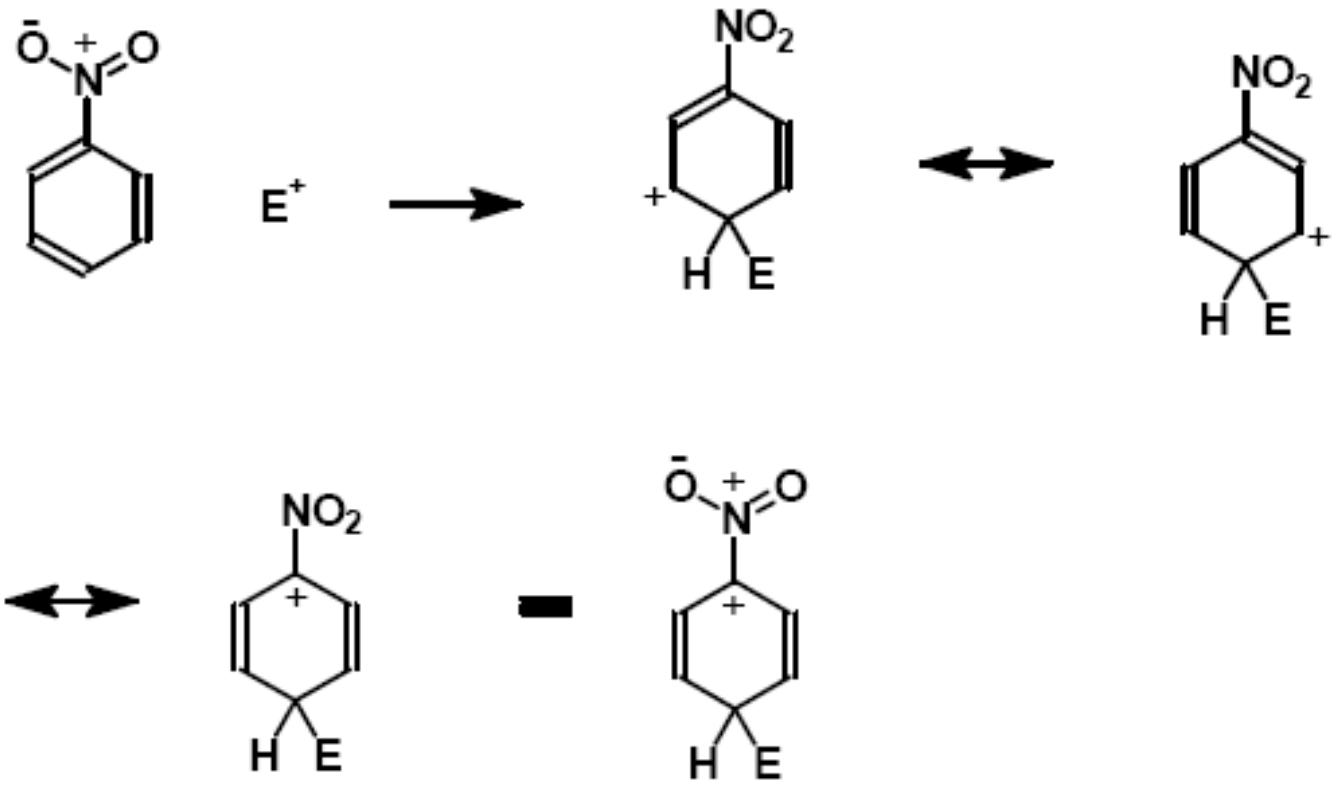




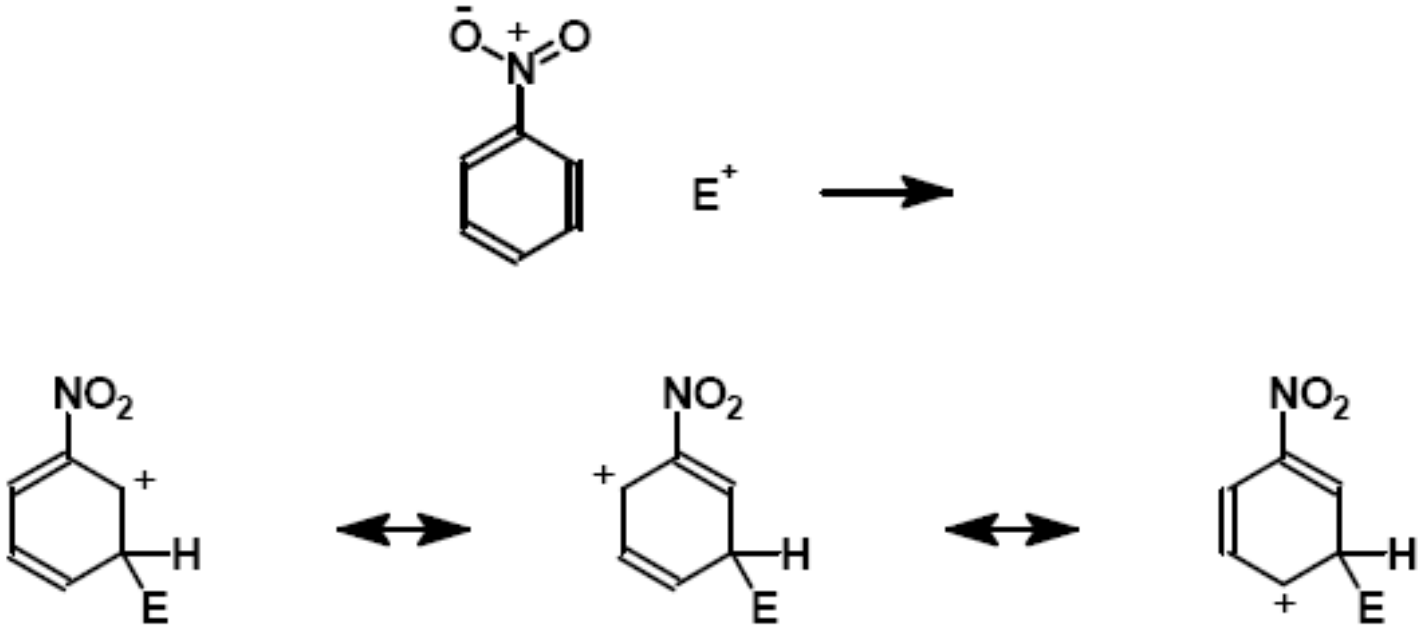
Intermediates, *ortho* attack:



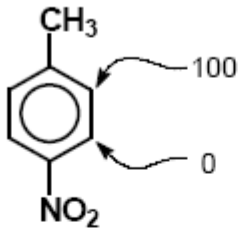
para attack:

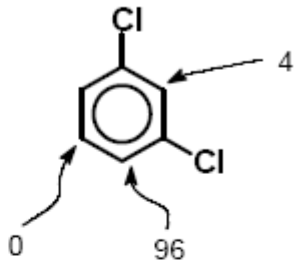


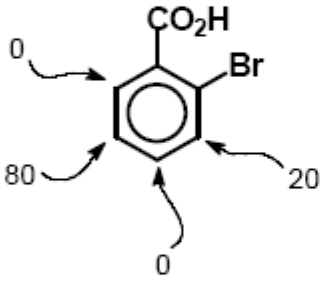
But, *meta* attack:

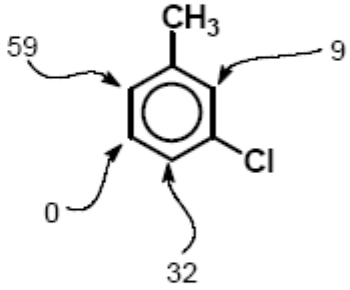


Multiple Substituents









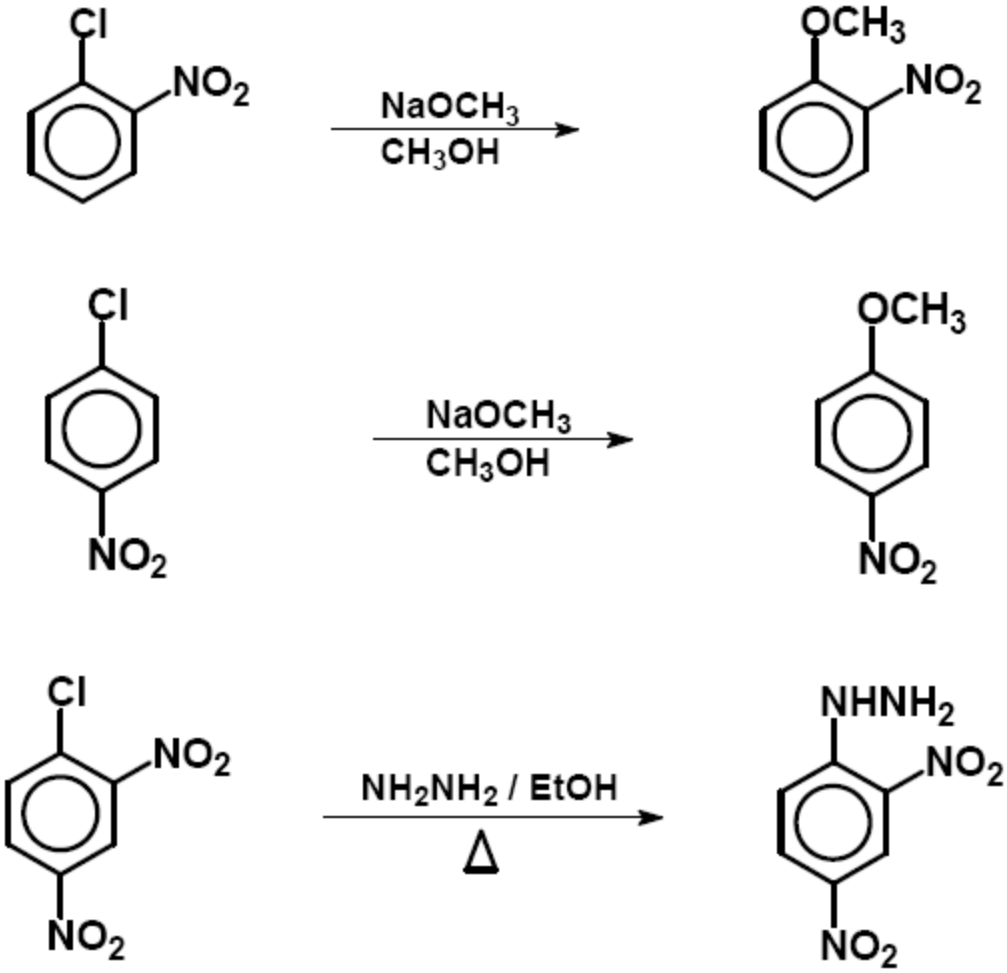
"Directing Power"

1) **Great electron donors: -NR_2, -OR, -OH**

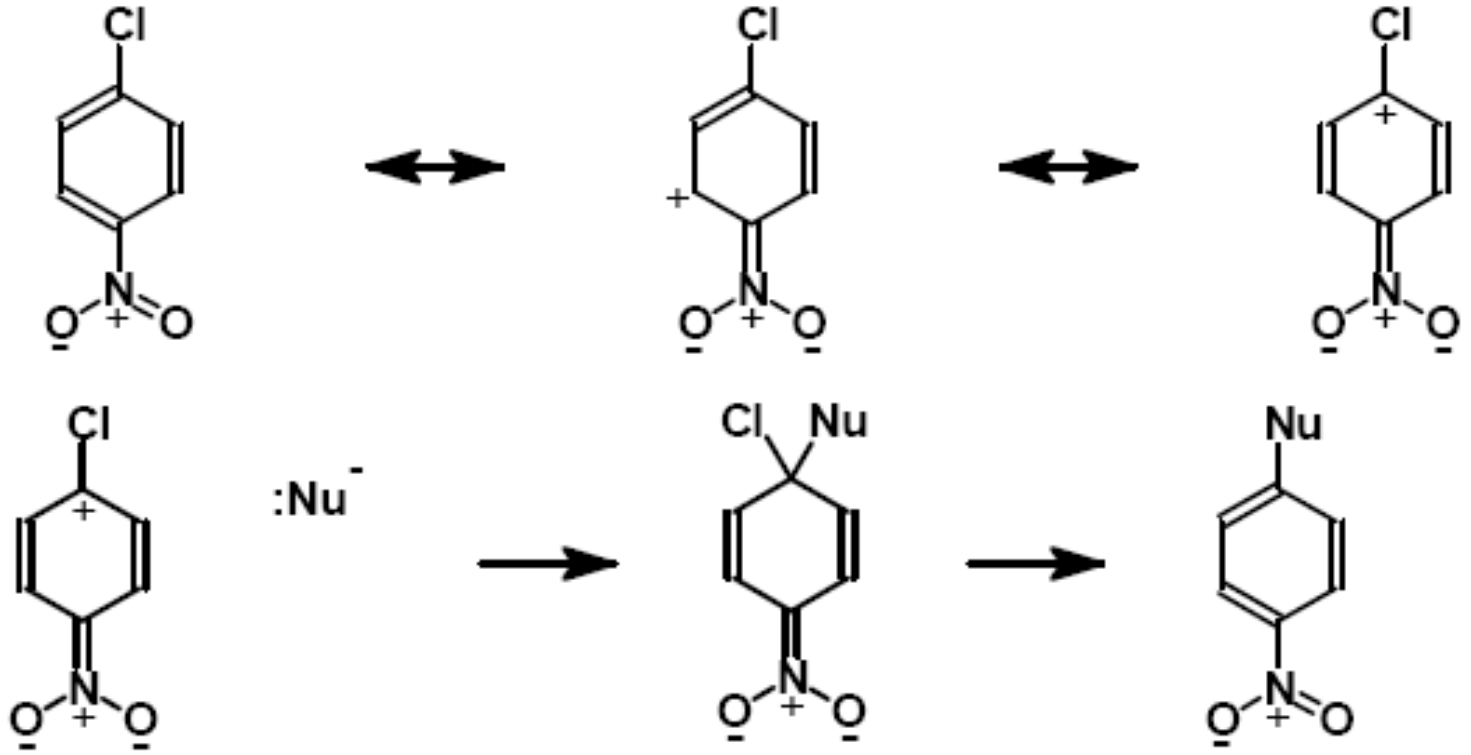
2) **-Cl, -Br, Alkyl**

3) ***meta* Directors**

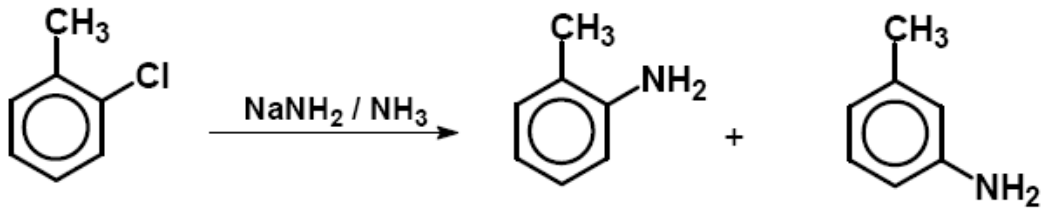
Nucleophilic Aromatic Substitution (Aryl Halides)



Mechanism:



However...



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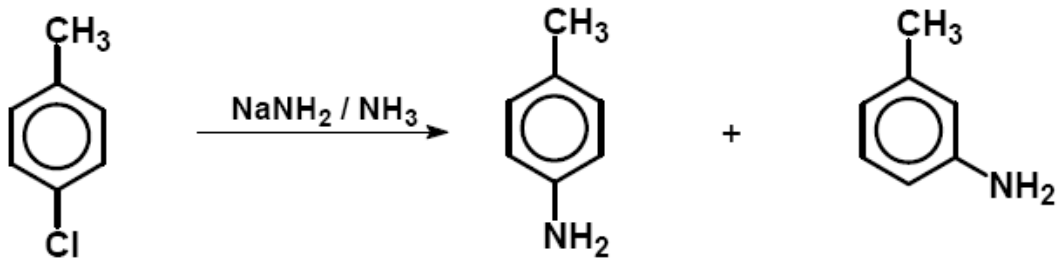
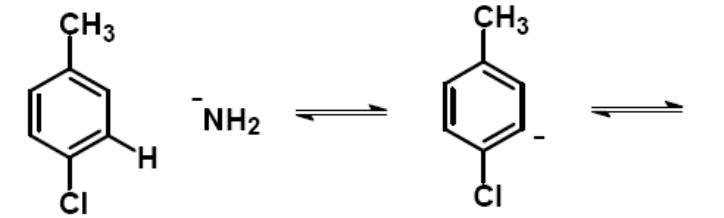
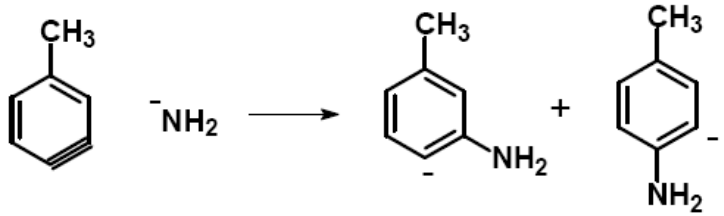


Mechanism:

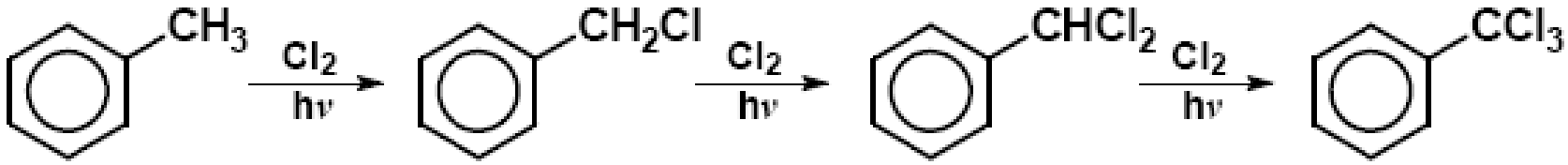




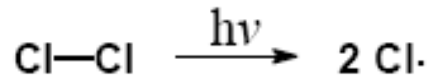
"Benzyne"

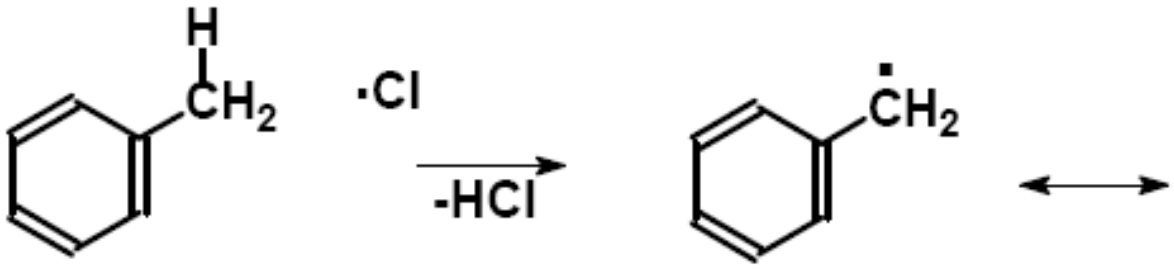
Side-Chain Reactions

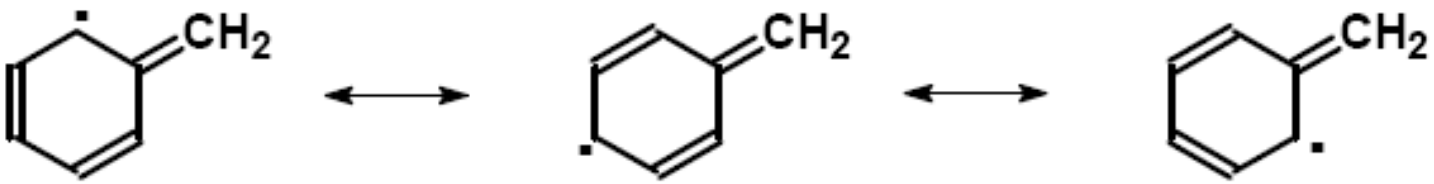
Free Radical Halogenation

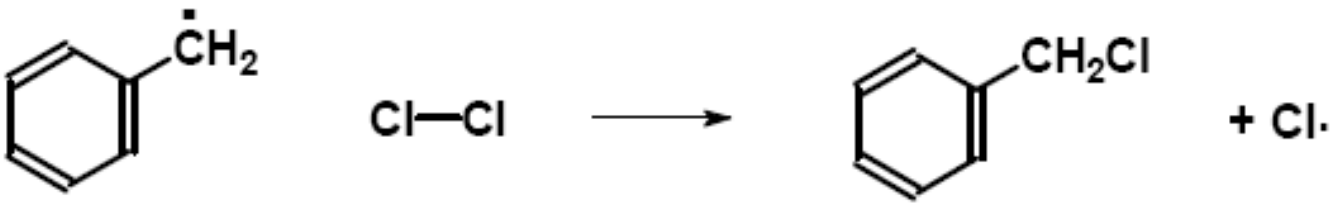


Mechanism:

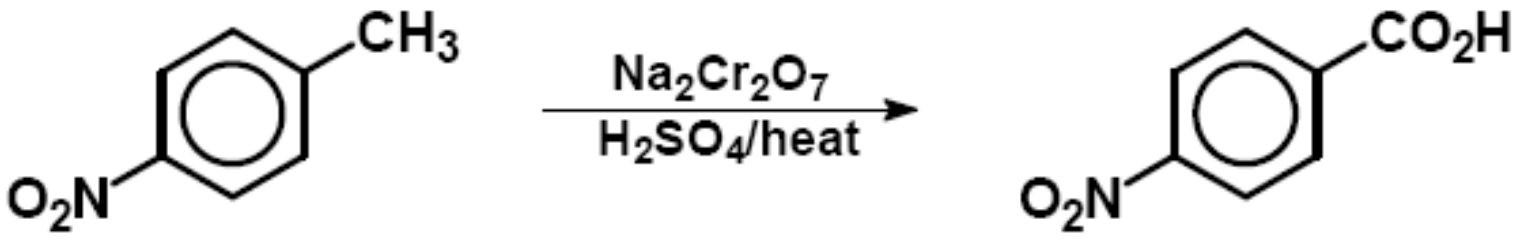




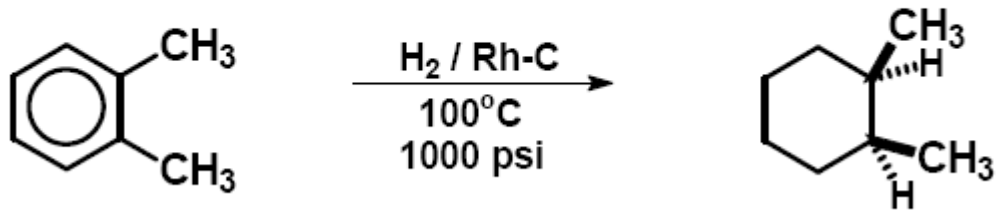




Oxidation



Hydrogenation of Aromatic Ring--- Possible but difficult:



Hydrogenolysis