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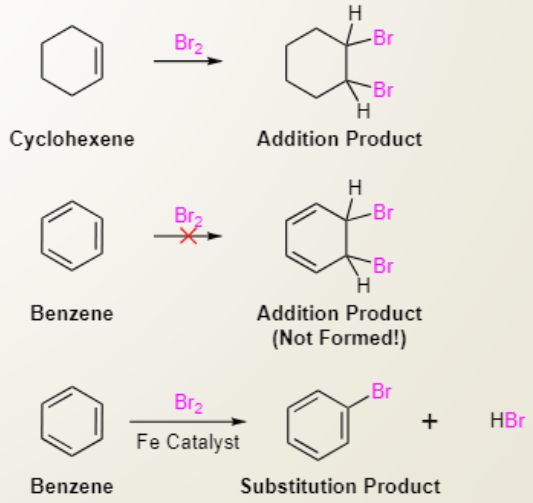
Benzene undergoes **substitution reactions** rather than the addition reactions!



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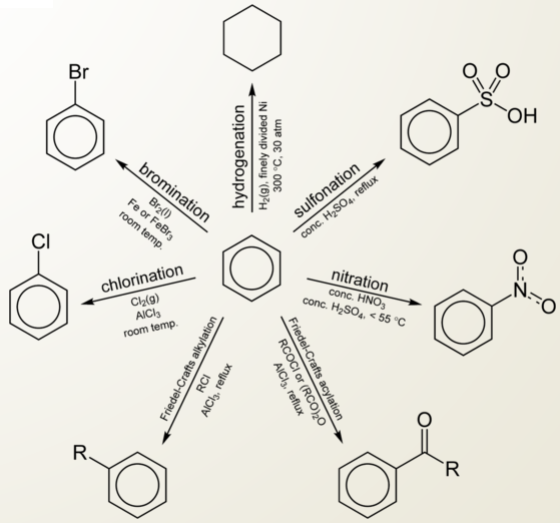
Benzene can undergo substitution reactions



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Substitution Reactions of Benzene

Reaction Type	Typical Equation			Electrophile $E^{(+)}$
Halogenation:	C_6H_6 + Cl_2 & heat $FeCl_3$ catalyst	——>	C_6H_5Cl + HCl Chlorobenzene	$Cl^{(+)}$ or $Br^{(+)}$
Nitration:	C_6H_6 + HNO_3 & heat H_2SO_4 catalyst	——>	$C_6H_5NO_2$ + H_2O Nitrobenzene	$NO_2^{(+)}$
Sulfonation:	C_6H_6 + H_2SO_4 + SO_3 & heat	——>	$C_6H_5SO_3H$ + H_2O Benzenesulfonic acid	$SO_3H^{(+)}$
Alkylation: Friedel-Crafts	C_6H_6 + R-Cl & heat $AlCl_3$ catalyst	——>	C_6H_5-R + HCl An Arene	$R^{(+)}$
Acylation: Friedel-Crafts	C_6H_6 + RCOCl & heat $AlCl_3$ catalyst	——>	C_6H_5COR + HCl An Aryl Ketone	$RCO^{(+)}$

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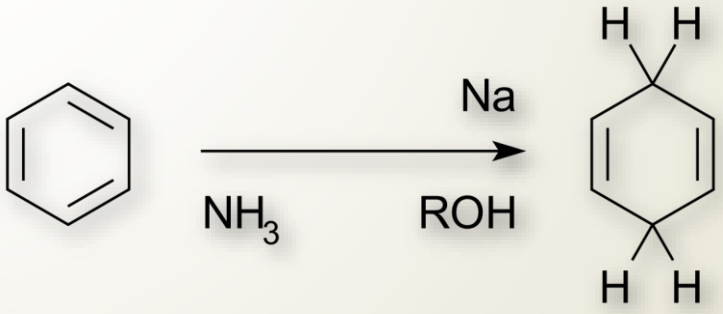
A redução de Birch



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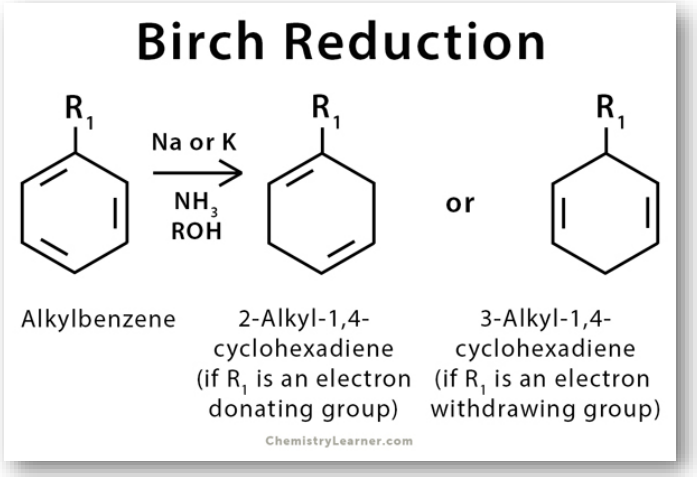

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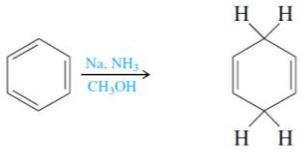
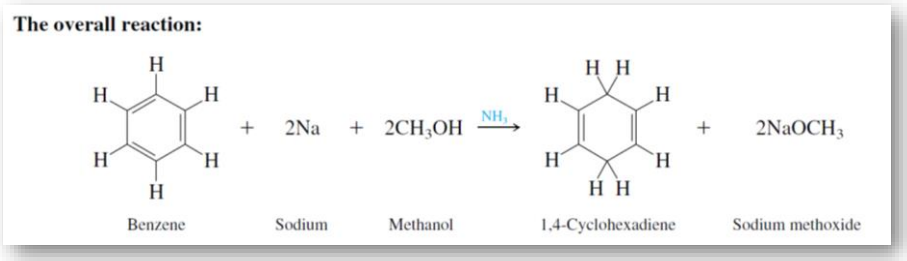
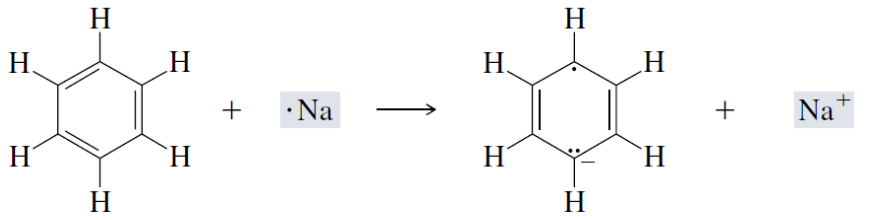
A redução de Birch





https://chemtips.wordpress.com/

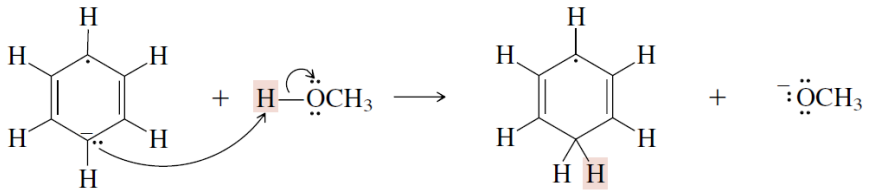
Mecanismo da reação



Benzene | Sodium | Benzene anion radical | Sodium ion

Mecanismo da reação...

Passo 2:



Benzene anion radical | Methanol | Cyclohexadienyl radical | Methoxide ion

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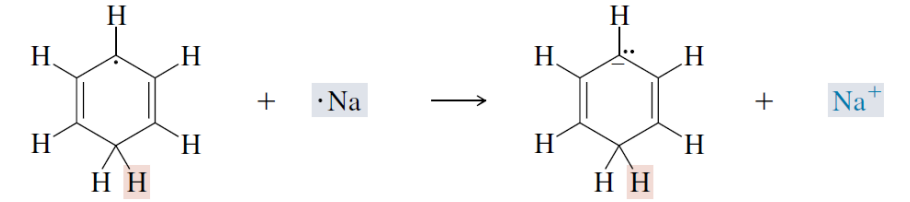
Mecanismo da reação...

Passo 3:



Cyclohexadienyl radical | Sodium | Cyclohexadienyl anion | Sodium ion

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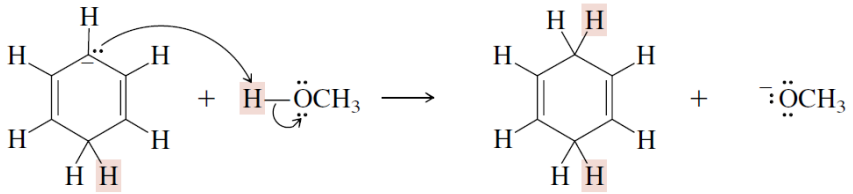
Mecanismo da reação...

Passo 4:



Cyclohexadienyl anion | 1,4-Cyclohexadiene | Methoxide ion

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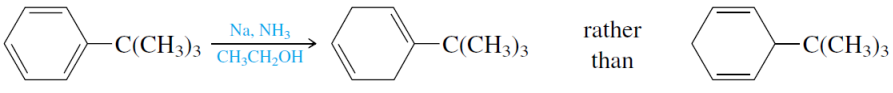
Ex: Explique a formação do produto da reação de Birch



tert-Butylbenzene

1-*tert*-Butyl-1,4-cyclohexadiene (86%)

3-*tert*-Butyl-1,4-cyclohexadiene

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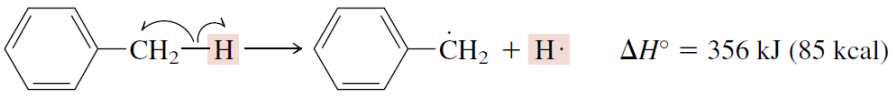
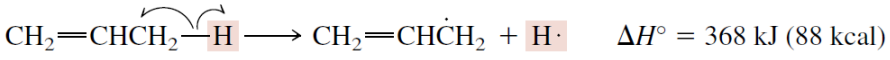
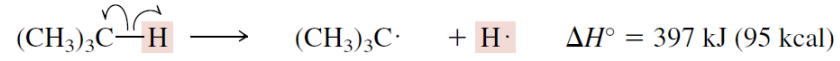
Halogenação de alquilbenzenos via radical livre



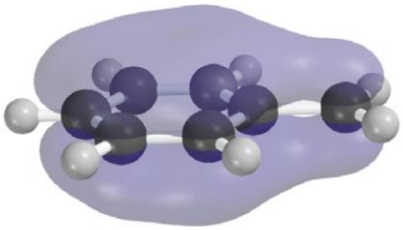
Toluene — Benzyl radical



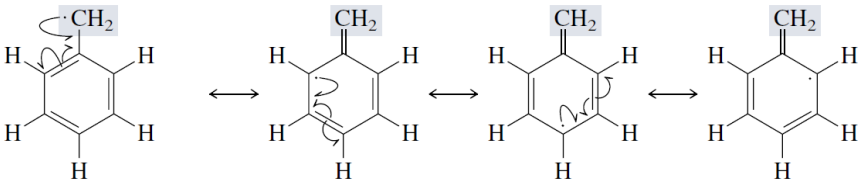
Propene — Allyl radical



2-Methylpropane — *tert*-Butyl radical

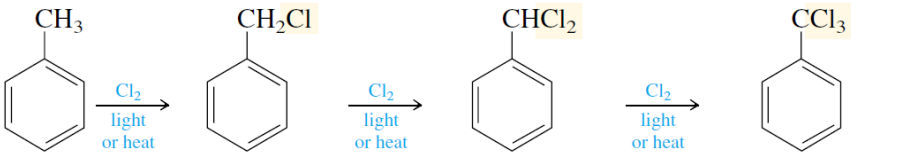


O radical é estabilizado por sobreposição do orbital *p* semi-preenchido com o sistema π do anel aromático.

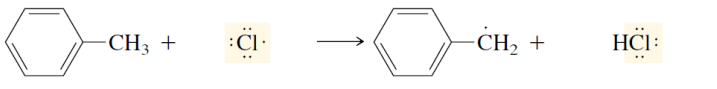


Most stable Lewis structure of benzyl radical

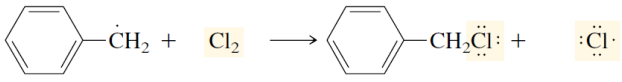
Benzotricloreto é usado para fazer tinturas e outros produtos químicos.



Toluene — Benzyl chloride — (Dichloromethyl)-benzene — (Trichloromethyl)-benzene



Toluene — Chlorine atom — Benzyl radical — Hydrogen chloride



Benzyl radical — Chlorine — Benzyl chloride — Chlorine atom

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A EPA classificou o benzotricloreto como provável carcinógeno humano.

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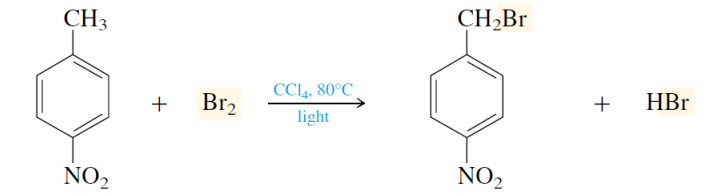
Ex: escreva os passos para a bromação benzílica em condições de iniciação fotoquímica



p-Nitrotoluene | Bromine | *p*-Nitrobenzyl bromide (71%) | Hydrogen bromide

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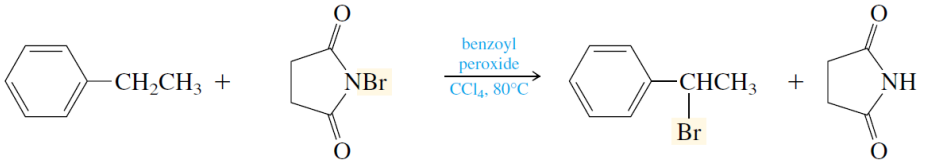
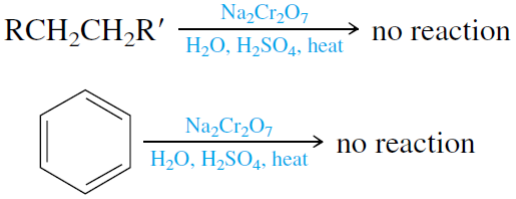
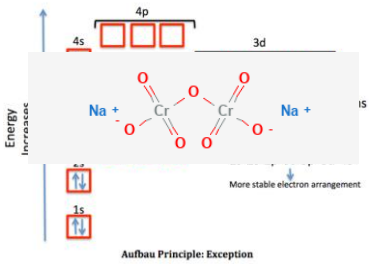
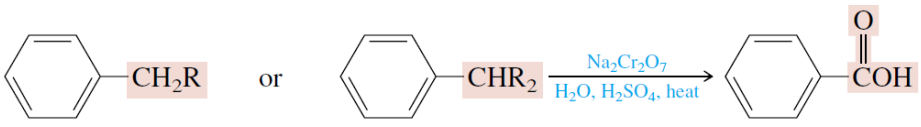
O NBS é um agente conveniente para a reação de bromação via radical-livre. Escreva os passos para a seguinte reação



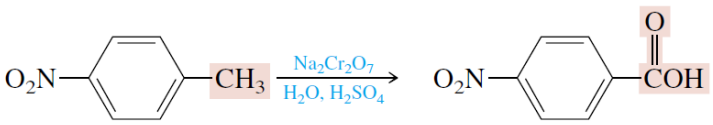
Ethylbenzene | *N*-Bromosuccinimide (NBS) | 1-Bromo-1-phenylethane (87%) | Succinimide







Alkylbenzene | Benzoic acid



p-Nitrotoluene | *p*-Nitrobenzoic acid (82–86%)

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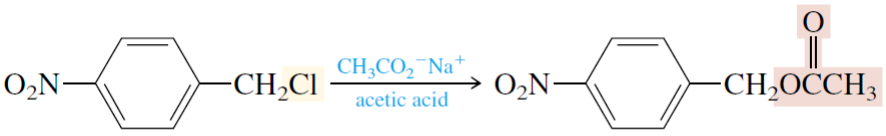
Substituição em haletos benzílicos



p-Nitrobenzyl chloride — *p*-Nitrobenzyl acetate (78–82%)

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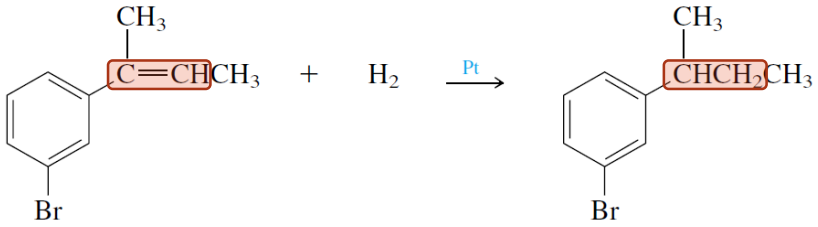
Reações de adição em alquenilbenzenos



2-(*m*-Bromophenyl)-2-butene — Hydrogen — 2-(*m*-Bromophenyl)butane (92%)

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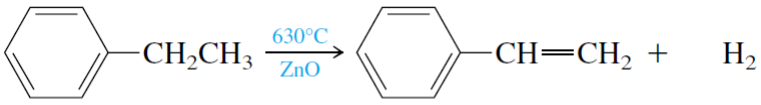
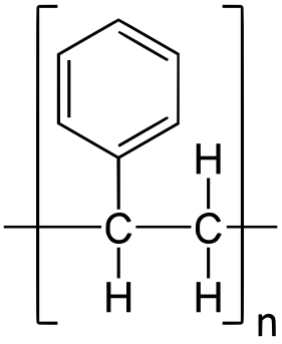
Preparação de alquenilbenzenos

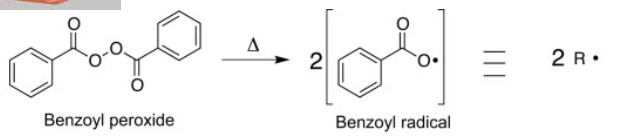


Ethylbenzene — Styrene — Hydrogen

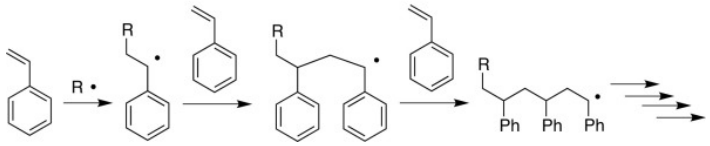
O etilbenzeno ocorre naturalmente no alcatrão de carvão e no petróleo.

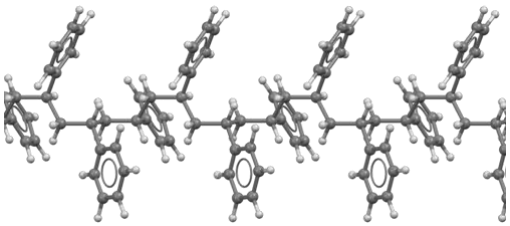


Síntese do poliestireno



Benzoyl peroxide — Benzoyl radical





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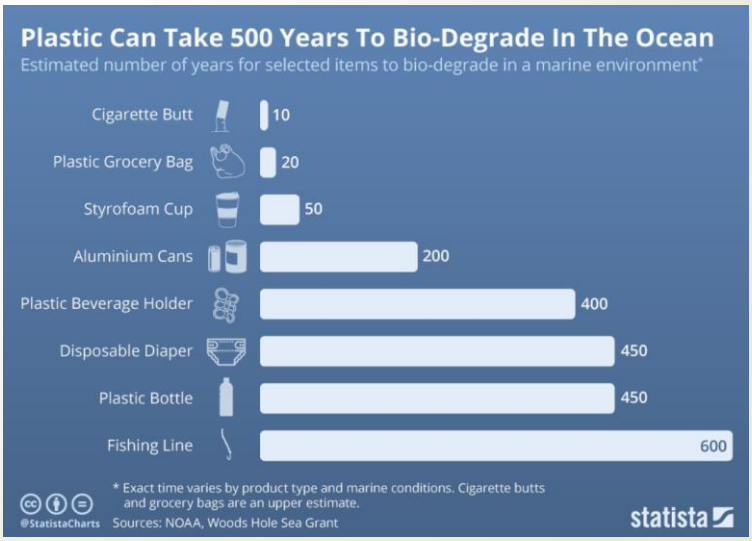
This is how long everyday plastic items last in the ocean! World Economic Forum



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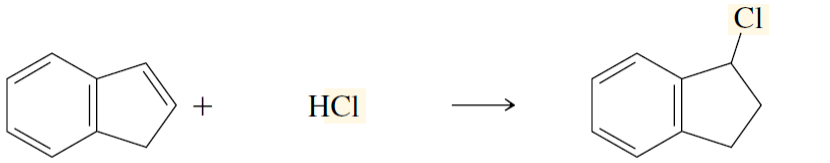
Explique a regiosseletividade de adição do HCl ao indeno



Indene + Hydrogen chloride → 1-Chloroindane (75–84%)

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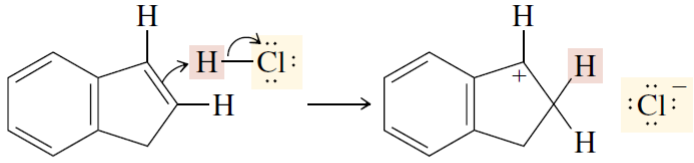
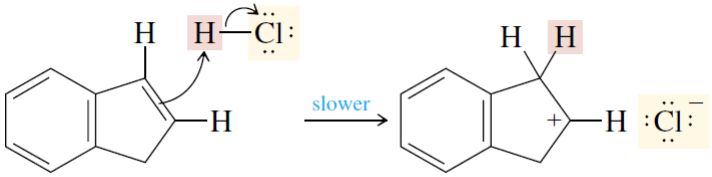
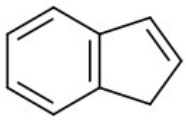
Solução



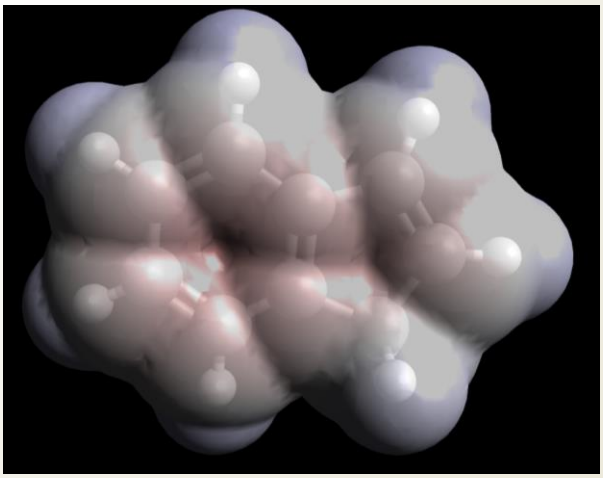
Carbocation that leads to observed product

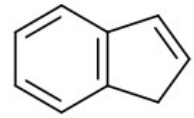


Less stable carbocation

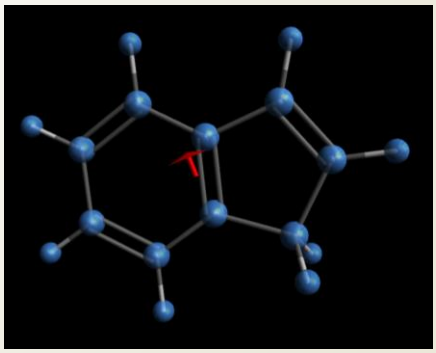


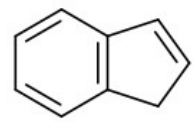
Aprenda por modelos via mapas de potencial eletrostático



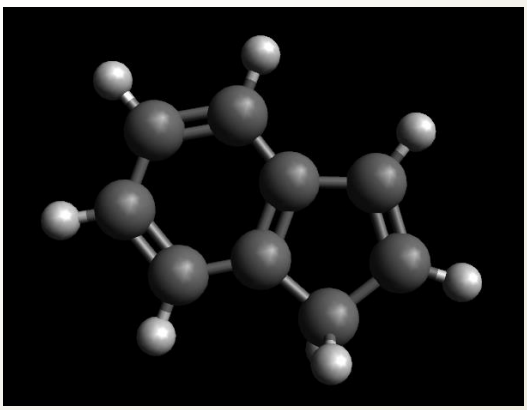


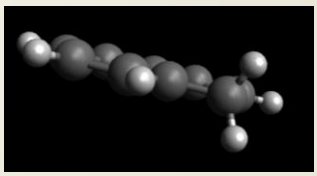
Aprenda por modelos via mapas de potencial eletrostático

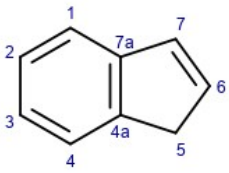




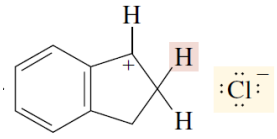
Aprenda por modelos via mapas de potencial eletrostático



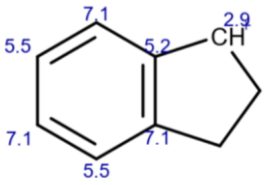


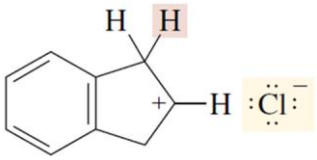


Eletronegatividade do orbital π

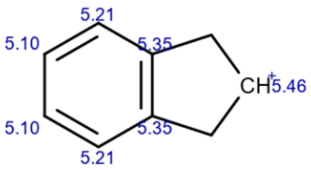


Carbocation that leads to observed product



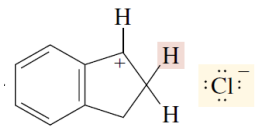


Less stable carbocation

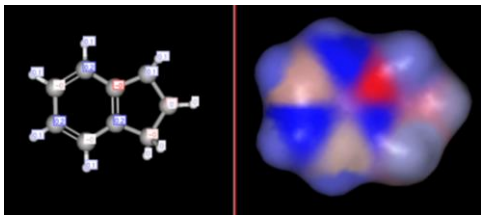


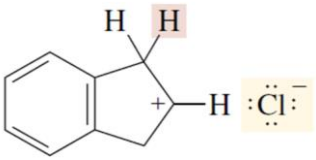
C 2.6

Cargas totais

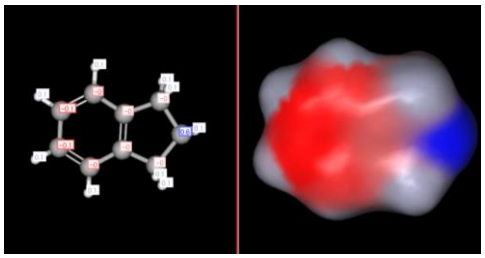


Carbocation that leads to observed product





Less stable carbocation



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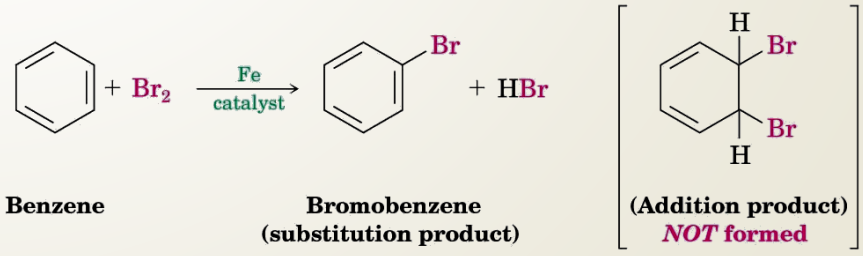
Estrutura e estabilidade do benzeno

- O benzeno reage lentamente com Br_2 para produzir bromobenzeno (Br substitui H)
- Esta é a **substituição** ao invés da reação de **adição** rápida comum aos compostos com C = C, sugerindo que no benzeno há uma barreira de energia mais alta



Benzene | **Bromobenzene (substitution product)** | **(Addition product) *NOT* formed**

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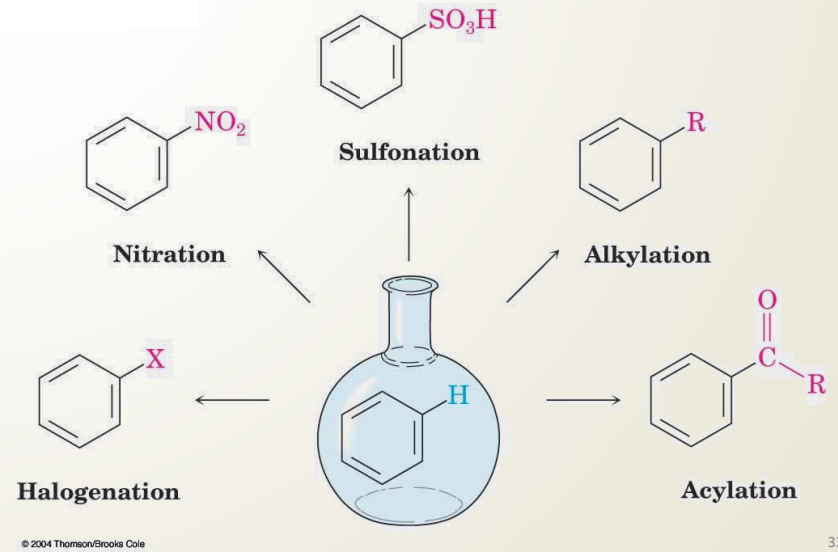
Reações do benzeno



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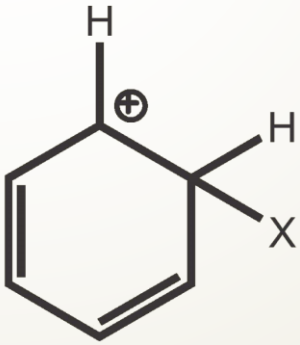
Substituições Aromáticas



George Willard Wheland

1907-1974

- A reação com o bromo envolve um mecanismo semelhante a muitas outras reações do benzeno com eletrófilos
- O intermediário catiônico foi proposto pela primeira vez por G. W. **Wheland**, da Universidade de Chicago e é frequentemente chamado de intermediário Wheland

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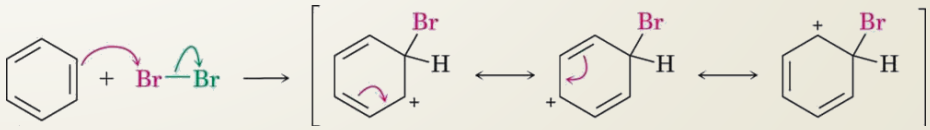
Bromação

- A adição de bromo ocorre em duas etapas
- Na primeira etapa, os elétrons π agem como um nucleófilo em direção ao Br_2 (em complex com o $FeBr_3$)
- O intermediário não é aromático e, portanto, possui alto teor de energia:



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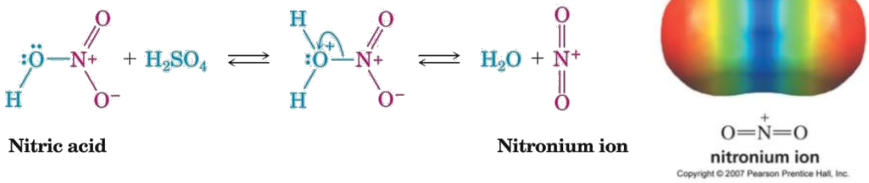
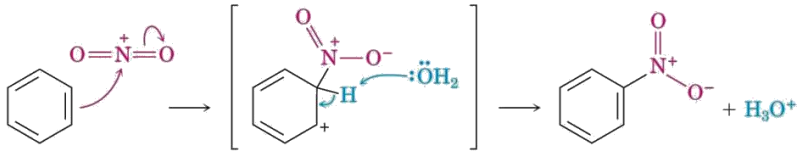
Nitração Aromática

- A combinação de ácido nítrico e ácido sulfúrico produz NO_2^+ (íon nitrônio)
- A reação com benzeno produz nitrobenzeno:





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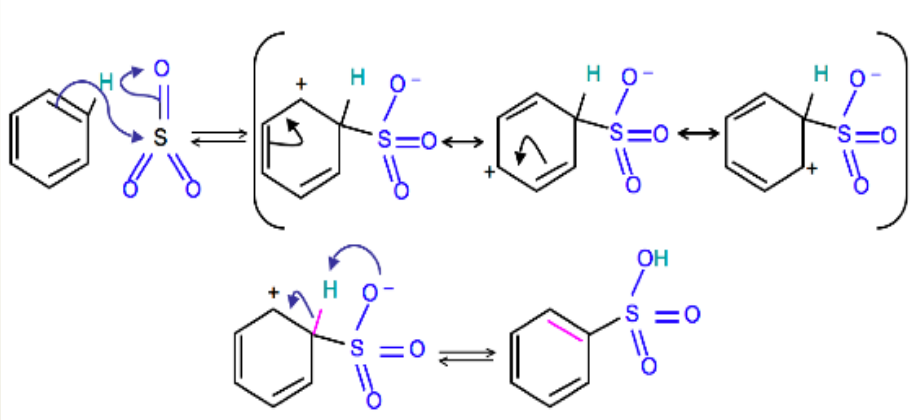
Sulfonação Aromática

- Substituição de H por SO_3 (sulfonação)
- Reação com uma mistura de ácido sulfúrico e SO_3
- A espécie reativa é o trióxido de enxofre ou seu ácido conjugado
- A reação ocorre via intermediário de Wheland e é reversível



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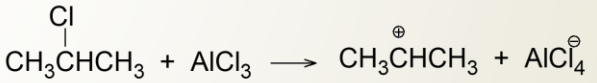
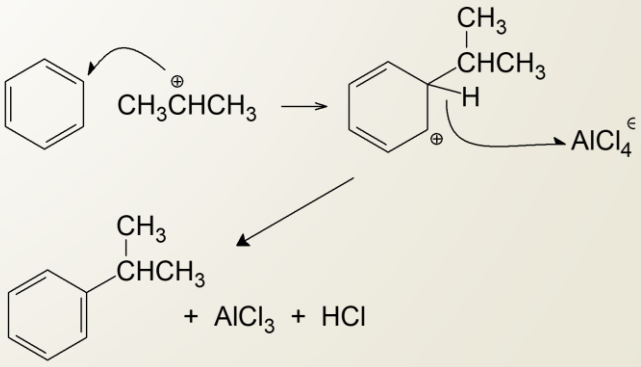
Alquilação de anéis aromáticos: a reação de Friedel-Crafts



- Substituição aromática de um R^+
- O cloreto de alumínio promove a formação do carbocátion



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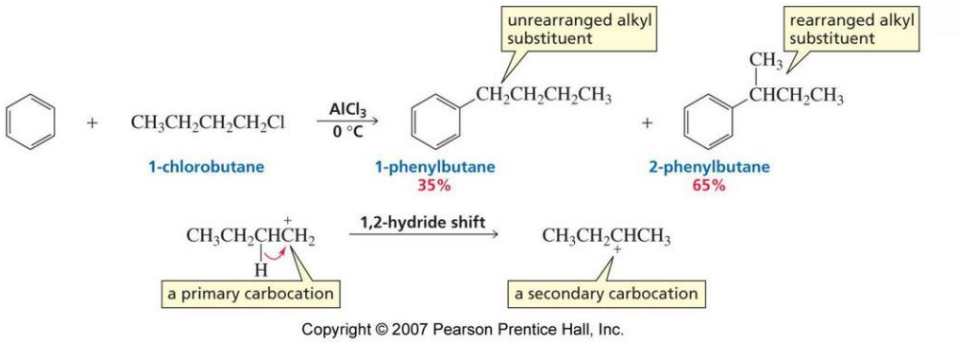
Alquilação de anéis aromáticos: a reação de Friedel-Crafts



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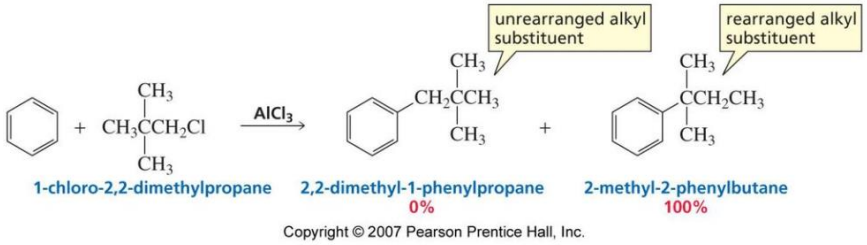
Alquilação de anéis aromáticos: a reação de Friedel-Crafts

Explique por que há formação apenas do 2-metil-2-fenilbutano



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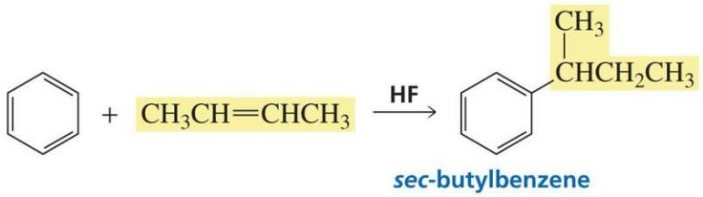
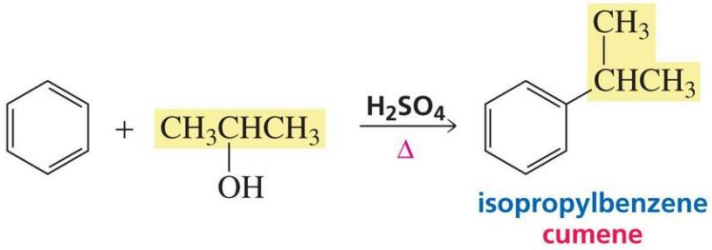
alkylation of benzene by an alkene



alkylation of benzene by an alcohol



Constituinte do óleo bruto e de combustíveis refinados.

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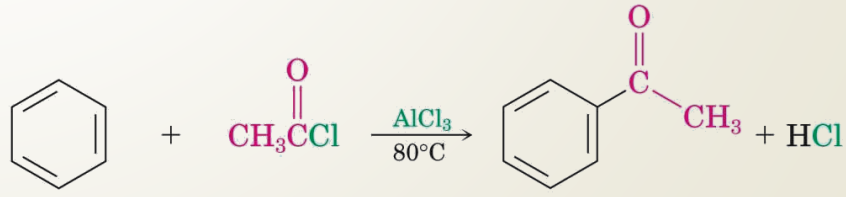
Acilação de Fiedel-Crafts

- A reação de um cloreto de ácido (RCOCl) e um anel aromático na presença de $AlCl_3$ introduz o grupo acila, —COR
  - Benzeno com cloreto de acetila produz acetofenona



Benzene **Acetyl chloride** **Acetophenone (95%)**

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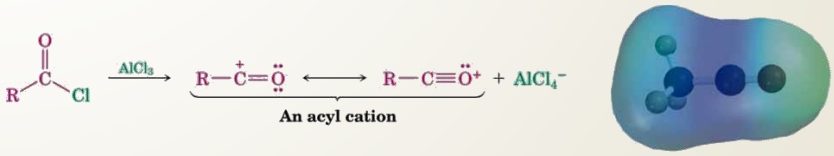
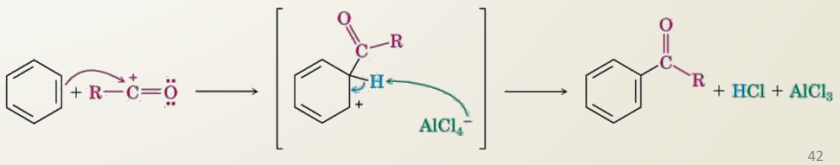
Mecanismo de acilação de Friedel-Crafts

- Semelhante à alquilação
- Eletrófilo reativo: cátion de acila estabilizado por ressonância
- Um cátion acila não se reorganiza





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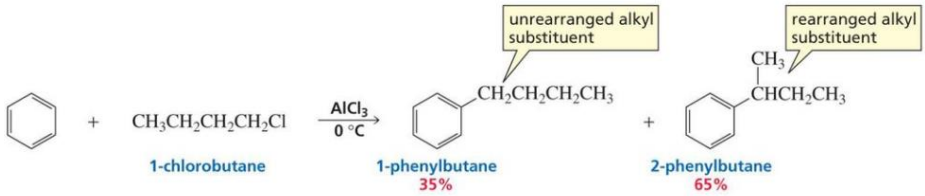
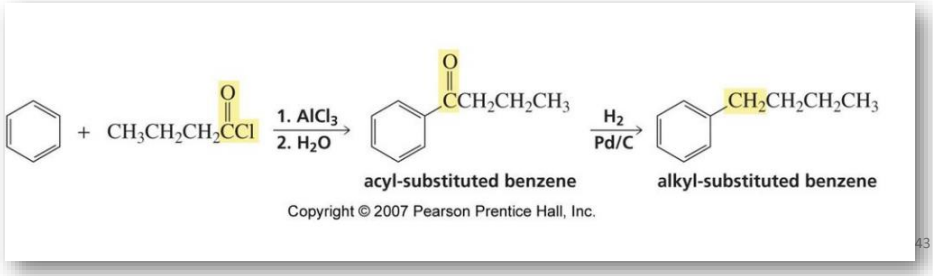
Como produzir 1-fenilbutano?





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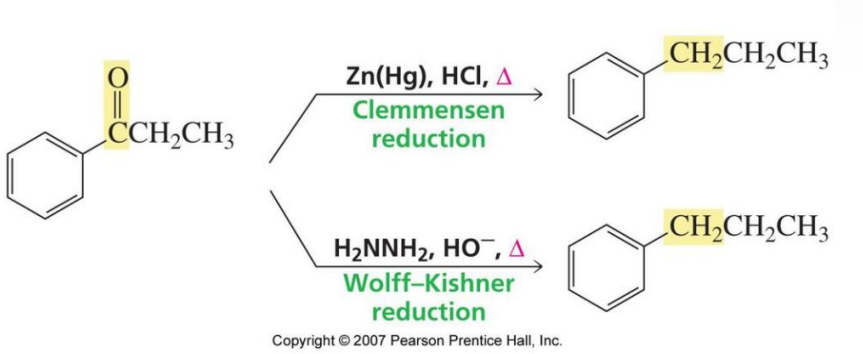
Redução da carbonila



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Reações do benzeno

Reaction and comments	Equation
1. Nitration Warming benzene with a mixture of nitric acid and sulfuric acid gives nitrobenzene. A nitro group (—NO_2) replaces one of the ring hydrogens.	Benzene + HNO_3 (H_2SO_4, 30–40°C) → Nitrobenzene (95%) + H_2O (Water)
2. Sulfonation Treatment of benzene with hot concentrated sulfuric acid gives benzenesulfonic acid. A sulfonic acid group (—SO_2OH) replaces one of the ring hydrogens.	Benzene + $HOSO_2OH$ (heat) → Benzenesulfonic acid (100%) + H_2O (Water)
3. Halogenation Bromine reacts with benzene in the presence of iron(III) bromide as a catalyst to give bromobenzene. Chlorine reacts similarly in the presence of iron(III) chloride to give chlorobenzene.	Benzene + Br_2 ($FeBr_3$) → Bromobenzene (65–75%) + HBr (Hydrogen bromide)
4. Friedel–Crafts alkylation Alkyl halides react with benzene in the presence of aluminum chloride to yield alkylbenzenes.	Benzene + $(CH_3)_3CCl$ (*tert*-Butyl chloride) ($AlCl_3$, 0°C) → *tert*-Butylbenzene (60%) + HCl (Hydrogen chloride)
5. Friedel–Crafts acylation An analogous reaction occurs when acyl halides react with benzene in the presence of aluminum chloride. The products are acylbenzenes.	Benzene + CH_3CH_2COCl (Propanoyl chloride) ($AlCl_3$, 40°C) → 1-Phenyl-1-propanone (88%) + HCl (Hydrogen chloride)

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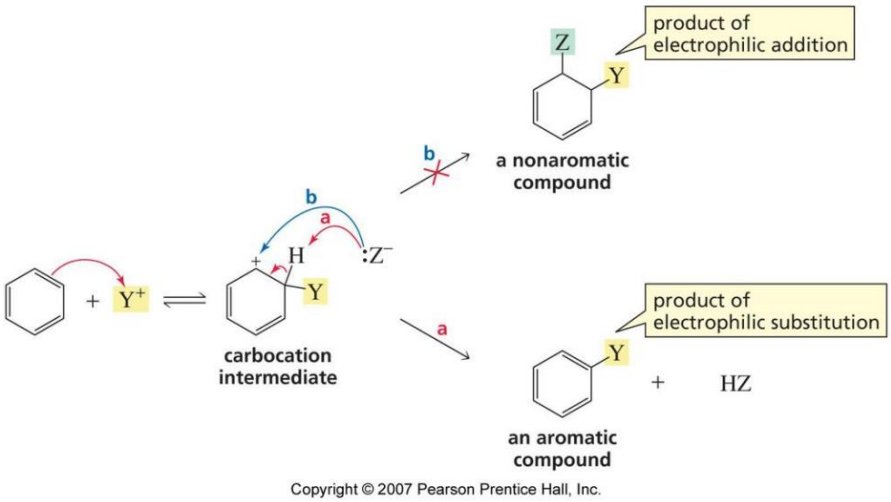
Caminho comum



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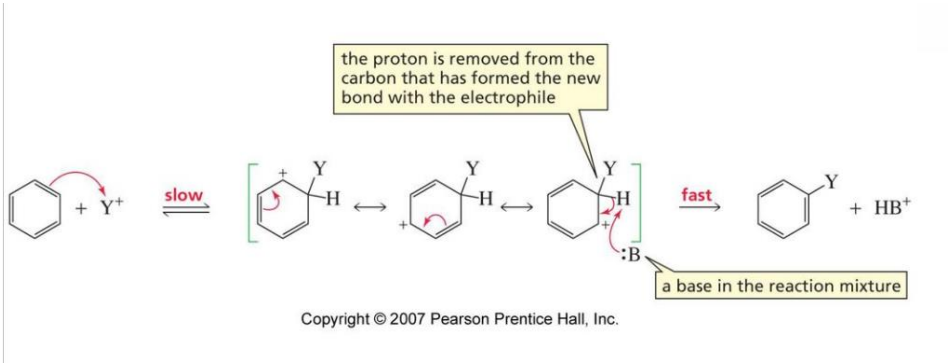
Caminho comum



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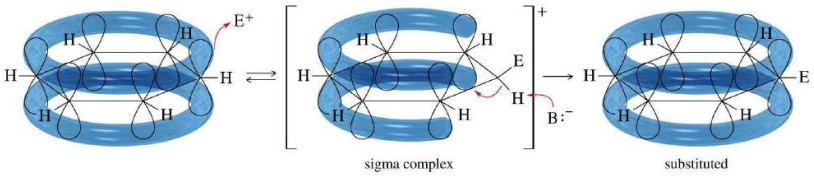
O complexo σ



Ion benzênio
E.g. ion arênio

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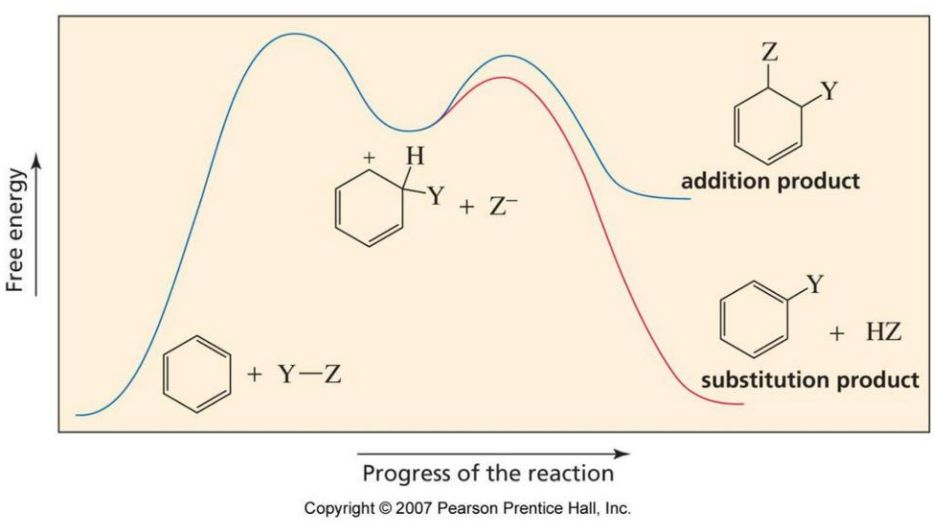
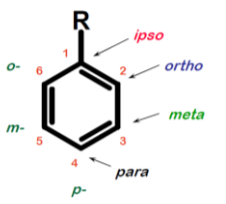
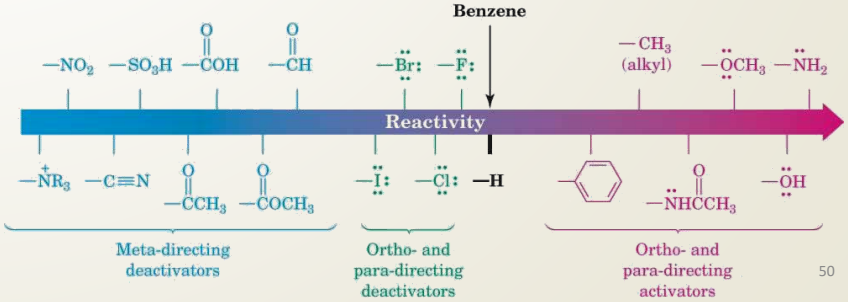
Caminho comum





Efeitos substituintes em anéis aromáticos

- Os substituintes podem fazer com que um composto seja (muito) mais ou (muito) menos reativo do que o benzeno
- Os substituintes afetam a orientação da reação - a relação posicional é controlada
- Ativadores orto e para-direcionadores, desativadores orto e para-direcionadores e desativadores meta-direcionadores



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Ativadores / Desativadores

Effect on rate	Substituent		Effect on orientation
Very strongly activating	$-\ddot{N}H_2$	(amino)	Ortho, para-directing
	$-\ddot{N}HR$	(alkylamino)	
	$-\ddot{N}R_2$	(dialkylamino)	
	$-\ddot{O}H$	(hydroxyl)	
Strongly activating	$-\ddot{N}HCR$ (O)	(acylamino)	Ortho, para-directing
	$-\ddot{O}R$	(alkoxy)	
	$-\ddot{O}CR$ (O)	(acyloxy)	
Activating	$-R$	(alkyl)	Ortho, para-directing
	$-Ar$	(aryl)	
	$-CH{=}CR_2$	(alkenyl)	
Standard of comparison	$-H$	(hydrogen)	
Deactivating	$-X$ (X = F, Cl, Br, I)	(halogen)	Ortho, para-directing
	$-CH_2X$	(halomethyl)	
Strongly deactivating	$-CH$ (O)	(formyl)	Meta-directing
	$-CR$ (O)	(acyl)	
	$-COH$ (O)	(carboxylic acid)	
	$-COR$ (O)	(ester)	
	$-CCl$ (O)	(acyl chloride)	
	$-C{\equiv}N$	(cyano)	
	$-SO_3H$	(sulfonic acid)	
Very strongly deactivating	$-CF_3$	(trifluoromethyl)	Meta-directing
	$-NO_2$	(nitro)	

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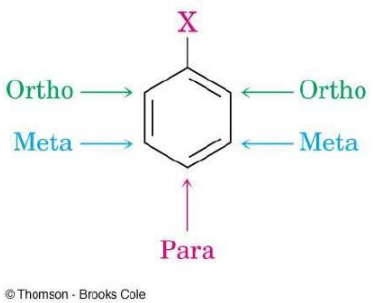
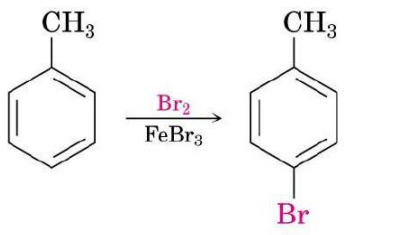
Ativadores, dirigem o,*p*



© Thomson - Brooks Cole

Bromação do tolueno



Toluene **p-Bromotoluene**

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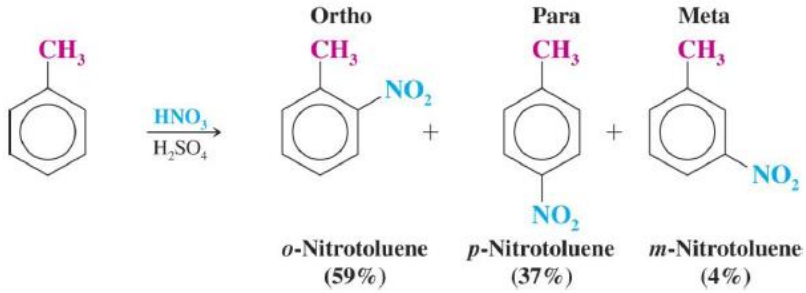
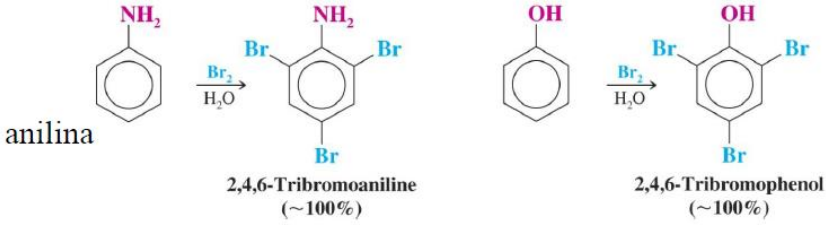

Ortho
Para
Meta
CH3
HNO3
H2SO4
NO2
o-Nitrotoluene
(59%)
p-Nitrotoluene
(37%)
m-Nitrotoluene
(4%)


NH2
anilina
Br2
H2O
Br
2,4,6-Tribromoaniline
(~100%)
OH
2,4,6-Tribromophenol
(~100%)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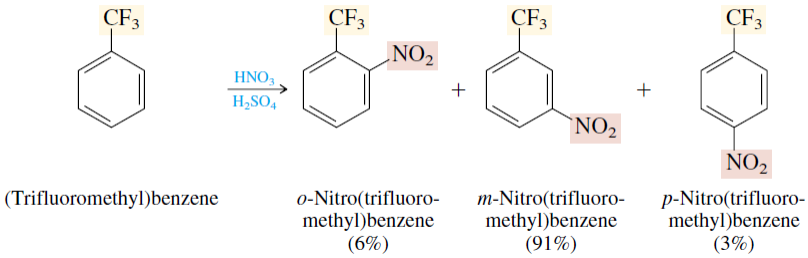
CF3
HNO3
H2SO4
NO2
(Trifluoromethyl)benzene
o-Nitro(trifluoro-
methyl)benzene
(6%)
m-Nitro(trifluoro-
methyl)benzene
(91%)
p-Nitro(trifluoro-
methyl)benzene
(3%)

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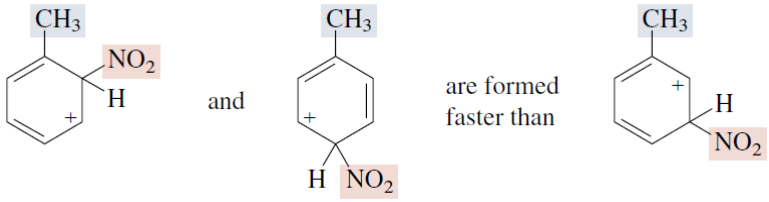
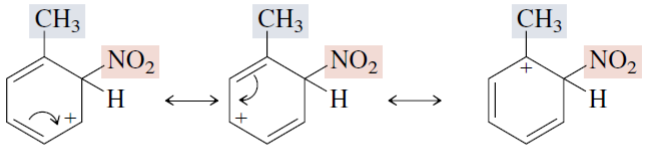
Velocidade e regiosseletividade na nitração do tolueno



Ortho attack



This resonance form is a tertiary carbocation

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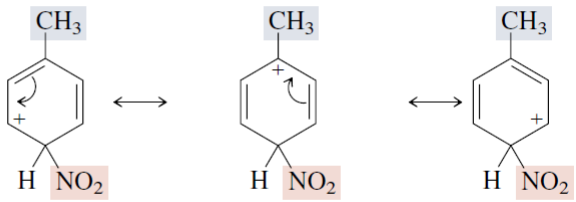
Para attack



This resonance form is a tertiary carbocation

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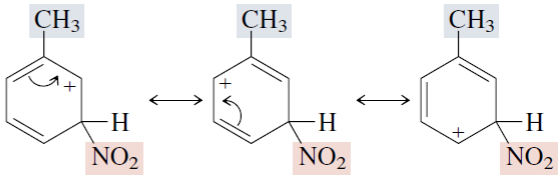
Meta attack



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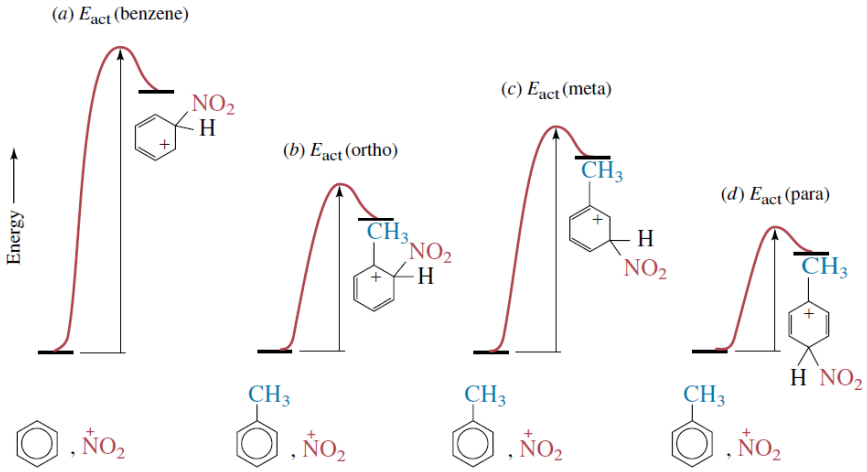
Diagramas comparativos de energia para ataque do íon nitrônio



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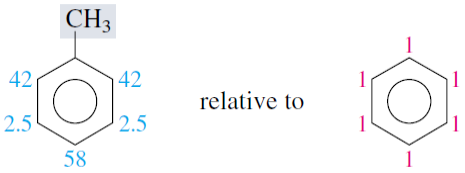
Velocidades relativas de ataque ao tolueno



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Faça uma análise similar para a nitração do (trifluorometil)benzeno

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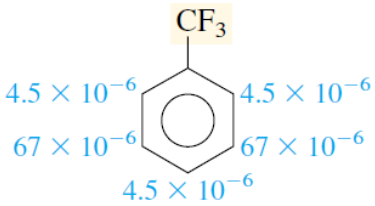
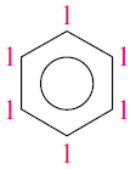
Velocidades relativas de ataque ao (trifluorometil)benzeno



compared with



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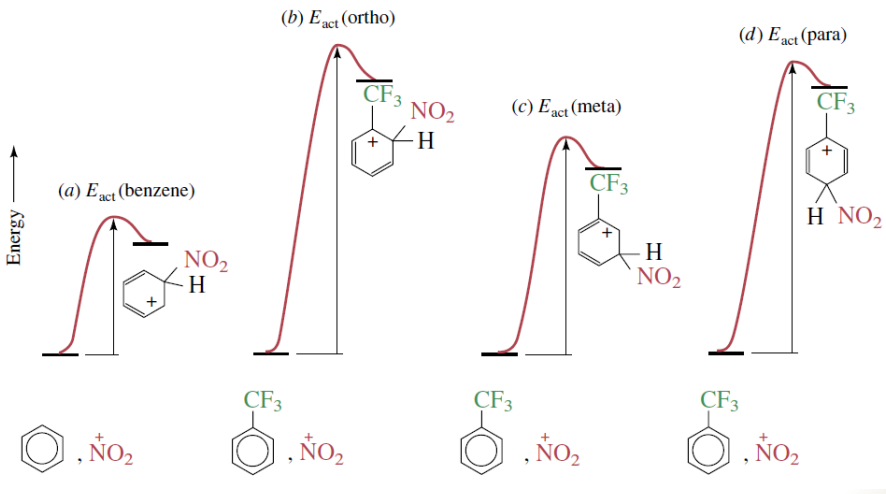
Diagramas comparativos de energia para ataque do íon nitrônio



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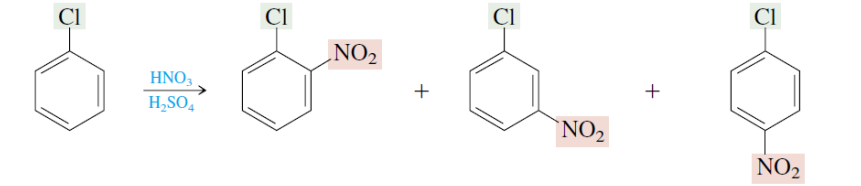
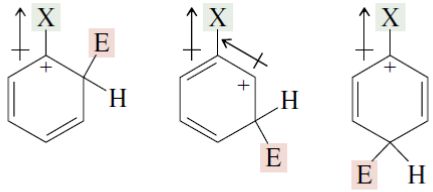
Halogênios?



Chlorobenzene | *o*-Chloronitrobenzene (30%) | *m*-Chloronitrobenzene (1%) | *p*-Chloronitrobenzene (69%)



All these ions are less stable when X = F, Cl, Br, or I than when X = H

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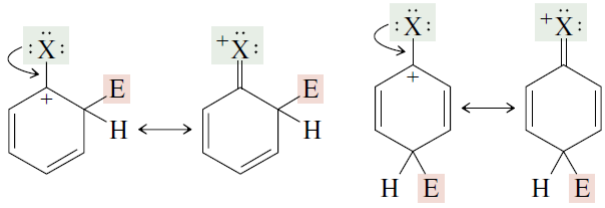
Ortho attack ***Para attack***



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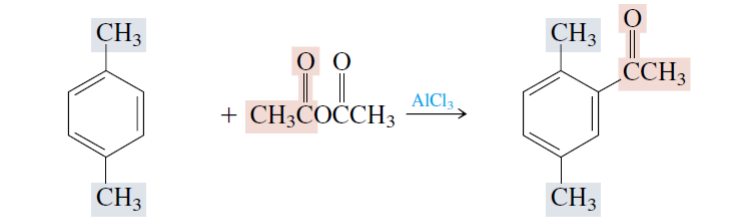
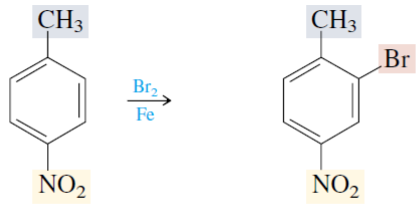
Efeitos múltiplos



1,4-Dimethylbenzene (*p*-xylene)

2,5-Dimethylacetophenone (99%)



p-Nitrotoluene

2-Bromo-4-nitrotoluene (86–90%)

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A partir do benzeno, mostre como sintetizar o *m*-cloroetilbenzeno