

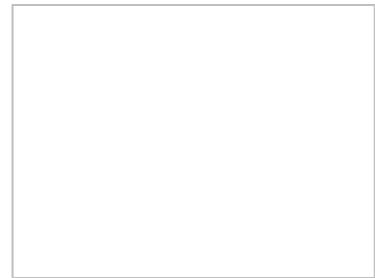


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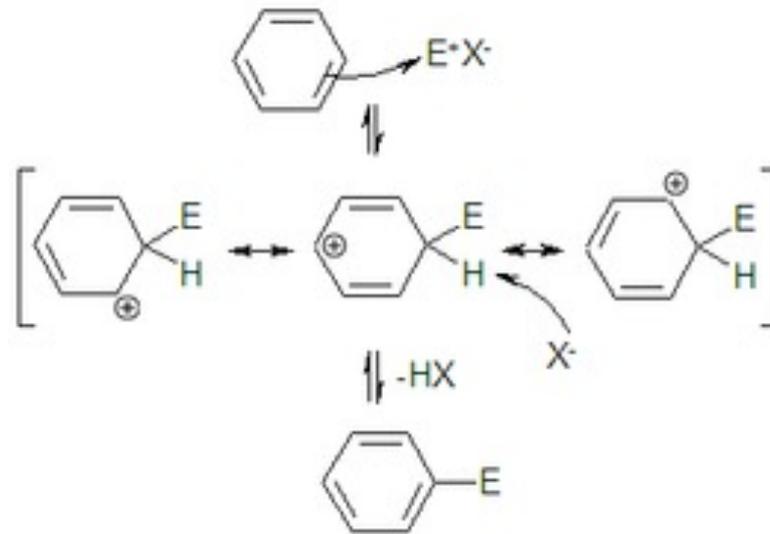
QFL 0450

Química Geral e Orgânica para Biomedicina

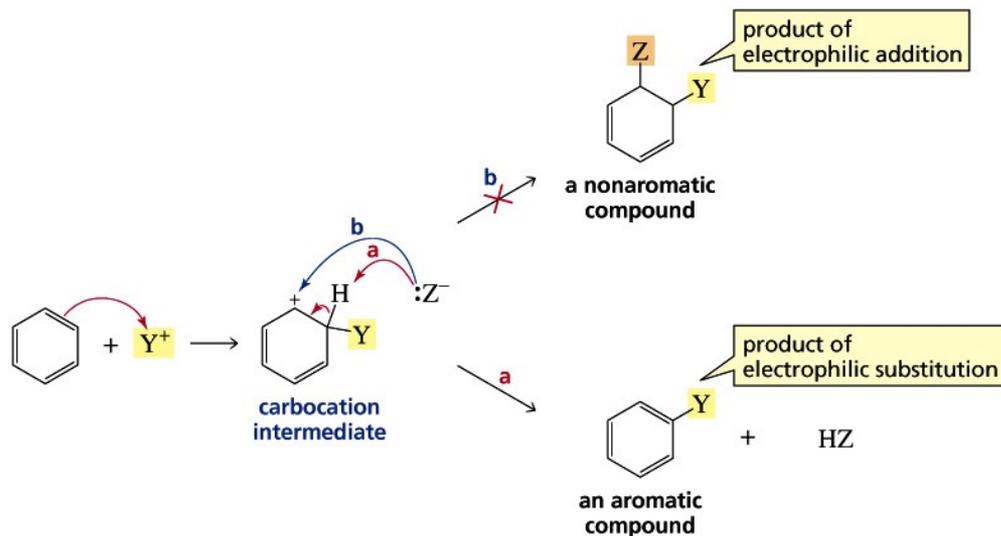
Substituição eletrofílica aromática



Substituição Aromática Eletrofílica

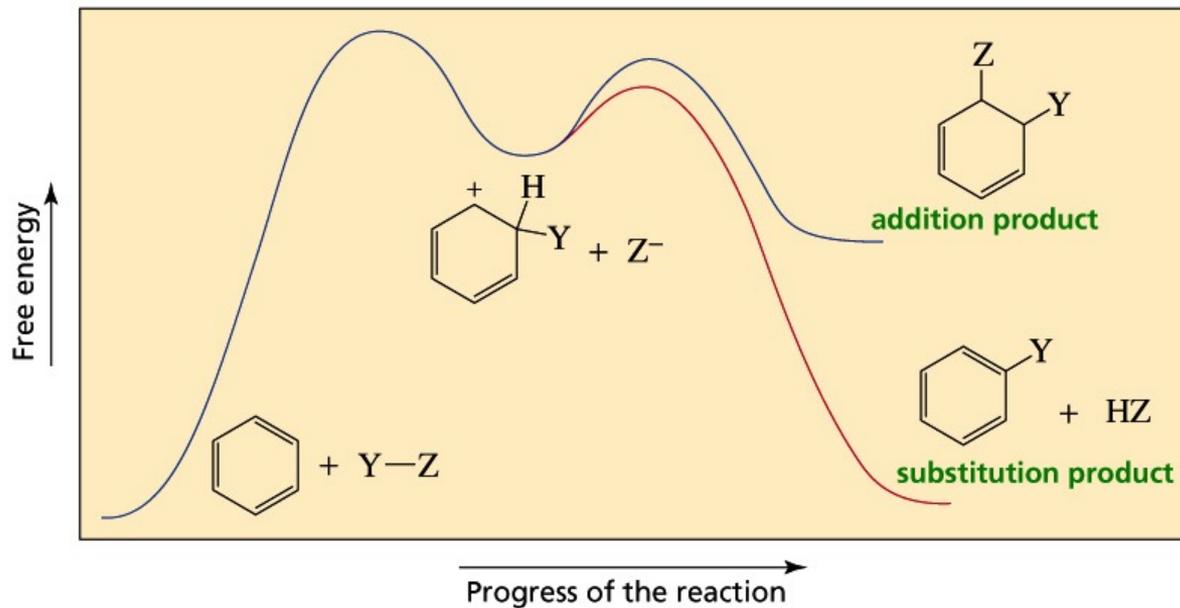


As reações características dos arenos são as reação de substituição que ocorrem quando eles reagem com reagentes eletrofílicos.



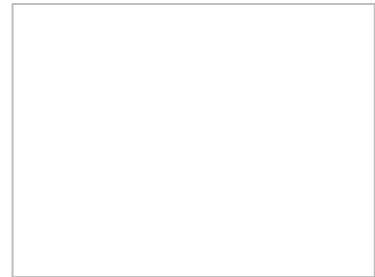
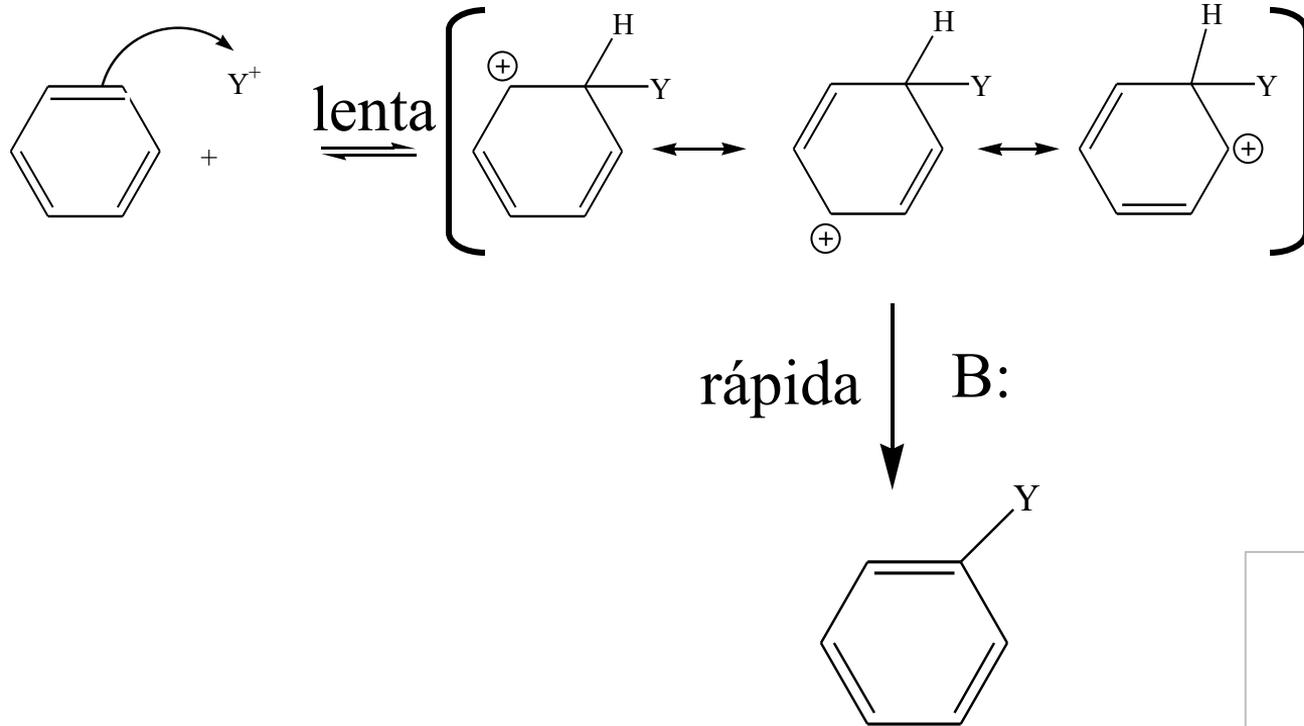
Os eletrófilos são ou um íon positivo (Y^+) ou alguma outra espécie deficiente de elétrons com grande carga positiva parcial.

O anel aromático é mantido na reação de substituição:



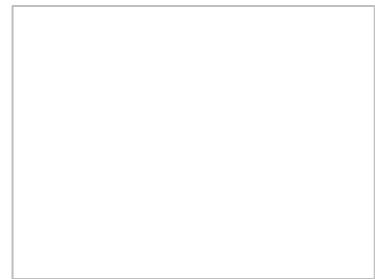
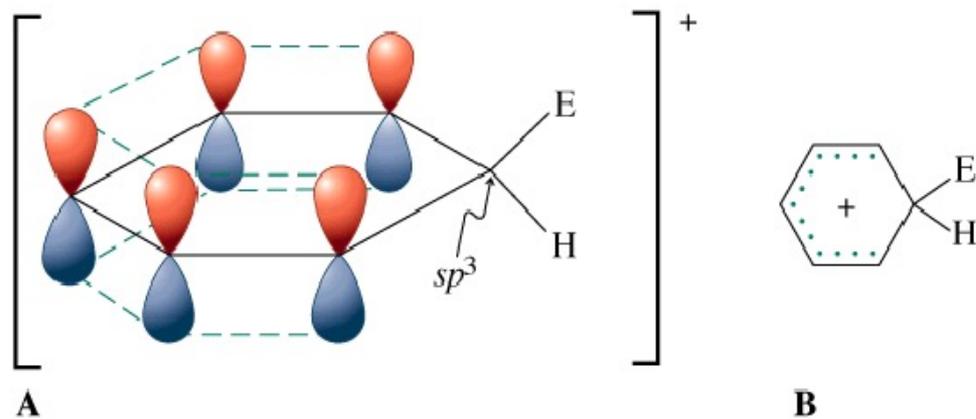


Mecanismo Geral da SEAr



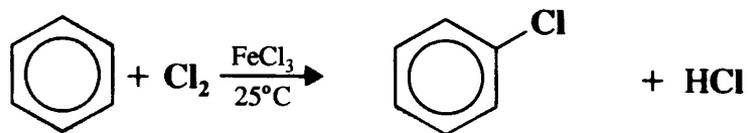


Intermediário da reação não é aromático:

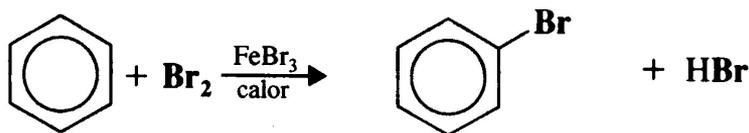




Halogenação do Benzeno



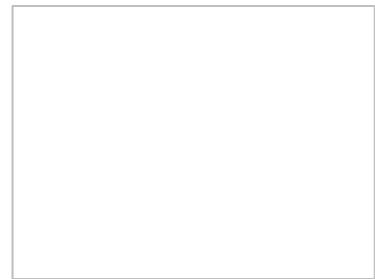
Clorobenzeno (90%)



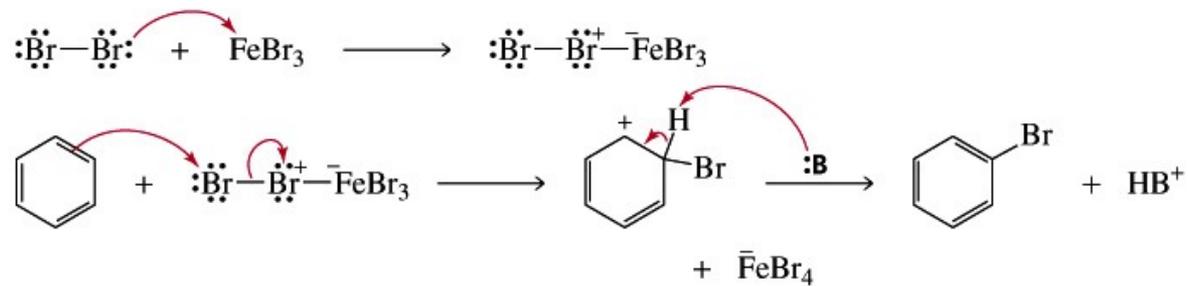
Bromobenzeno (75%)

Ácidos de Lewis mais utilizados: FeCl_3 , FeBr_3 e AlCl_3 .

Função do ácido de Lewis: polarizar a ligação X-X.

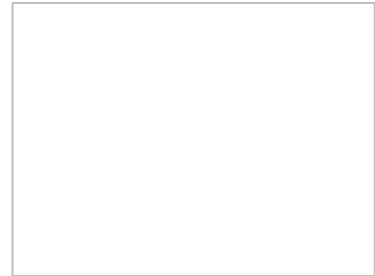
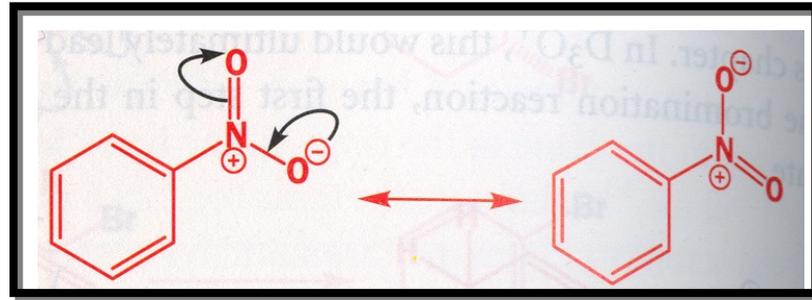
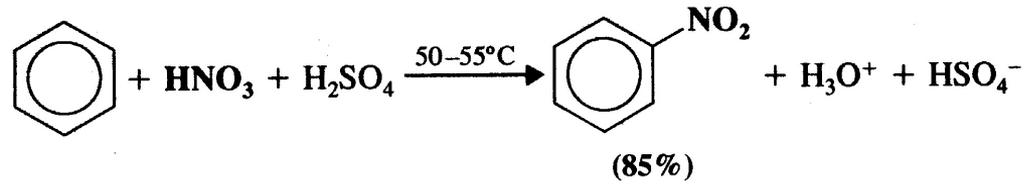


mechanism for bromination

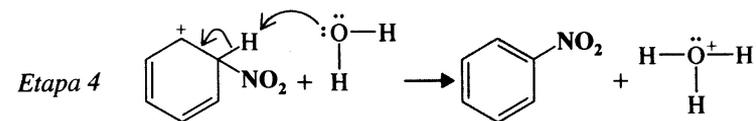
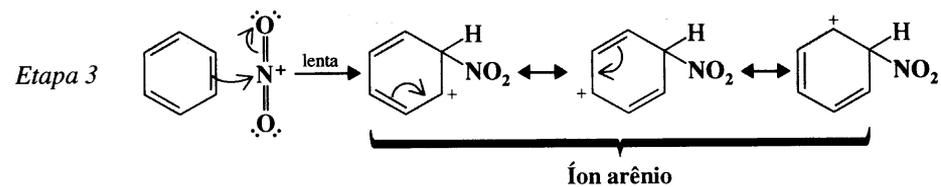
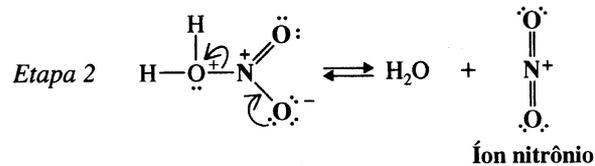
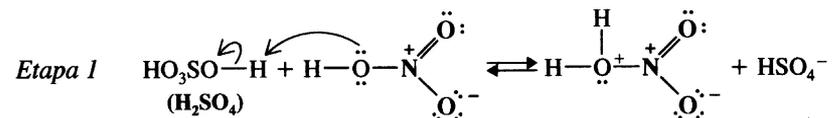




Nitração do Benzeno

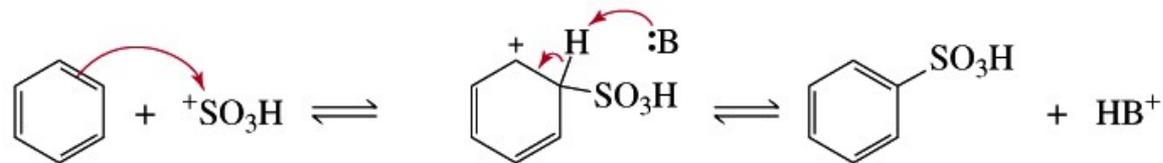
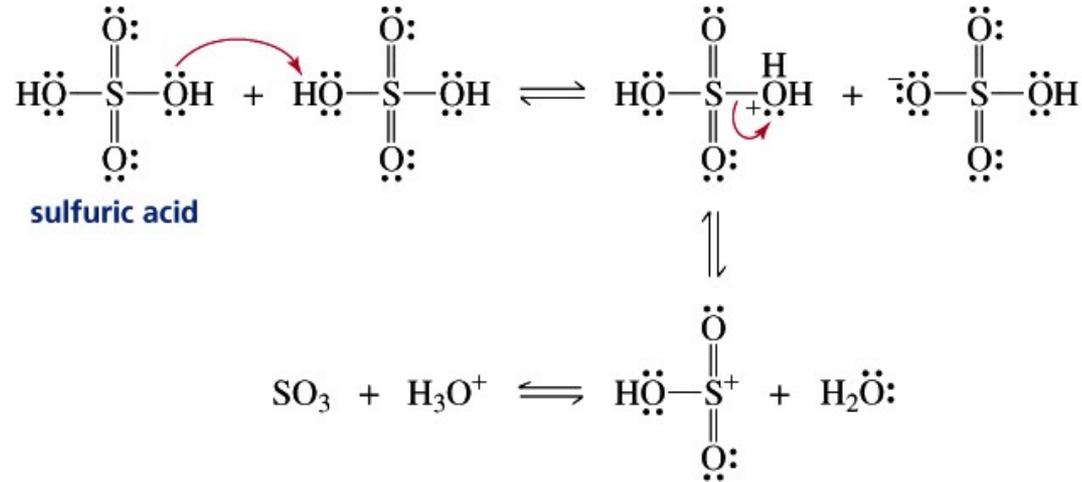


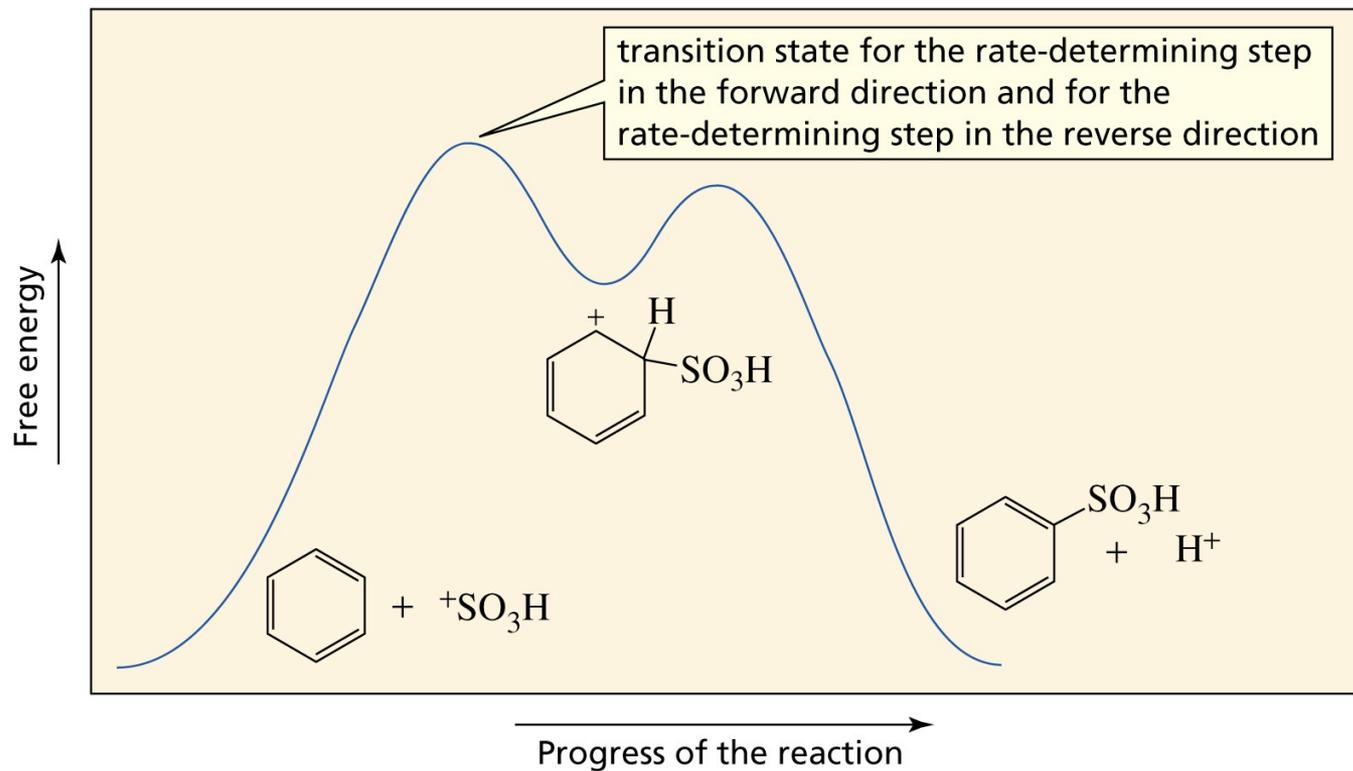
Nitração de Benzeno



Sulfonação do Benzeno

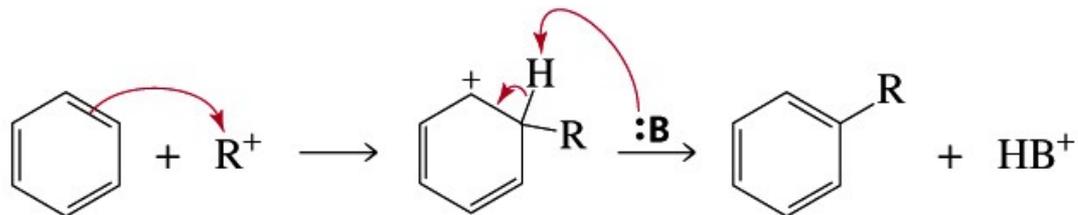
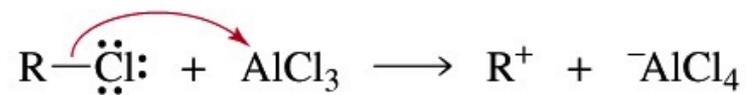
mechanism for sulfonation





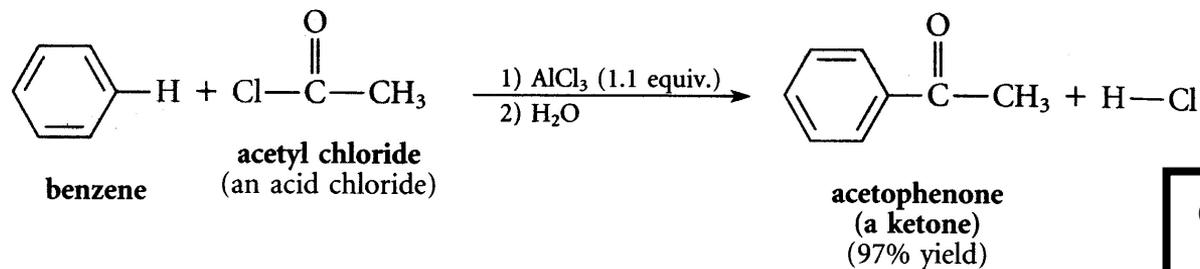
Alquilação de Friedel-Crafts

mechanism for the Friedel-Crafts alkylation

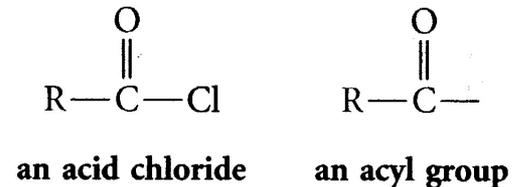


Acilação de Friedel-Crafts

Exemplo:

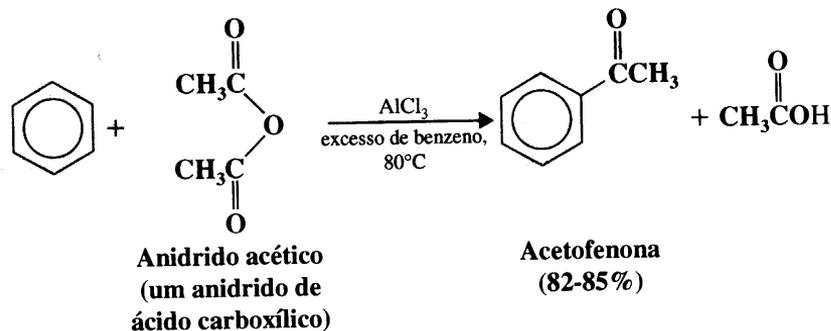


Grupo acila:



Anidridos também
podem ser utilizados
nas acilações.

Exemplo:



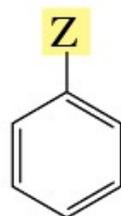


Di- e Poli-substituição

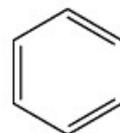
- Grupos existentes em um anel benzênico influenciam a substituição adicional na **orientação** e **velocidade**
- **Orientação:**
 - certos substituintes dirigem preferencialmente para as posições orto & para;
 - outros dirigem preferencialmente para as posições meta
 - substituintes são classificados como
 - **orto-para dirigentes** **ou**
 - **meta dirigentes**
- **Velocidade:**
 - certos substituintes causam que a velocidade da segunda substituição seja maior que para o benzeno; outros causam que a velocidade seja menor
 - substituintes são classificados como
 - **ativantes em relação à substituição adicional, ou**
 - **desativantes**



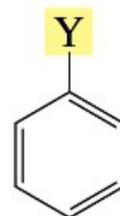
relative rates of electrophilic substitution



>

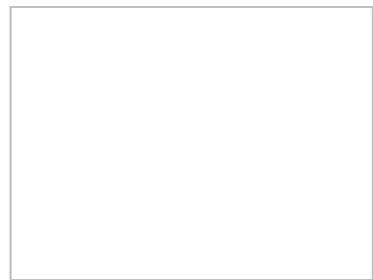


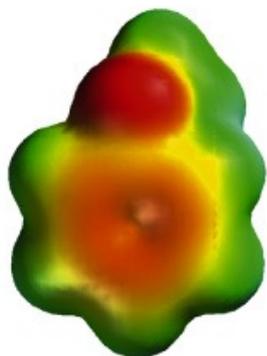
>



Z donates electrons
into the benzene ring

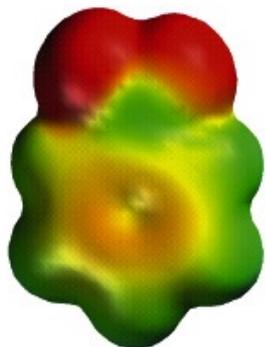
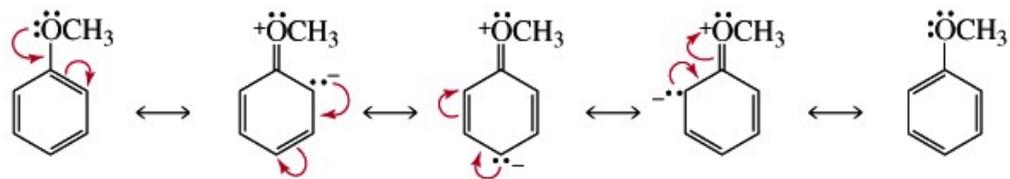
Y withdraws electrons
from the benzene ring





anisole

donation of electrons into a benzene ring by resonance



nitrobenzene

withdrawal of electrons from a benzene ring by resonance

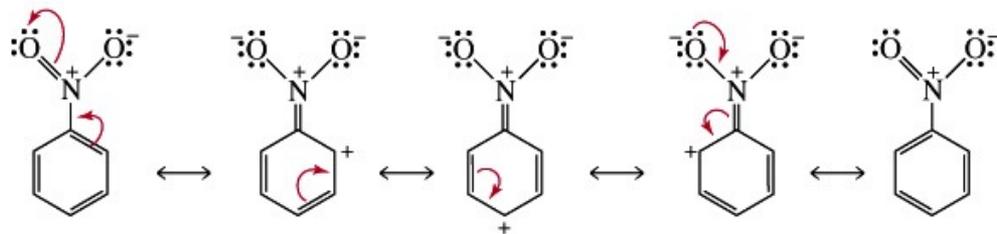




Table 16.1 The Effects of Substituents on the Reactivity of a Benzene Ring Toward Electrophilic Substitution

Activating substituents	Most activating				
↓	-NH ₂	Strongly activating	Ortho/para directing		
	-NHR				
	-NR ₂				
	-OH				
	-OR				
		-NHCO-		Moderately activating	
		-OCO-		Weakly activating	
		-R			
		-Ar			
		-CH=CHR			
Standard of comparison →	-H				
↓	-F	Weakly deactivating	Meta directing		
	-Cl				
	-Br				
	-I				
		-CHO		Moderately deactivating	
		-CO-			
		-COR			
		-COH			
		-COCl			
		-C≡N			
		-SO ₃ H		Strongly deactivating	
		-NH ₃ ⁺			
		-NHR ₂ ⁺			
		-NR ₃ ⁺			
		-NO ₂			
	Most deactivating				

