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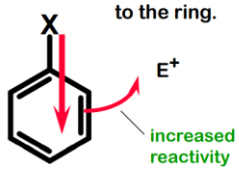
Diretividade de substituintes simples do benzeno

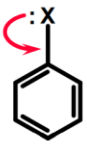
ortho, para - Directing Groups

Groups that donate electron density to the ring.



These groups also "activate" the ring, or make it more reactive.

PROFILE:



+I Substituent	+R Substituent
CH_3-	CH_3-$\ddot{O}$-
R-	CH_3-$\ddot{N}$-
	-$\ddot{N}H_2$
	-$\ddot{O}$-H

The +R groups activate the ring more strongly than +I groups.

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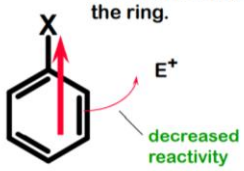
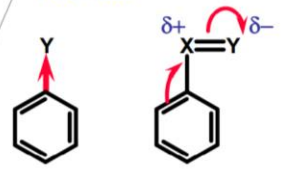
meta - Directing Groups

Groups that withdraw electron density from the ring.

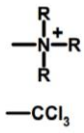


These groups also "deactivate" the ring, or make it less reactive.

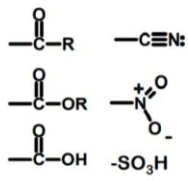
PROFILE:



-I Substituent

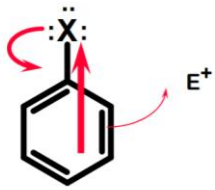


-R Substituent



THE EXCEPTION

Halides - *o,p* Directors / Deactivating



+R / -I / *o,p* / deactivating

-F
-Cl
-Br
-I

Halides represent a special case:

They are *o,p* directing groups that are deactivating

They are *o,p* directors (+R effect)

They are deactivating (-I effect)

Most other other substituents fall into one of these four categories:

1) +R / *o,p* / activating
2) +I / *o,p* / activating
3) -R / *m* / deactivating
4) -I / *m* / deactivating

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Diretividade de substituintes múltiplos do benzeno

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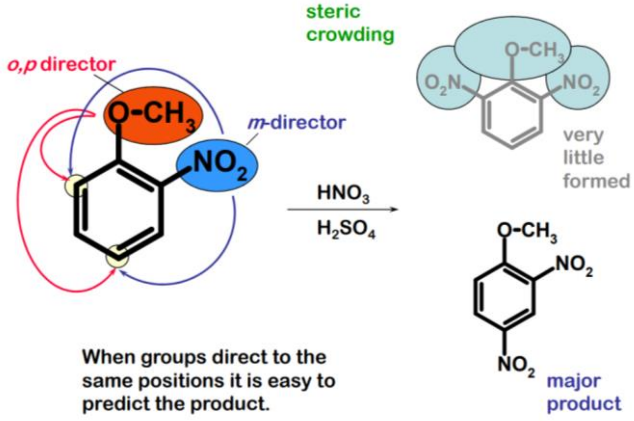
GROUPS ACTING IN CONCERT



When groups direct to the same positions it is easy to predict the product.

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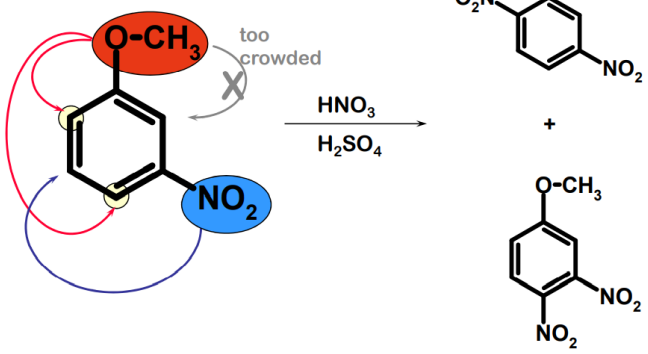
GROUPS COMPETING

o,p-directing groups win over *m*-directing groups



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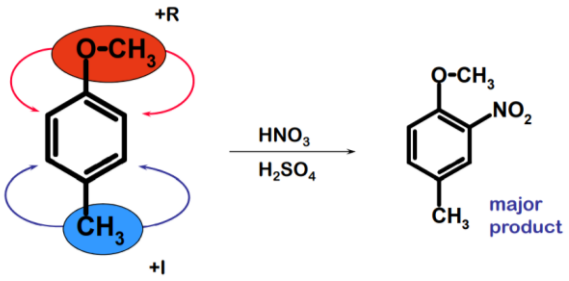
RESONANCE VERSUS INDUCTIVE EFFECT



resonance effects are more important than inductive effects

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Efeito de campo de vários grupos em relação ao hidrogênio

+I		−I	
O^-	NR_3^+	COOH	OR
COO^-	SR_2^+	F	COR
CR_3	NH_3^+	Cl	SH
CHR_2	NO_2	Br	SR
CH_2R	SO_2R	I	OH
CH_3	CN	OAr	C≡CR
D	SO_2Ar	COOR	Ar
			$C{\equiv}CR_2$

[a]The groups are listed approximately in order of decreasing strength for both –I and +I groups. [Reprinted with permission from Ceppi, E.; Eckhardt, W.; Grob, C.A. *Tetrahedron Lett.* **1973**, 3627.

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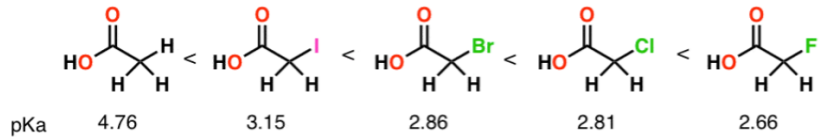
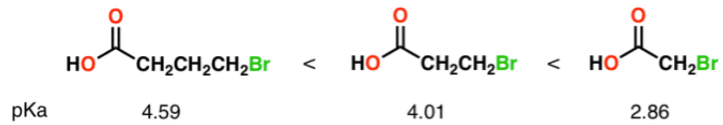
Efeitos Indutivo (campo) e Ressonância

Two principles - electron-withdrawing substituents can increase acidity of a nearby atom, which *increases with electronegativity* and *decreases with increasing distance to the atom*.

Electronegativity increases in the order F > Cl > Br > I :



More acidic



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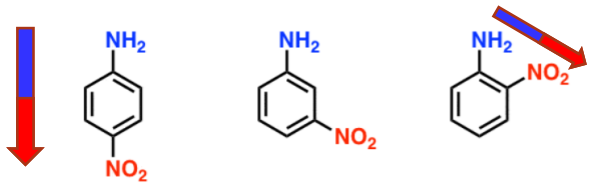
Por que a meta-nitroanilina é mais básica do que a para-nitroanilina, embora o grupo NO_2 esteja mais próximo da amina?



	p-nitroaniline	*m*-nitroaniline	*o*-nitroaniline
pK_aH	1.0	2.46	−0.26

most basic of the three amines pictured

Inductive effects alone can't explain this!

pK_aH, é o pK_a do ácido conjugado!

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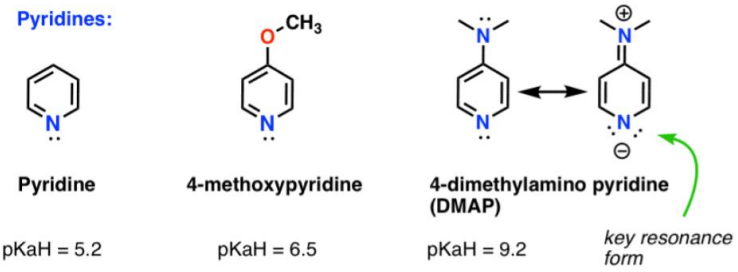
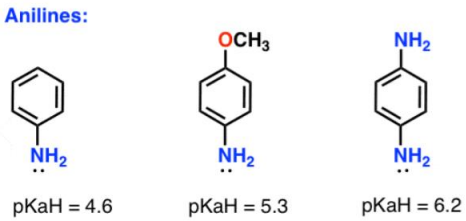
Em sistemas aromáticos, *EDG (ERG)* podem aumentar a basicidade





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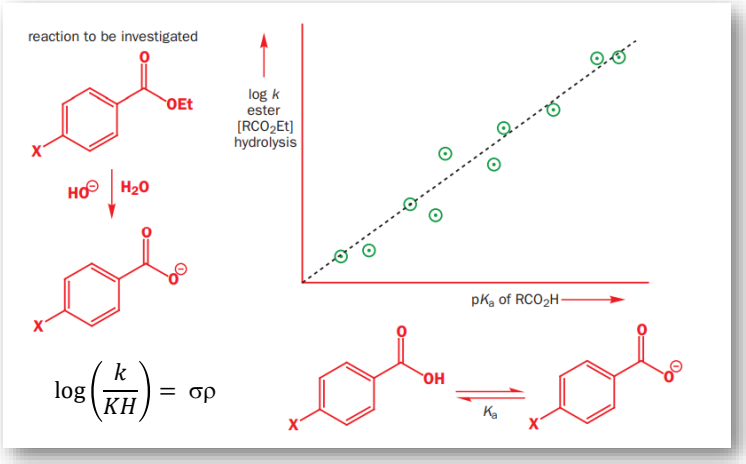
A correlação de Hammett



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A correlação de Hammett