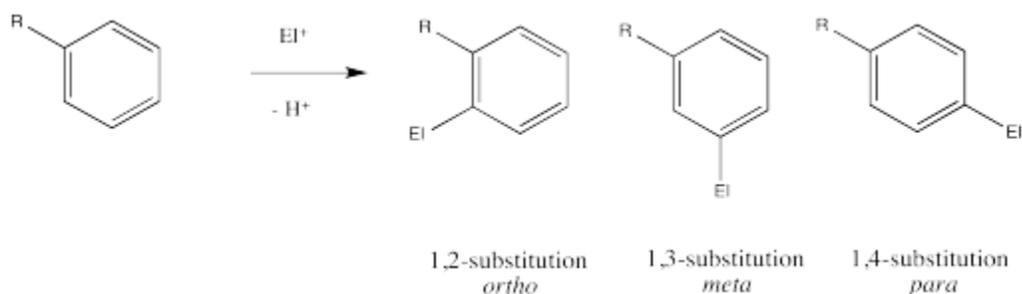


DIRECTING EFFECTS

In addition to exerting an effect on the speed of reaction, substituents on the benzene ring also influence the regiochemistry of the reaction. That is, they control *where* the new substituent appears in the product.

Remember, there are three different positions on the benzene ring where a new substituent can attach, relative to the original substituent. Substitution could actually occur on five positions around the ring, but two pairs are related by symmetry. Isomerism in disubstituted benzenes can be described by numbering the substituents (1,2- etc) or by the relationships *ortho*-, *meta*- and *para*-. There are two positions *ortho*- to the initial substituent and two positions *meta*- to it.



Ingold and colleagues investigated the question of regiochemistry in nitration. They reported the following observations:

Substitution patterns during nitration of benzene derivatives

R in C ₆ H ₅ R	% <i>o</i> - product	% <i>m</i> - product	% <i>p</i> - product
CH ₃	56	3	41
F	10	0	90
Cl	30	0	70
Br	38	0	62
OH	10	0	90
CHO	19	72	9
CO ₂ Et	28	68	3
CN	17	81	2
NO ₂	6	94	0

In looking at the table, you might see that there are two groups of substituents. One group reacts to make mixtures of *ortho*- and *para*- products. There may be different ratios of *ortho*- to *para*- and there may be small amounts of *meta*-, but don't get

bogged down in the details right now. Focus on the bigger picture. Some groups are "*ortho*-/*para*-directors".

The other group reacts to make mostly *meta*-substituted products. There may be small amounts of *ortho*- and *para*- products, but don't worry about that. Focus on the bigger picture. Some groups are "*meta*-directors".

These regiochemical effects are very closely related to the activating and directing effects we have already seen. If we want to understand this data, we need to think about things like π -donation, π -acceptance, inductive effects and cation stability.

Source: <http://employees.csbsju.edu/cschaller/Reactivity/romadd/ARdirect.htm>