

12.12

Substituent Effects in Electrophilic  
Aromatic Substitution:  
Activating Substituents

## *Table 12.2*

### Classification of Substituents in Electrophilic Aromatic Substitution Reactions

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Very strongly activating

Strongly activating

Activating

Standard of comparison is H

Deactivating

Strongly deactivating

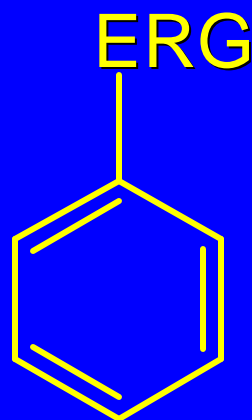
Very strongly deactivating

## *Generalizations*

1. All activating substituents are ortho-para directors.
2. Halogen substituents are slightly deactivating but ortho-para directing.
3. Strongly deactivating substituents are meta directors.

## *Electron-Releasing Groups (ERGs)*

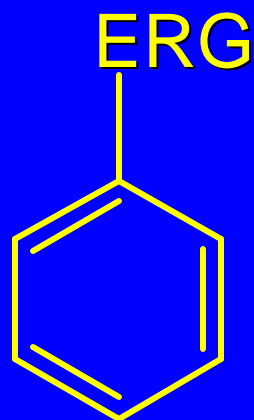
are ortho-para directing and activating



ERGs include  $\text{—R}$ ,  $\text{—Ar}$ , and  $\text{—C=C}$

## *Electron-Releasing Groups (ERGs)*

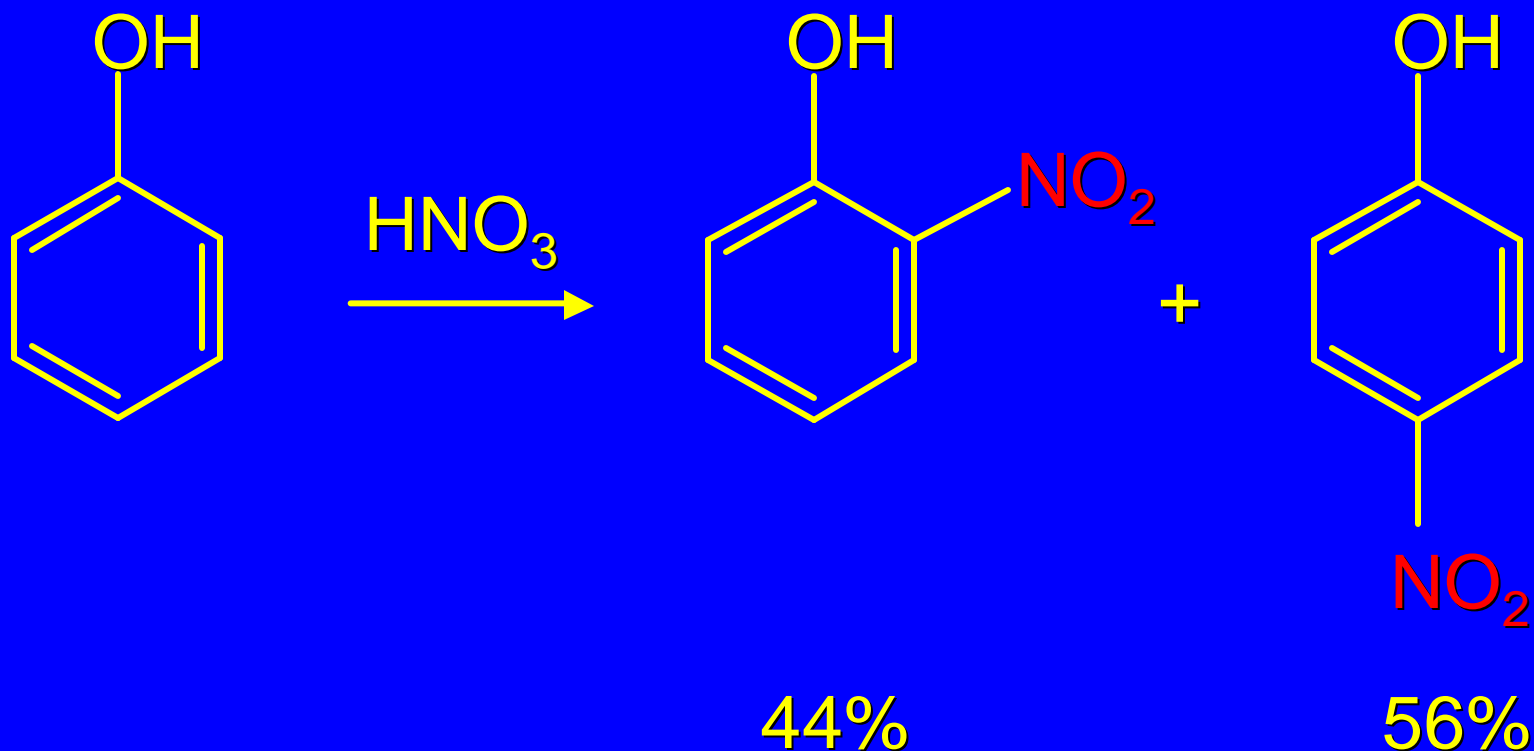
are ortho-para directing and strongly activating



ERGs such as —OH, and —OR  
are  
strongly activating

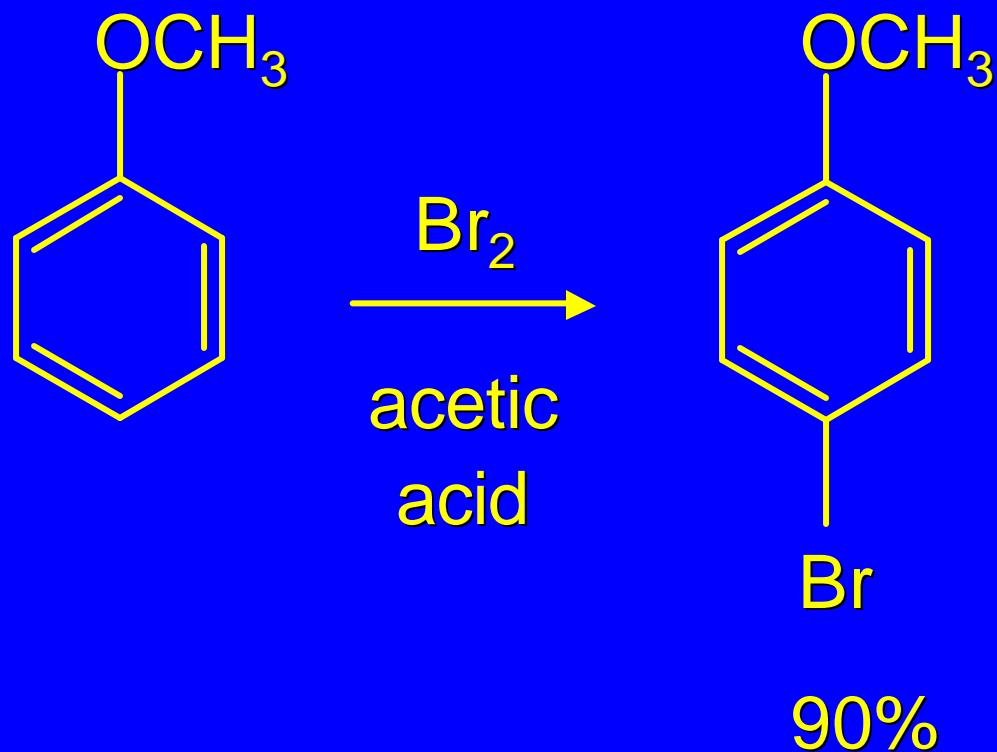
## Nitration of Phenol

occurs about 1000 times faster than nitration of benzene

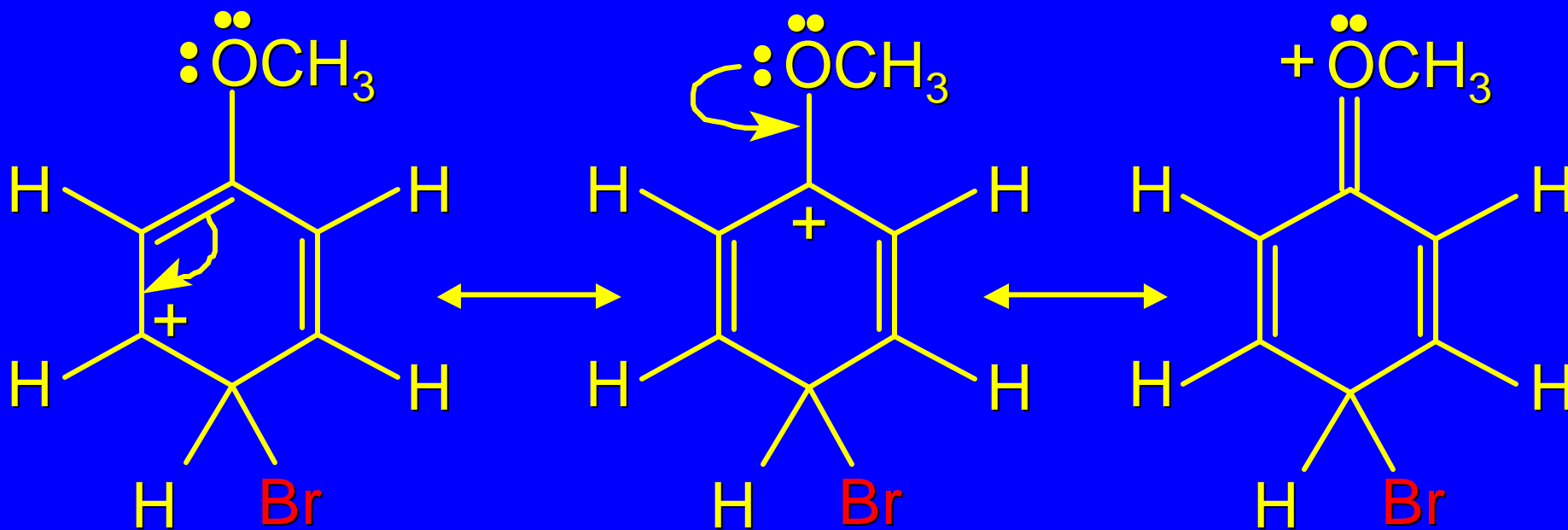


## *Bromination of Anisole*

FeBr<sub>3</sub> catalyst not necessary



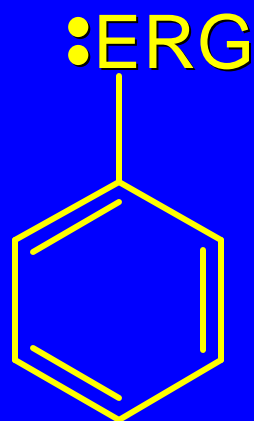
## Oxygen Lone Pair Stabilizes Intermediate



all atoms  
have octets

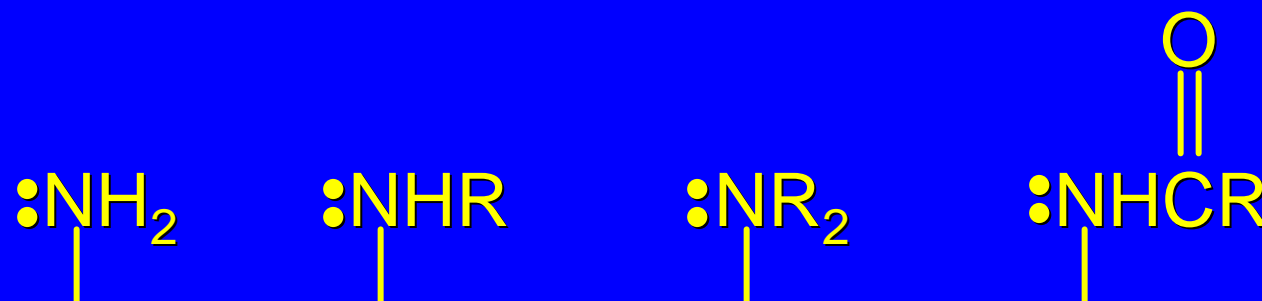
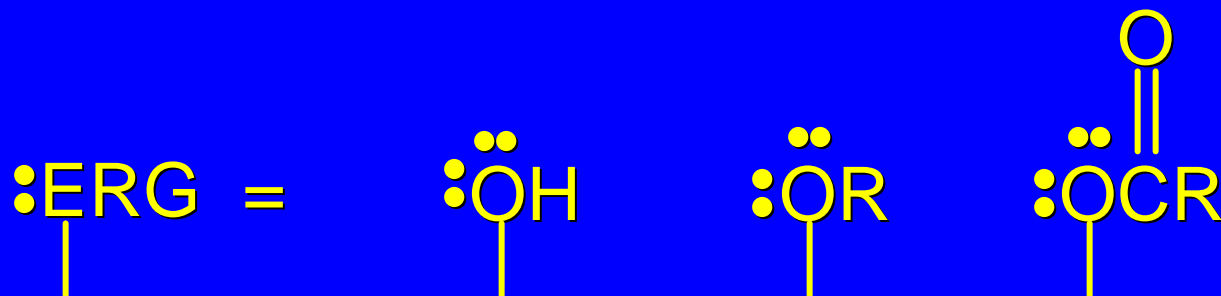


## *Electron-Releasing Groups (ERGs)*



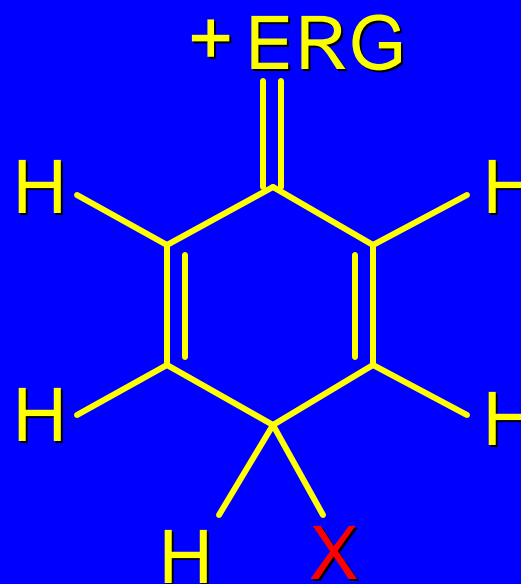
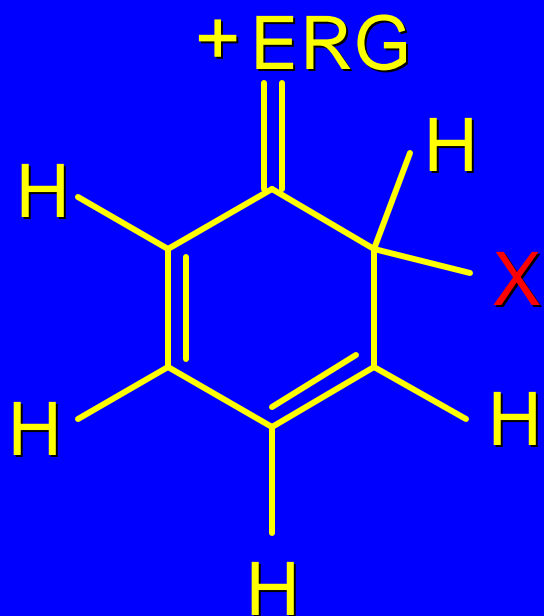
ERGs with a lone pair on the atom directly attached to the ring are ortho-para directing and strongly activating

## Examples



All of these are ortho-para directing  
and strongly to very strongly activating

*Lone Pair Stabilizes Intermediates for  
ortho and para Substitution*

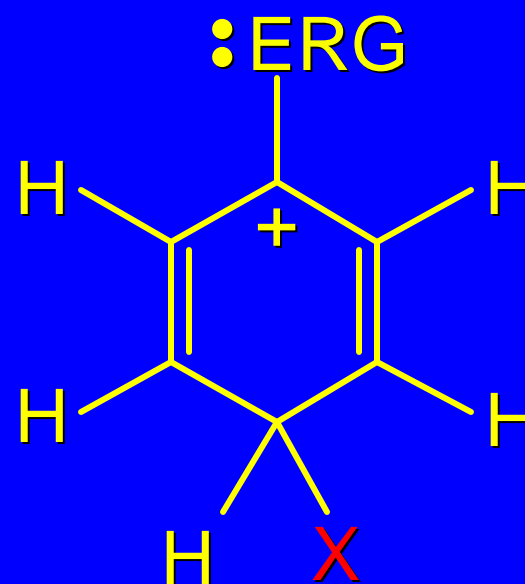
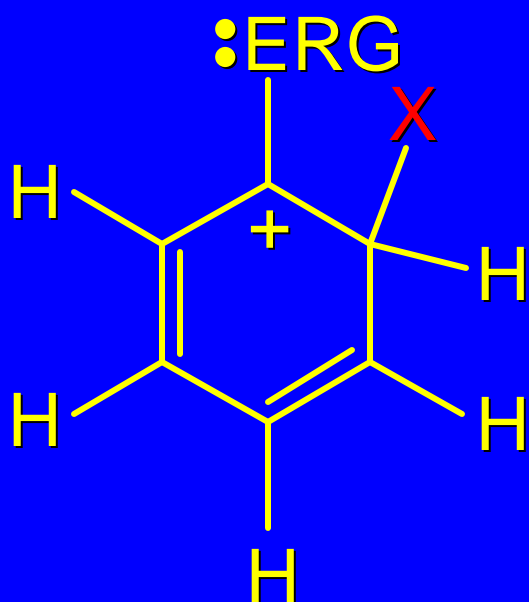


comparable stabilization not possible for  
intermediate leading to meta substitution

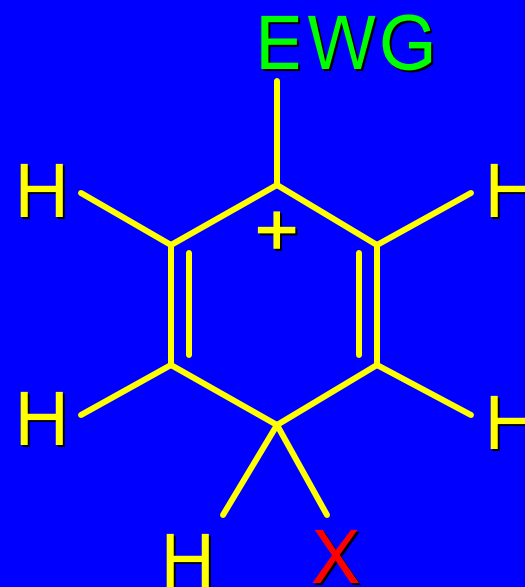
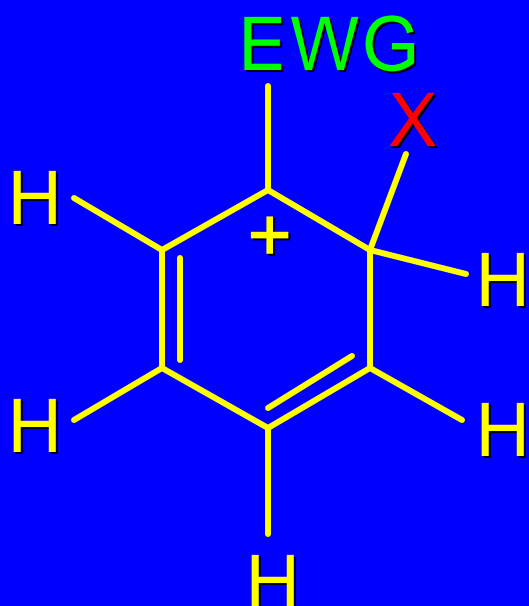
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Substituent Effects in Electrophilic  
Aromatic Substitution:  
Strongly Deactivating Substituents

*ERGs Stabilize Intermediates for  
ortho and para Substitution*

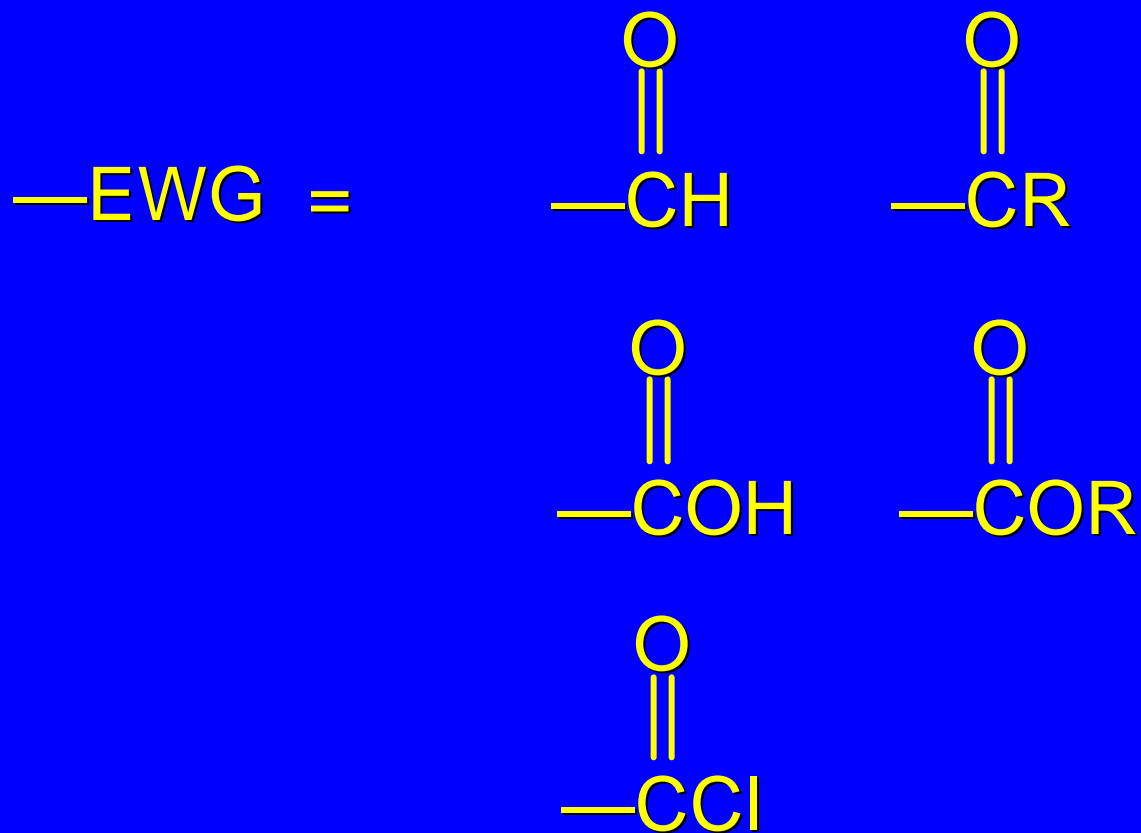


*Electron-withdrawing Groups (EWGs) Destabilize Intermediates for ortho and para Substitution*



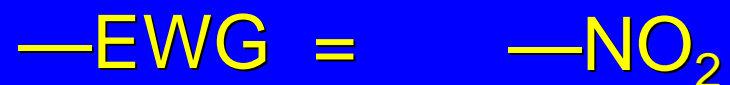
—CF<sub>3</sub> is a powerful EWG. It is strongly deactivating and meta directing

*Many EWGs Have a Carbonyl Group Attached Directly to the Ring*



All of these are meta directing and strongly deactivating

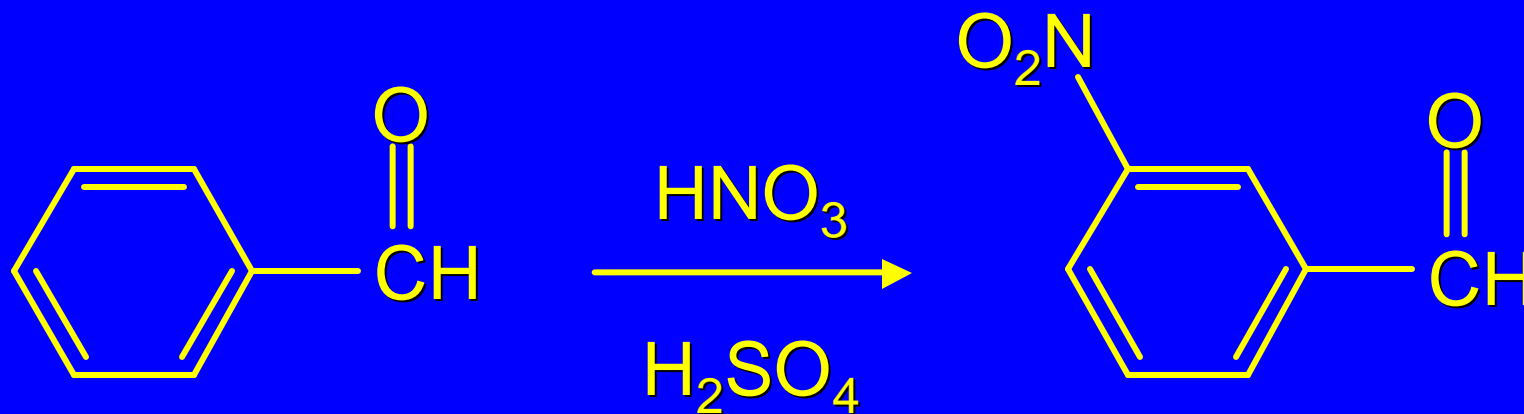
*Other EWGs Include:*



All of these are meta directing and strongly deactivating

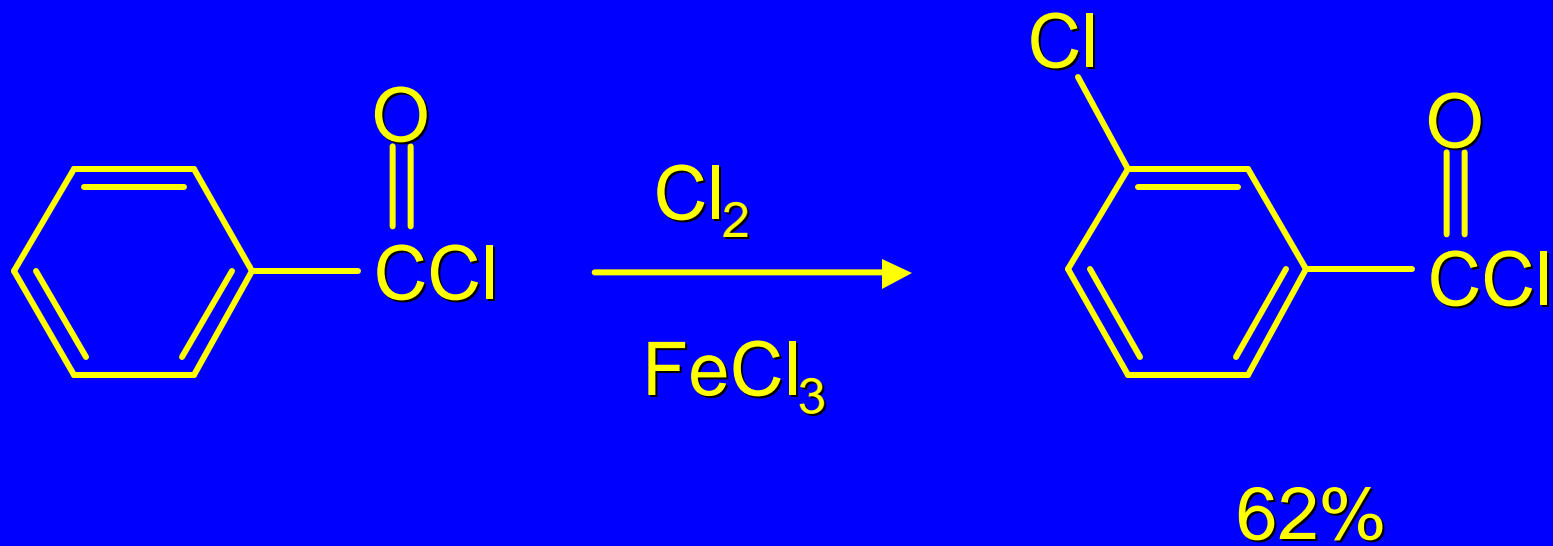


## Nitration of Benzaldehyde

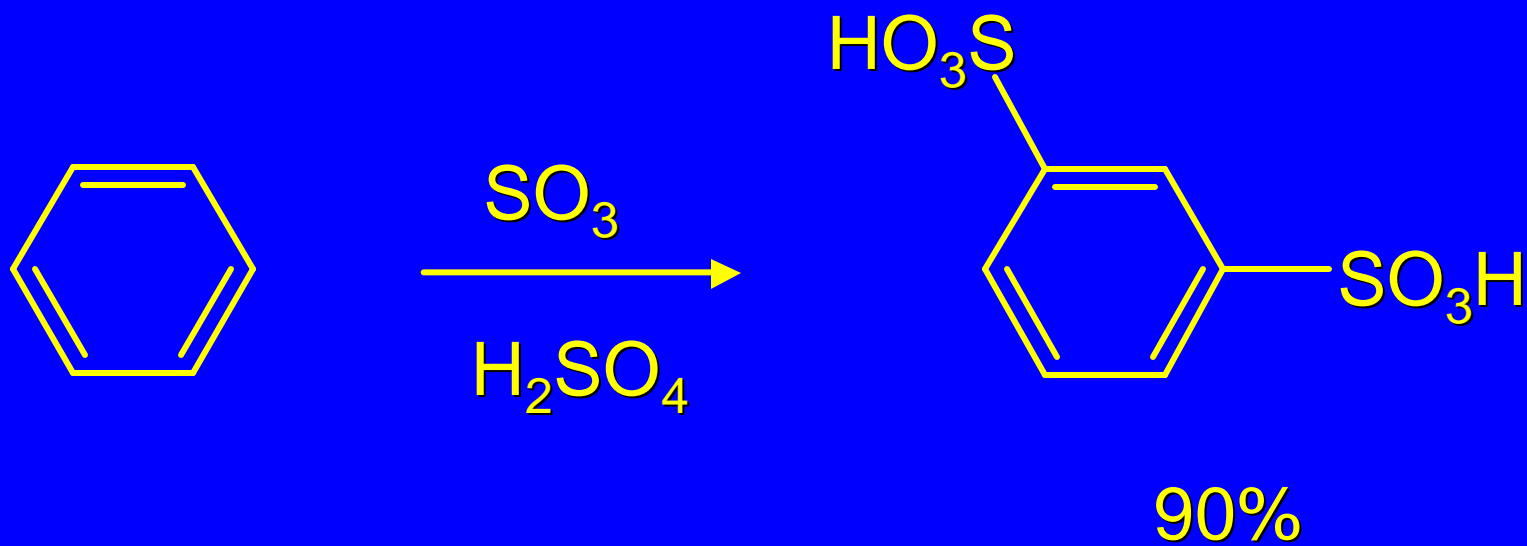


75-84%

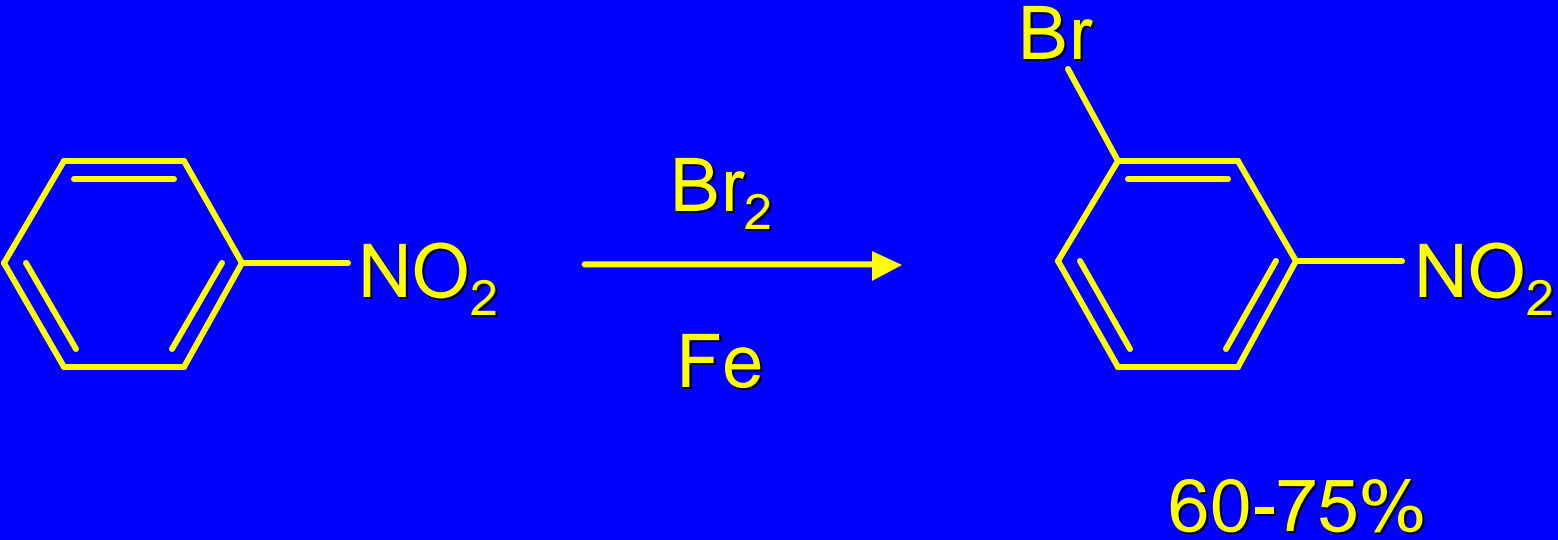
*Problem 12.14(a); page 468*



## Disulfonation of Benzene



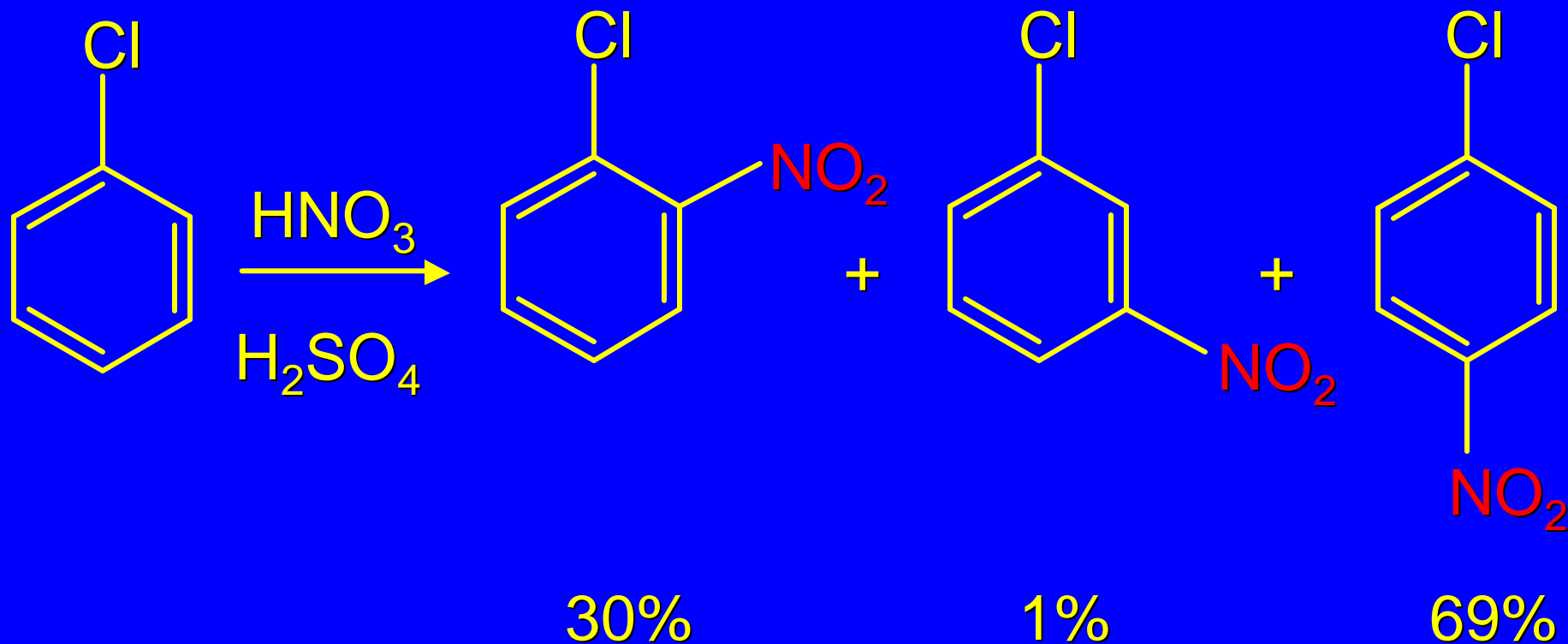
*Bromination of Nitrobenzene*



12.14  
Substituent Effects in Electrophilic  
Aromatic Substitution:  
Halogens

F, Cl, Br, and I are ortho-para directing,  
but deactivating

## Nitration of Chlorobenzene



The rate of nitration of chlorobenzene is about 30 times slower than that of benzene.

## Nitration of Toluene vs. Chlorobenzene

