Organic chemistry background II

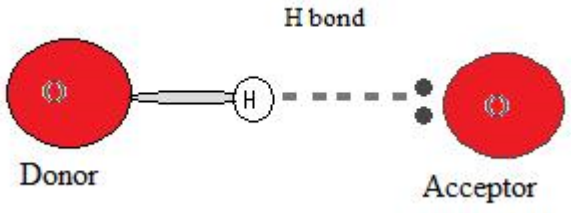
Hydrogen donors and acceptors

- Hydrogen (bond) donors:

  An ion or molecule which possesses a hydrogen atom attached to a relatively electronegative atom such that the hydrogen can participate in a hydrogen bond

- Hydrogen (bond) acceptors:

  An electronegative ion or molecule which possesses a lone electron pair in order to form a hydrogen bond



Electron donating and withdrawing groups

- A functional group attached to a carbon atom in an organic molecule may affect the reactivity of the molecule

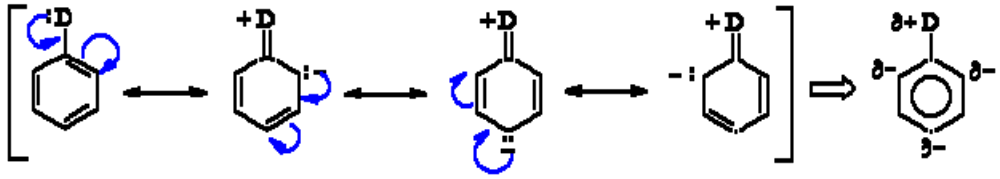
ex) Nitration of a substituted benzene

ortho meta para

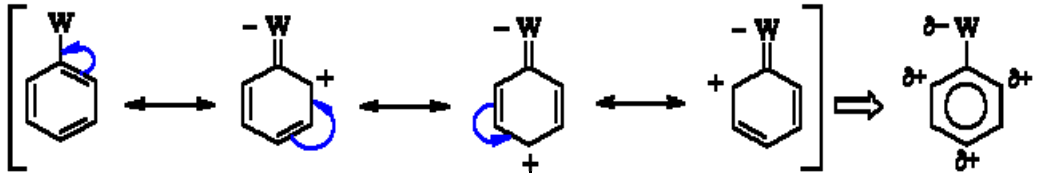
R	Reaction rate relative to benzene	Product ratio			Comments
		ortho	meta	para	
CH_3	25	63%	3%	34%	**Activated** (ortho/para directed)
CF_3	2.5×10^{-5}	6%	91%	3%	**Deactivated** (meta directed)

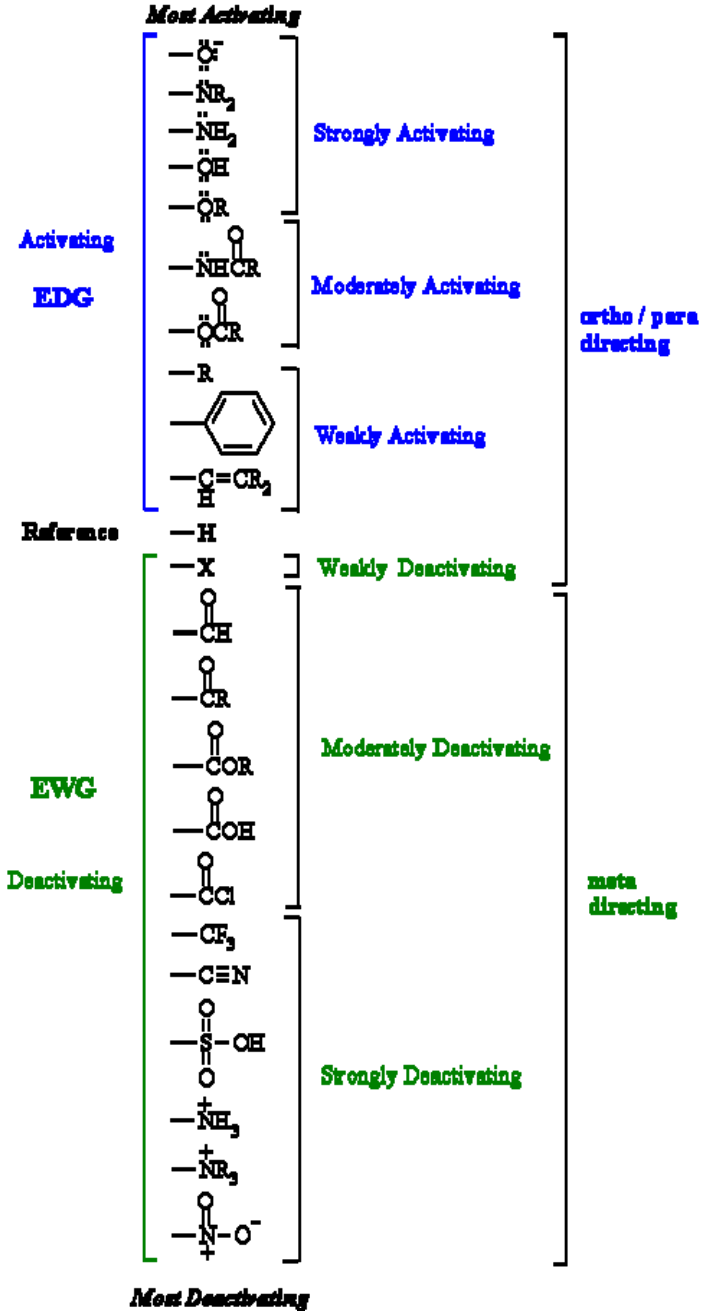
Electron donating and withdrawing groups

- **Electron donating groups**
  - Increase the electron density of the aromatic ring
  - Make the molecule more nucleophilic (activated)
  - The molecule tends to react with electrophiles at ortho- & para-sites



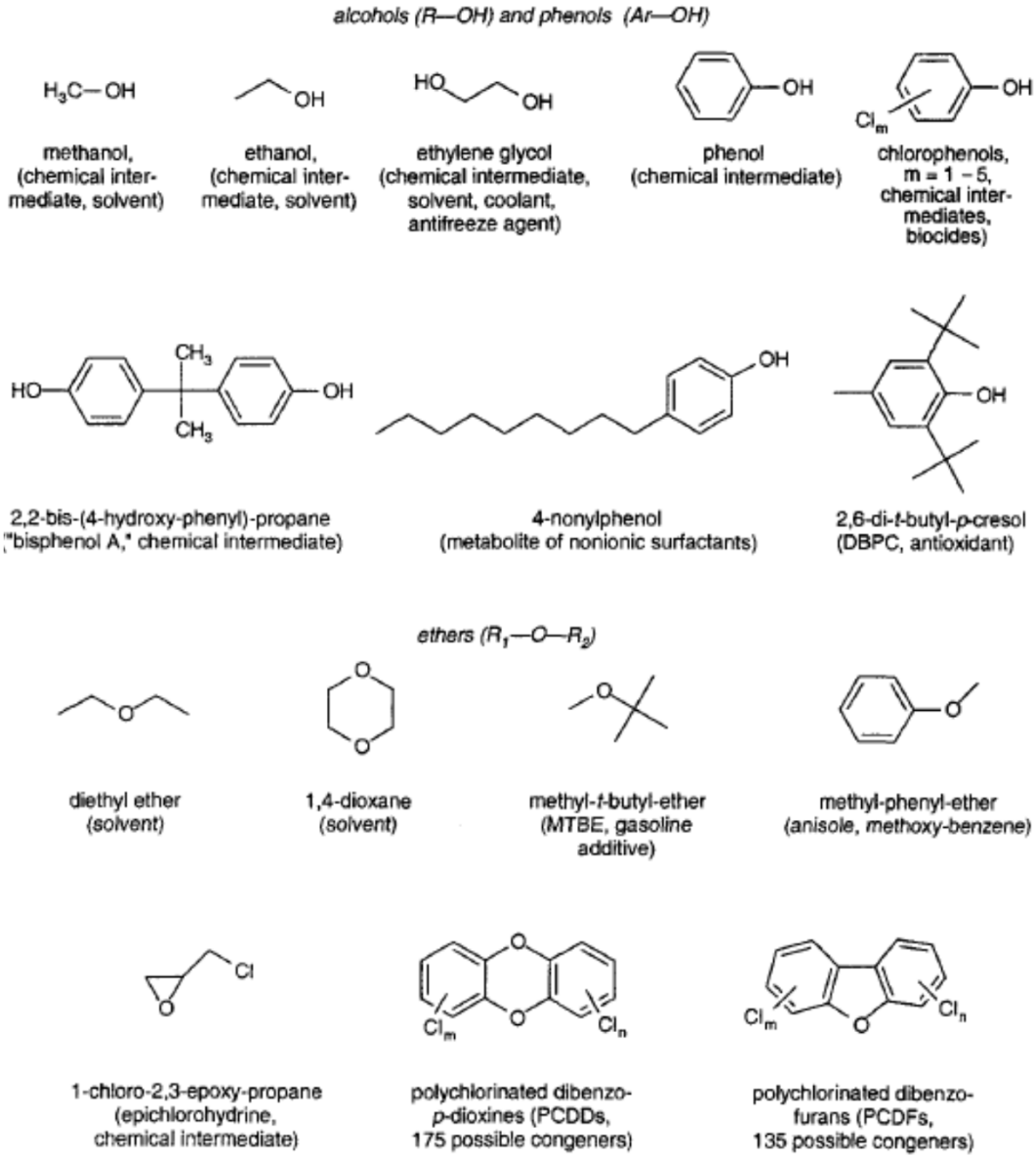
- **Electron withdrawing groups**
  - Decrease the electron density of the aromatic ring
  - Make the molecule less nucleophilic (deactivated)
  - The molecule tends to react with electrophiles at meta-sites




Most Activating
Activating
EDG
Strongly Activating
Moderately Activating
Weakly Activating
ortho / para directing
Reference
Weakly Deactivating
EWG
Deactivating
Moderately Deactivating
Strongly Deactivating
meta directing
Most Deactivating

Oxygen-containing functional groups

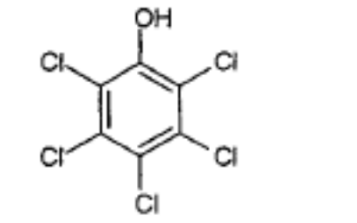
- **Alcohols, phenols, and ethers**
  - Alcohols: R-OH (R: alkyl group)
  - Phenols: R-OH (R: aromatic group)
  - Ethers: R_1-O-R_2



Oxygen-containing functional groups

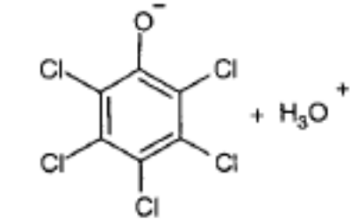
- **Alcohols, phenols, and ethers**
  - Oxygen atoms participate in hydrogen bonds: significant changes in physicochemical properties of the molecule
  - R-OH: may act as both H-donor and H-acceptor
  - R_1-O-R_2: acts only as an H-acceptor
  - Dissociation of a R-OH group
    - R-OH group may dissociate in water (renders H^+) → act as a weak acid
    - Especially for phenols
    - Greater dissociation tendency for phenols substituted with electron-withdrawing substituents

  ex) pentachlorophenol: mostly dissociated at pH=7.0



pentachlorophenol

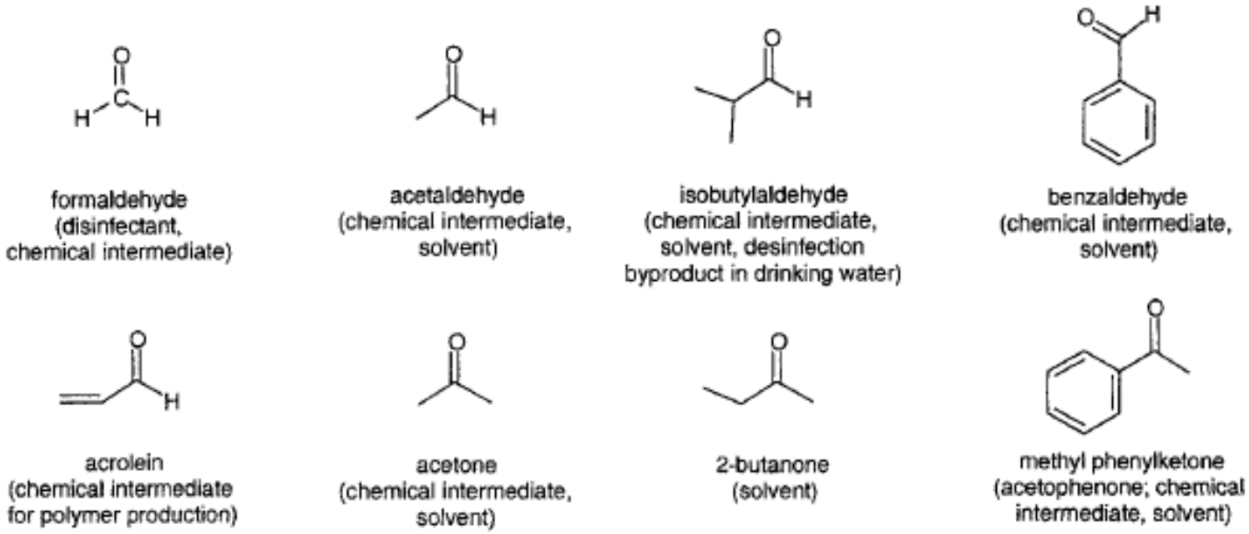
H_2O



pentachloro-phenolate ion

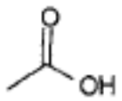
Oxygen-containing functional groups

- **Aldehyde and keto groups**
  - C=O bonds
  - Aldehyde: C-CHO; keto: R_1-CO-R_2
  - H-acceptors
  - Quite reactive

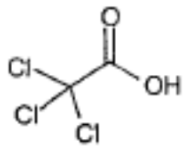


Oxygen-containing functional groups

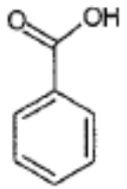
- **Carboxylic groups**
  - R-COOH
  - May dissociate in aqueous solution (pK_a in the range of 0-6)
  - Both strong H-donors and acceptors



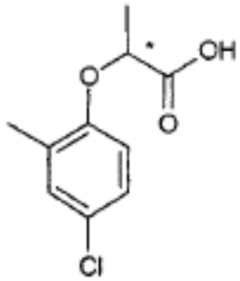
acetic acid



trichloroacetic acid (herbicide, atmospheric breakdown product of chlorinated solvents)



benzoic acid (food preservative, additive, chemical intermediate)

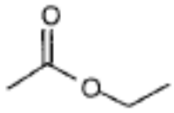


(R,S)-2-(4-chloro-2-methyl phenyl) - propionic acid ((R,S)-mecoprop; herbicide)

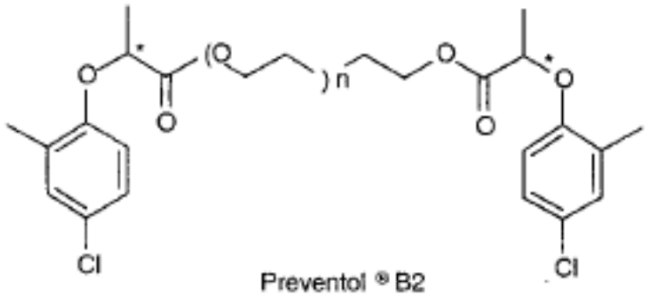
Oxygen-containing functional groups

- **Ester groups**
  - R_1-COO-R_2; -OH of a carboxylic acid is replaced by a –OR group
  - Act only as a H-acceptor (smaller impact on a compound's water solubility)

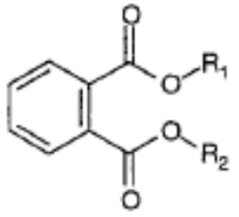
  ex) phthalates: often used as plasticizers



ethylacetate
(acetic acid ethyl ester; solvent)



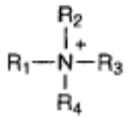
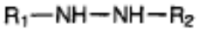
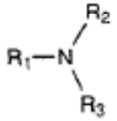
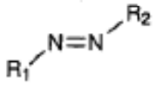
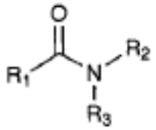
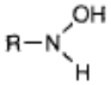
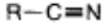
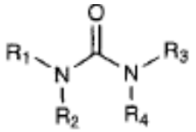
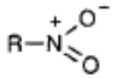
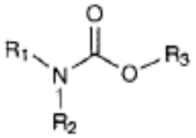
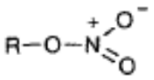
Preventol ® B2
(roof protection agent)



phthalates
(R_1, R_2 = C_1, to C_{10}; plasticizers)

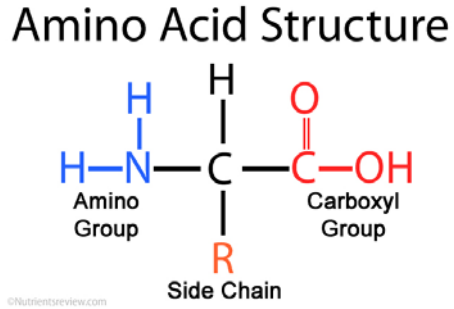
Nitrogen-containing functional groups

Table 2.5 Some Important Nitrogen-Containing Functional Groups Present in Anthropogenic Organic Compounds

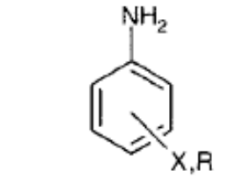
Group	Name (oxidation state of nitrogen)	Group	Name (oxidation state of nitrogen)
	ammonium (-III)		hydrazo (-II)
	amino[a] (-III) (amine)		azo (-I)
	carboxylic acid amide[a] (-III)		hydroxyl-amine (-I)
	cyano, nitrilo (-III)		nitroso (+I)
	urea (-III)		nitro (+III)
	carbamate (-III)		nitrato (+V) (nitrate)

[a]Primary if $R_2 = R_3 = H$; secondary if $R_2 = H$ and $R_3 \neq H$; tertiary if $R_2 \neq H$ and $R_3 \neq H$.

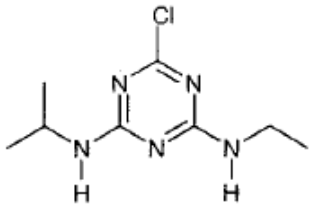
Nitrogen-containing functional groups



- **Amine groups**
  - Types: primary/secondary/tertiary
  - Natural/synthetic compounds
    - Natural example: amino acids
    - Synthetic example: anilines (intermediate for synthesis of dyes, pharmaceuticals, pesticides, antioxidants, …), atrazine (pesticide)
  - Acts as both H-acceptors and donors
    - H-acceptors: to a lesser extent
    - H-donors: only for primary and secondary amines
  - Slightly basic: acquire a proton in an aqueous solution to form a cationic ammonium species



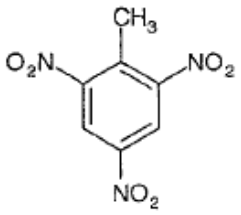
aniline and substituted anilines (chemical intermediates)



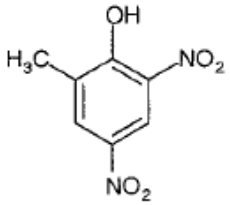
atrazine (a triazine herbicide)

Nitrogen-containing functional groups

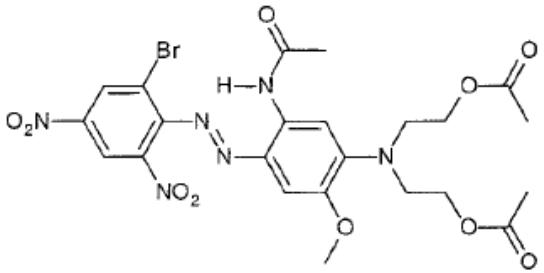
- **Nitro groups**
  - Widely used in the chemical industry
    - Explosives (ex: TNT), agrochemicals (ex: DNOC), dyes (ex: Dispersive Blue 79)
  - Strong electron-withdrawing characteristics
    - Significantly affect the electron distribution in a molecule
    - Significantly affect the chemical properties of the compound
  - Explosives: multiple nitro groups in the molecules
    - Nitro group as built-in oxidant
    - Very fast oxidation of the molecule



2,4,6-trinitrotoluene
(TNT, explosive)



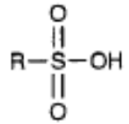
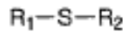
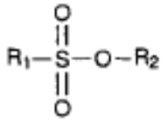
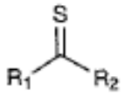
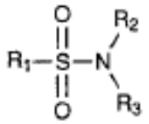
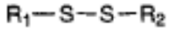
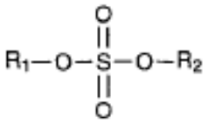
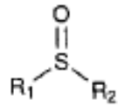
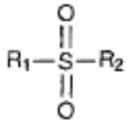
2,4-dinitro-*o*-cresol
(DNOC, herbicide)



Dispersive Blue 79
(textile dye)

Sulfur-containing functional groups

Table 2.6 Some Important Sulfur-Containing Functional groups Present in Anthropogenic Organic Compounds

Group	Name (oxidation state of sulfur)	Group	Name (oxidation state of sulfur)
	thiol, mercaptan (-II)		sulfonic acid (+IV)
	thioether, sulfide (-II)		sulfonic acid ester (+IV)
	thiocarbonyl (-II)		sulfonic acid amide, sulfonamide (+IV)
	disulfide (-I)		sulfuric acid ester, sulfate (+VI)
	sulfoxide (0)		
	sulfone (+II)		