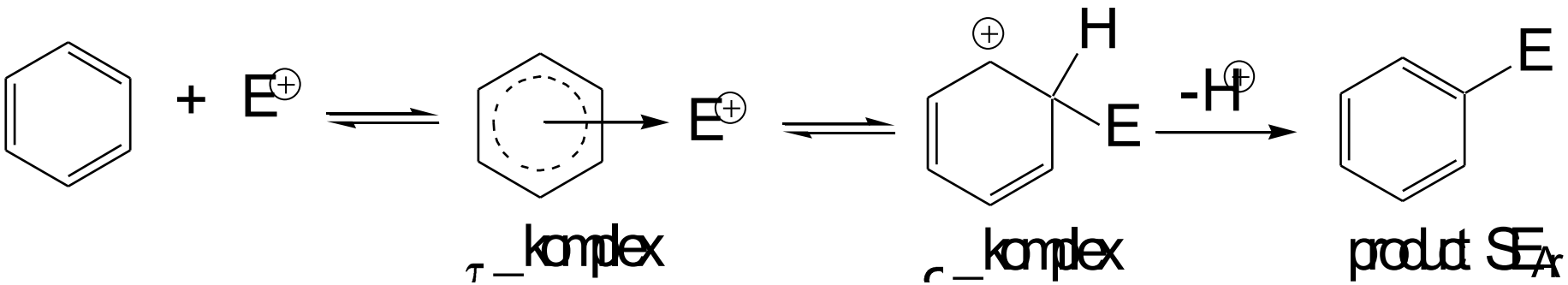
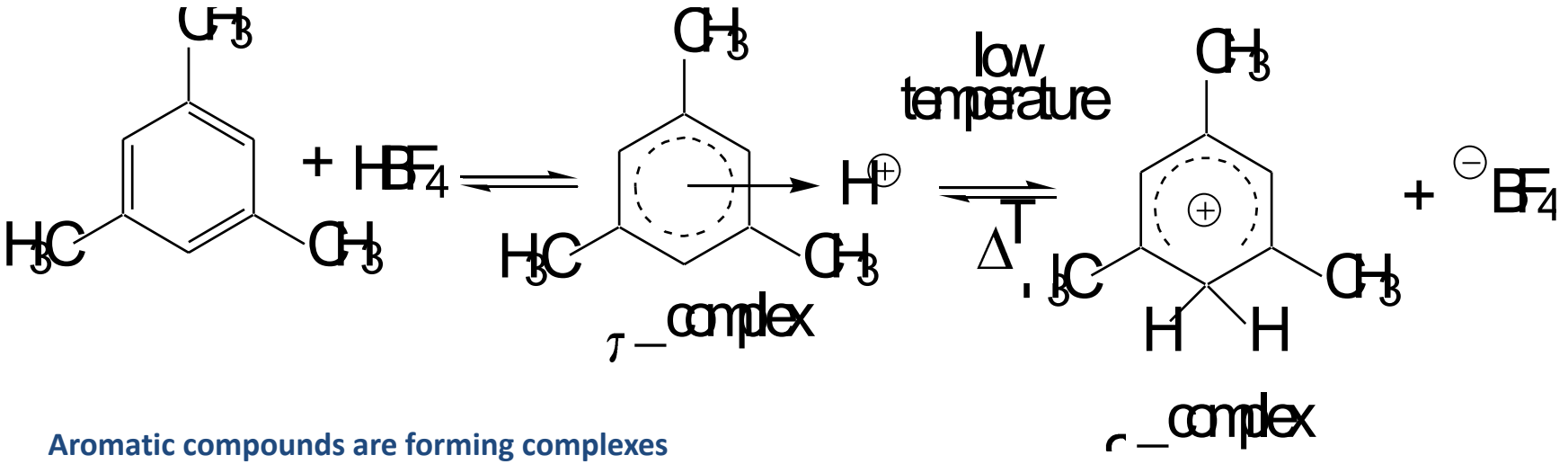
AROMATIC COMPOUNDS - REACTIVITY

TYPICAL REACTION OF AROMATIC COMPOUNDS - SUBSTITUTION ELEKTROPHILIC AROMATIC



Mechanizm of substitution electrophilic aromatic

AROMATIC COMPOUNDS - REACTIVITY



Aromatic compounds are forming complexes

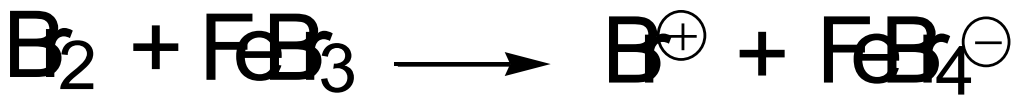
- crystaline compound
- X-ray analysis
- when heated it decomposes back

AROMATIC COMPOUNDS - REACTIVITY

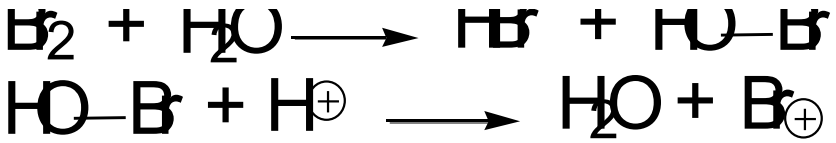
Preparation of electrophilic reagents

HALOGENATION is limited to chlorination and bromination

For the reaction Lewis acid is necessary



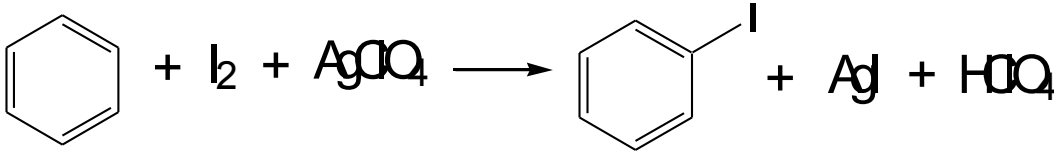
similarly aluminium halogenide is active, sometimes addition of powdered metal is used

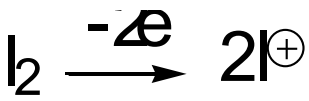


reactive aromates

Fluorination as SE_{Ar} is not applied, is carried out as Schiemann reaction (by decomposition of aromatic diazonium salts)

Iodine is less active and therefore elektrophilic reagent I^+ is generated directly in reaction mixture by iodine oxidation





oxidation by H_3AsO_4 , HNO_3

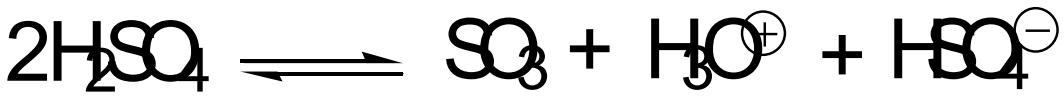
AROMATIC COMPOUNDS - REACTIVITY

NITRATION

- Nitration of activated aromatic systems is possible even by HNO_3
- I case of substituted derivatives it is necessary to také to consideration reaction of substituents with strong acid

SULFONATION

conc. sulfuric acid, oleum, sufur trioxide



the reagent is sulfur trioxide

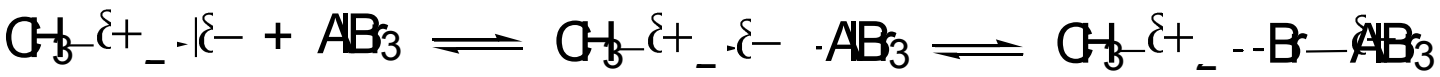
Sulfonation is reversible reaction

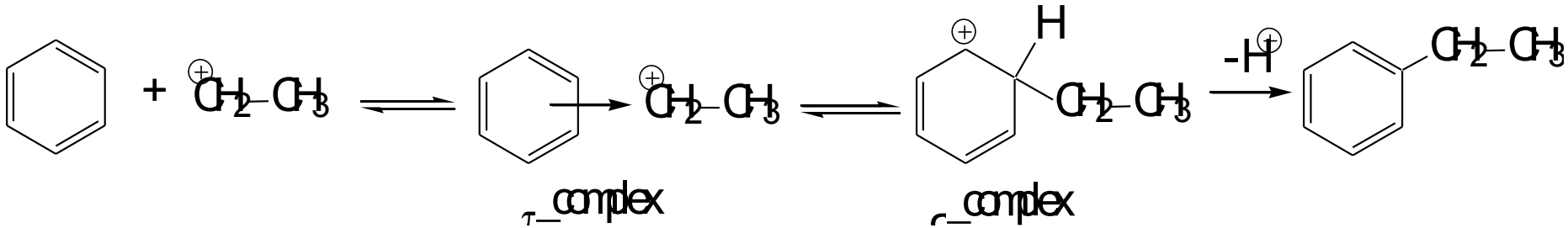
Conditions:
conc. acid, oleum
diluted acid + steam (overheated)

AROMATIC COMPOUNDS - REACTIVITY

FRIEDEL –CRAFTS reaction – alkylation and aryltion (1877 – Friedl (F), Crafts (US)

ALKYLATION

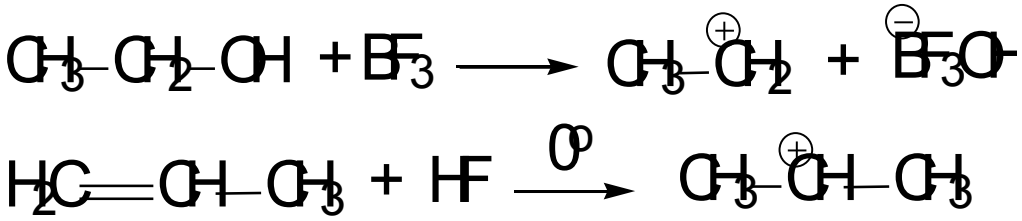




Differnt Lewis acids:

$AlCl_3$, BF_3, $TiCl_4$, $SnCl_4$, $ZnCl_2$, but also acids HF, H_2SO_4

Alkylation agents may be also alcohols and alkenes:



AROMATIC COMPOUNDS - REACTIVITY

FRIEDEL –CRAFTS reaction – alkylation and aryltion (1877 – Friedl (F), Crafts (US)

ALKYLATION

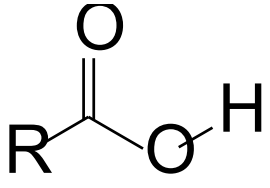
Conditions and restrictions:

1) **Reactions cannot be applied at aromatic systems with strong electronwithdrawing groups (-NO_2, -NH_3^+, - CN)**
2) **Halogen derivatives and vinyl derivatives do not work.**
3) **The formed alkylated system is always more reactive than the starting compound**
   ⟹ **a severalfold substitution can be observed**
4) **When you are trying alkylation with a longer chain – when carbocation is formed, often its rearrangement to the more stable cation is observed**
5) **Reactions cannot be applied at aromates with amino group because amino group interacts with Lewis acid forming complex with free electron pair of nitrogen and this way is desactivating aromatic system**

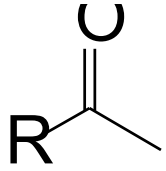
AROMATIC COMPOUNDS - REACTIVITY

FRIEDEL –CRAFTS reactions

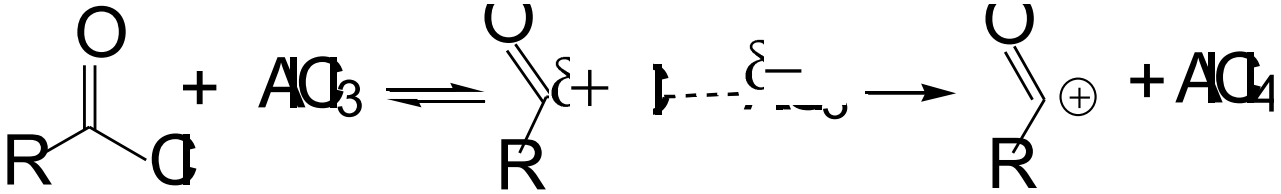
ACYLATION - formation of aromatic ketones

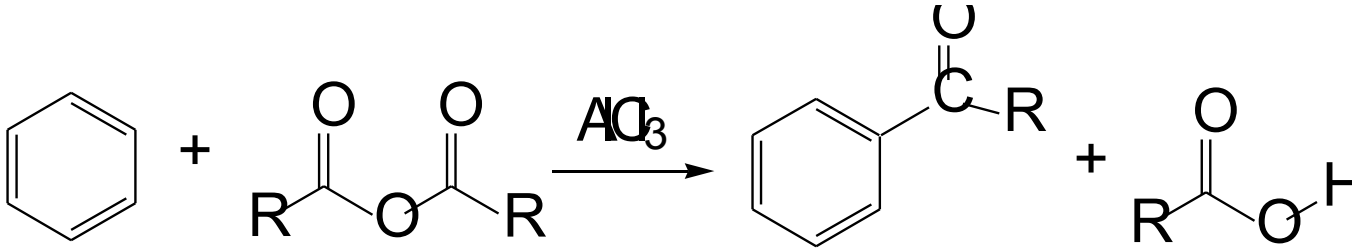


acid



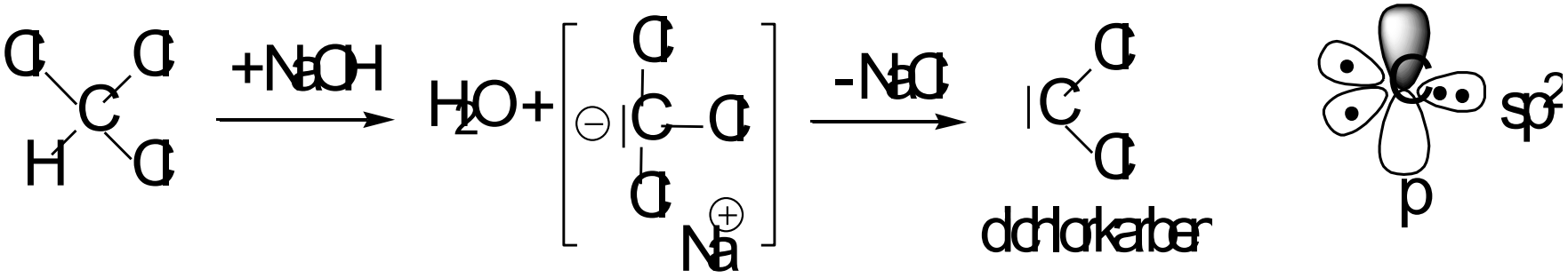
acyl - fragment of acid



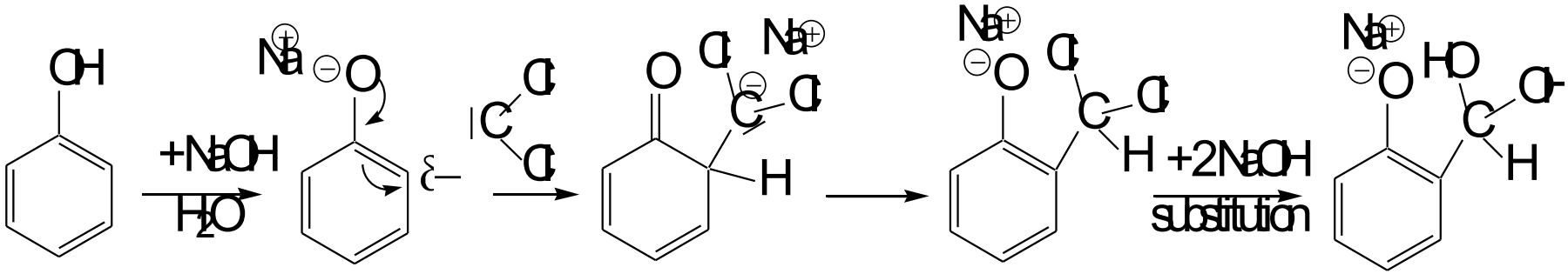


AROMATIC COMPOUNDS - REACTIVITY

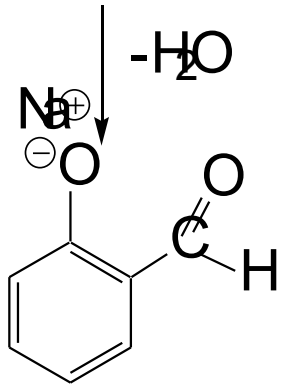
REIMER – TIEMAN reaction



dichlorkarben je electrophile

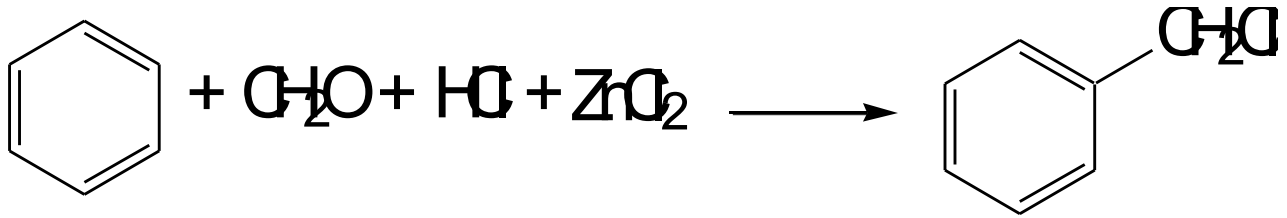


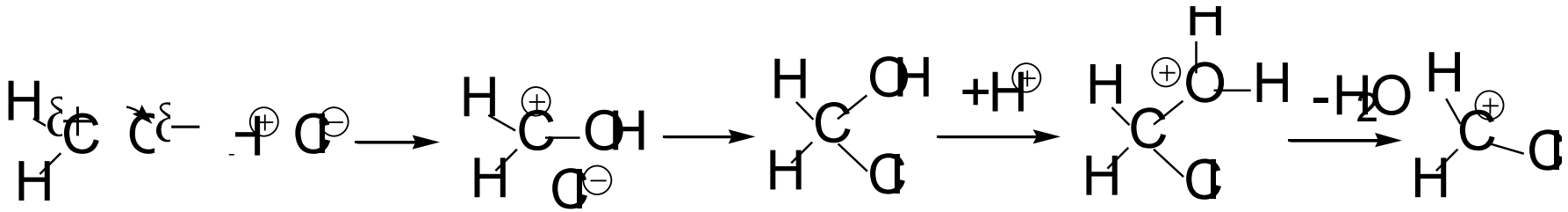
o- and p-substituted hydroxybenzaldehydes are formed



AROMATIC COMPOUNDS - REACTIVITY

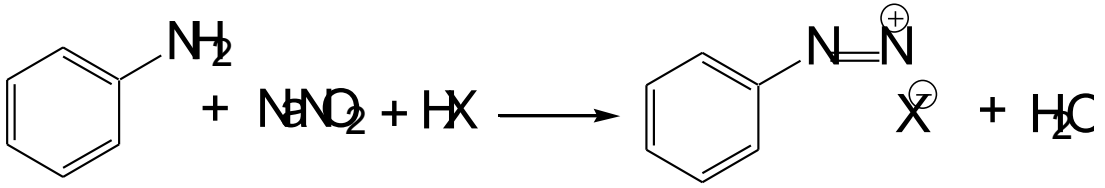
CHLORMETHYLATION - introduction of chlormethyl group

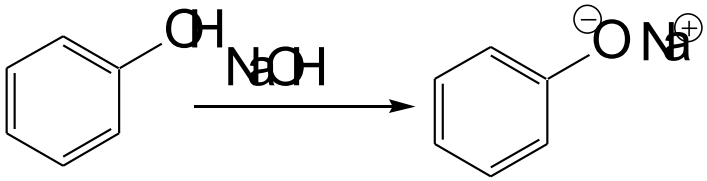


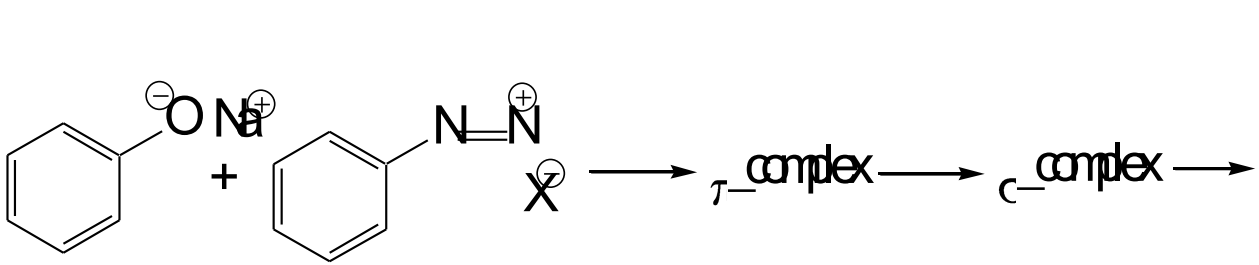


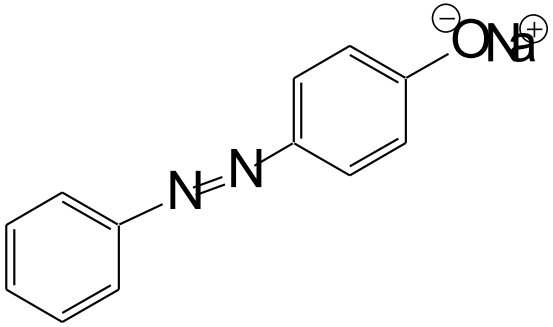
AROMATIC COMPOUNDS - REACTIVITY

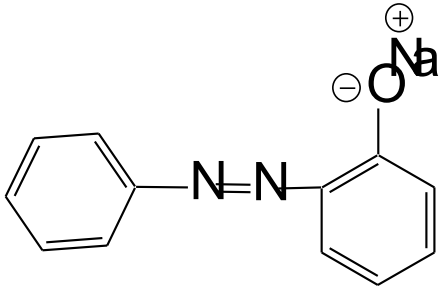
AZOKOPULATION - formation of azodyes





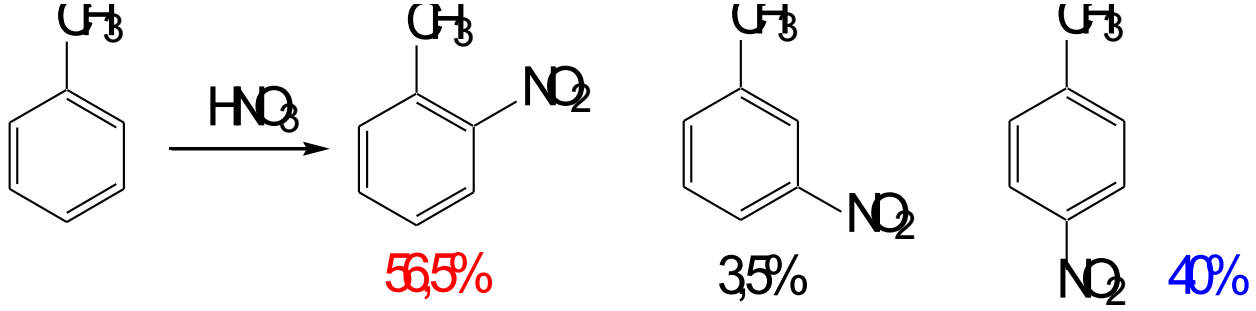






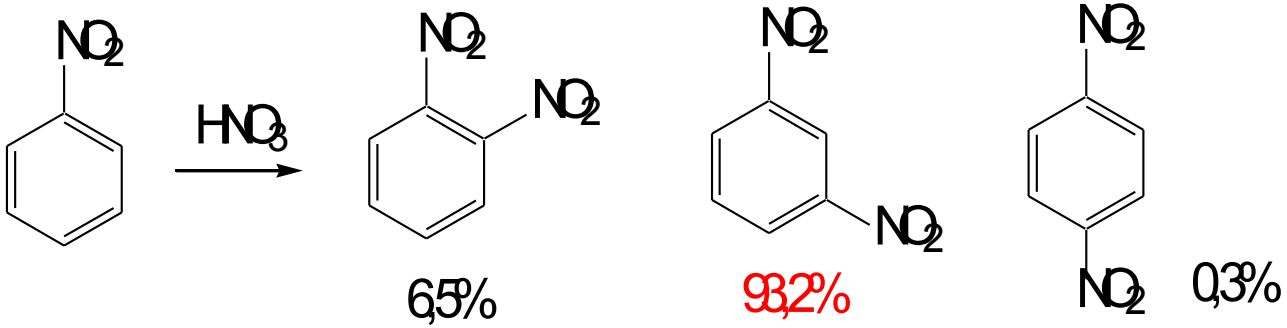
AROMATIC COMPOUNDS - REACTIVITY

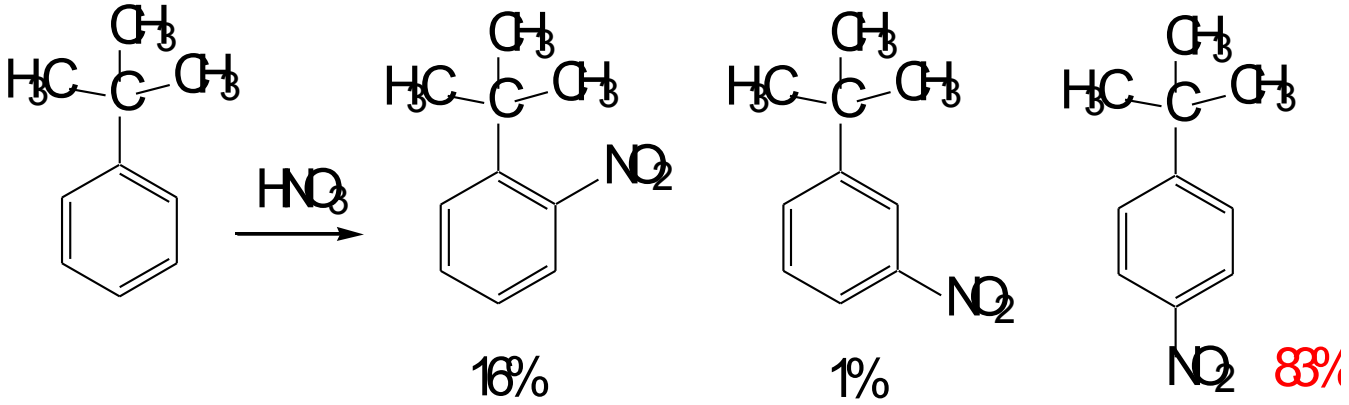
REACTIONS AT SUBSTITUTED AROMATICS - influence of substitution



STATISTICS:

o- 40%
m- 40%
p- 20%





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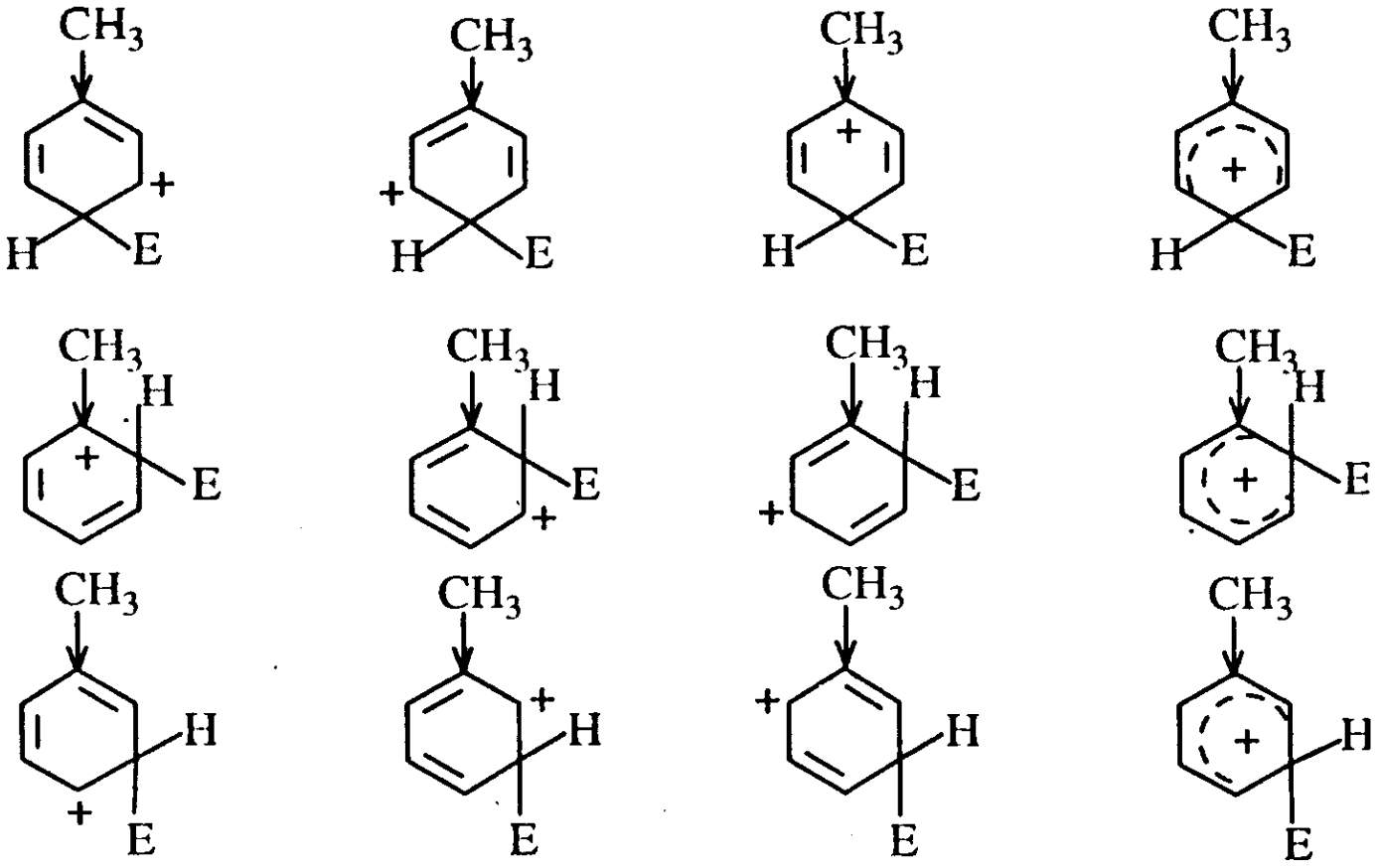

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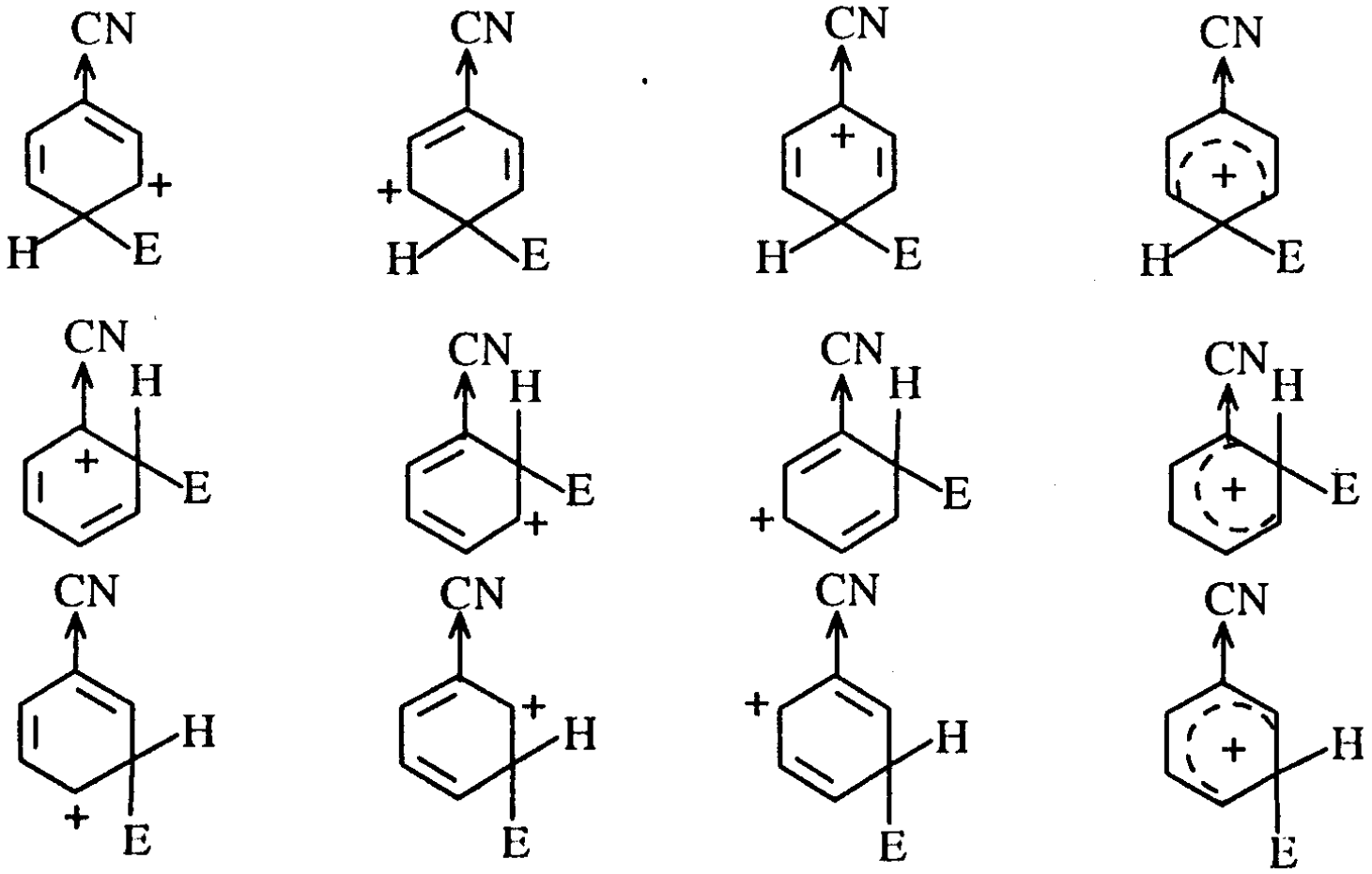

AROMATIC COMPOUNDS - REACTIVITY

			Poznámky
Donating o- and p-directing substituents		- NH_2, -NHR, - NR^1R^2	Pozor na změnu efektu v kyselém prostředí
	Strongly activating	- OH	Silně aktivující v alkalickém prostředí
		- OR, - OCH_3	Silně aktivující
	Weak activating	- $NHCOCH_3$, -NHCOR	Mírně aktivující
		- CH_3, - C_2H_5, ----- alkyly	
		- C_6H_5	
	desactivating	- F, -Cl, -Br, -I	
m - directing		- NO_2, -CN	Silně desaktivující
		- NR_3^+	
		- CF_3, - CCl_3	
		- SO_3H,	
		- COOH, -COOR	
		- CHO, -COR	

For the quantitative value of substituent influence consult Hammett constants

AROMATIC COMPOUNDS - REACTIVITY