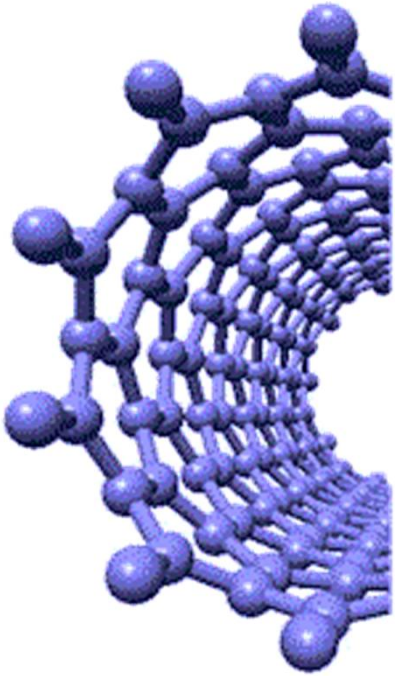
esf european social fund in the czech republic
EUROPEAN UNION
MINISTRY OF EDUCATION, YOUTH AND SPORTS
OP Education for Competitiveness
INVESTMENTS IN EDUCATION DEVELOPMENT

Innovation and Development of Study Field Nanomaterials at the Technical University of Liberec

nano.tul.cz



These materials have been developed within the ESF project: Innovation and development of study field Nanomaterials at the Technical University of Liberec

TECHNICAL UNIVERSITY OF LIBEREC
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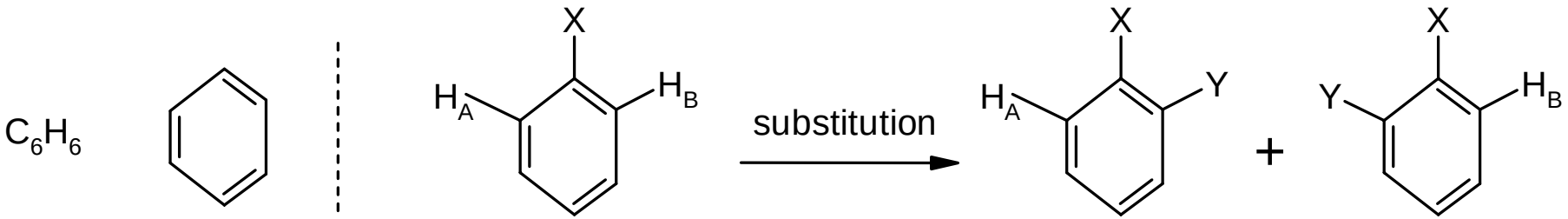
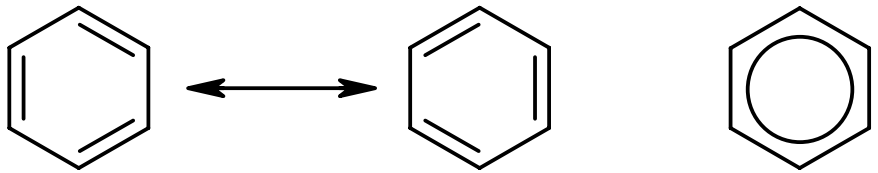
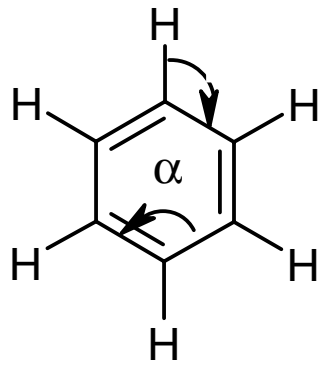
Organic Chemistry I – 13. Chemistry of aromatics

History

- discovery of benzene (M.Faraday – 1825)
- structure of benzene (F.A.Kekulé – 1864)
- conjugation, resonance structures



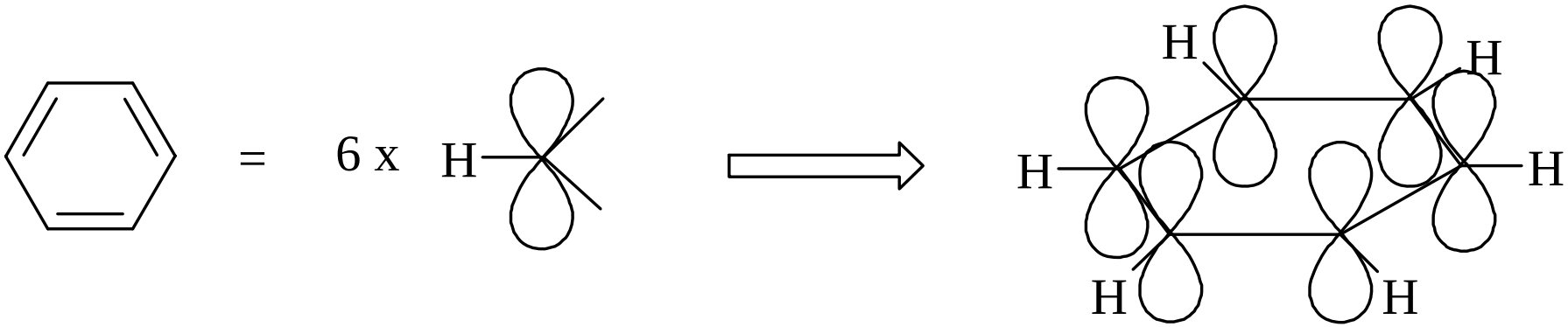




α = 120 °
C-H = 108,4 pm
C-C = 139,7 pm

Organic Chemistry – chemistry of aromatics

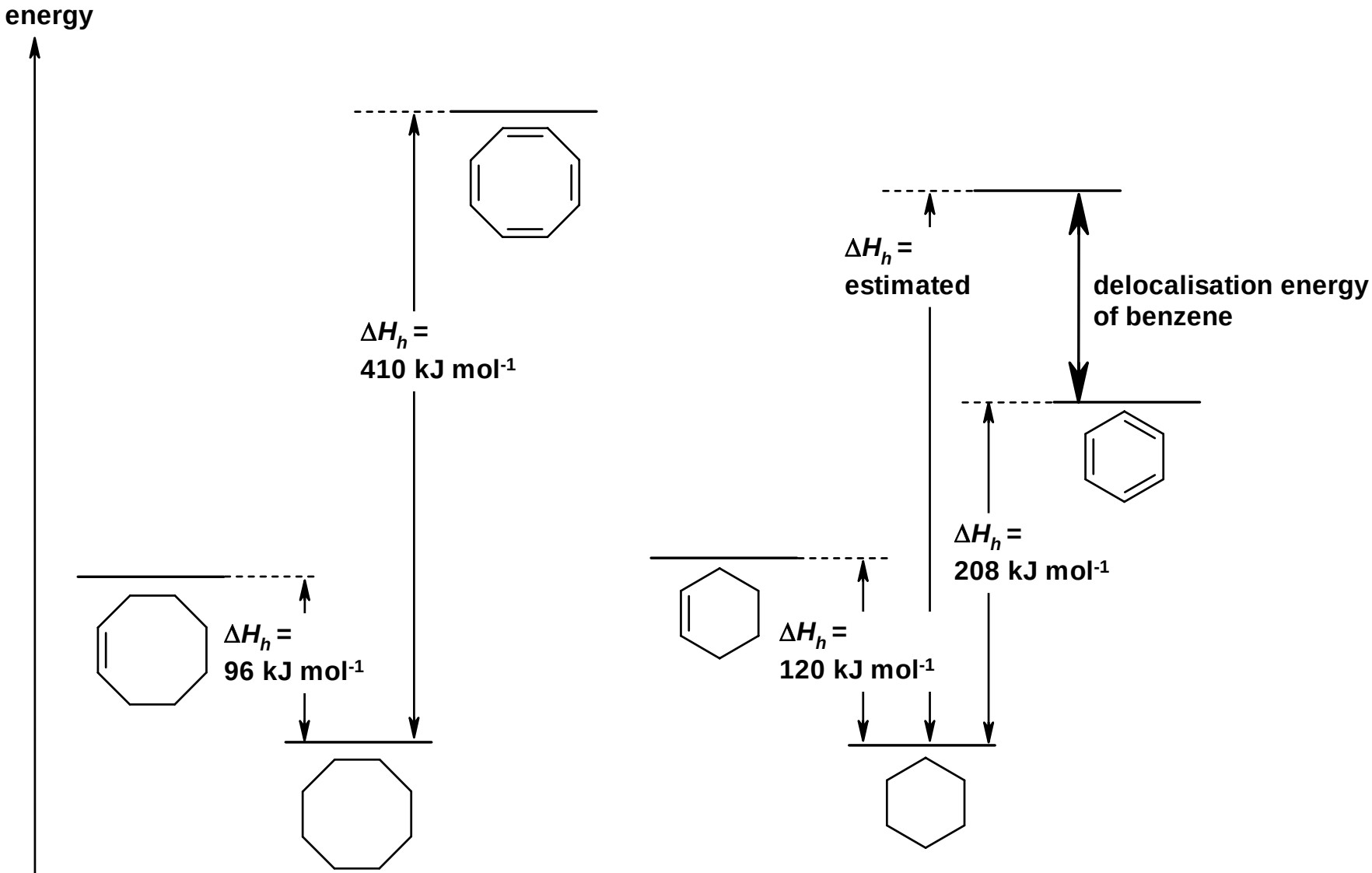
Aromaticity



Delocalisation of π – electrons

- is it favourfable process ???

Organic Chemistry – chemistry of aromatics



Organic Chemistry – chemistry of aromatics

Aromaticity

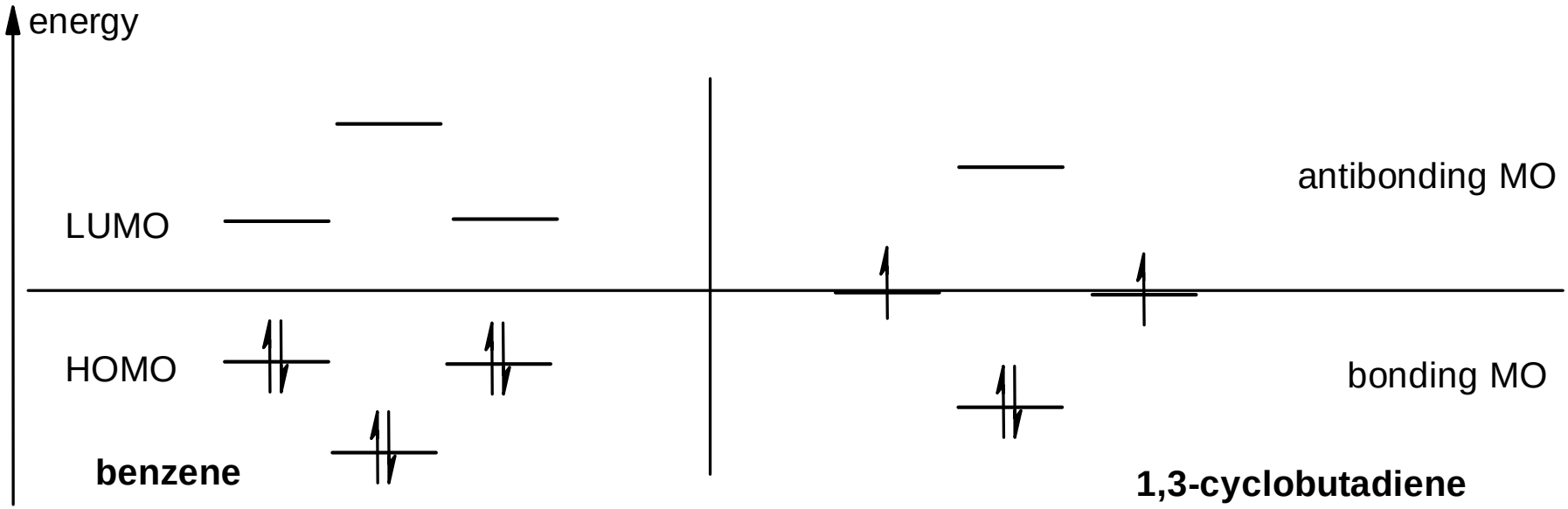
„Hückel rule“

Aromatic compounds have to have

- cyclic structure
- conjugated systém of double bonds
- $4n + 2$ ($n = 1,2,3,4\ldots$ Π – electrons
- planar structure (shape) of aromatic part

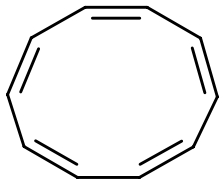
Organic Chemistry – chemistry of aromatics

Aromaticity – π - orbital picture

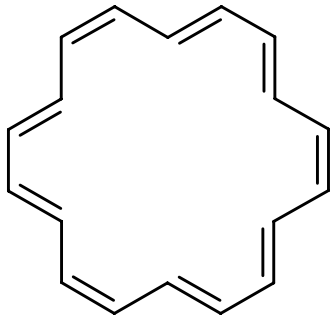


Organic Chemistry – chemistry of aromatics

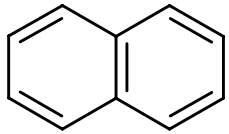
Aromatic compounds



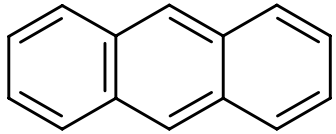
[10]-annulene



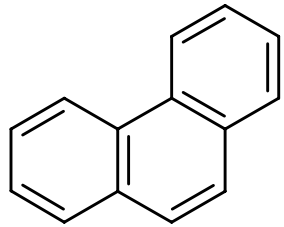
[18]-annulene



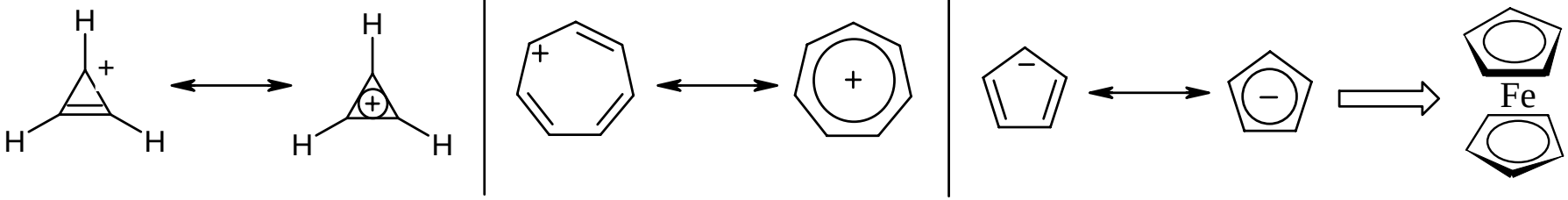
naphthalene



anthracene

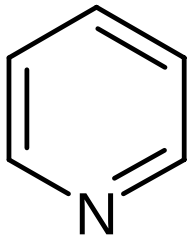


fenanthrene

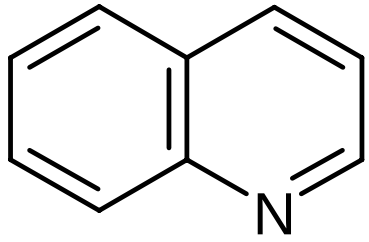


Organic Chemistry – chemistry of aromatics

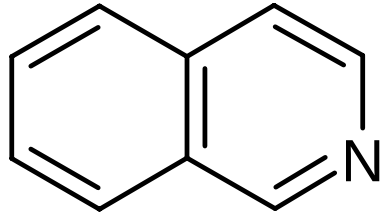
Heteroaromatic compounds



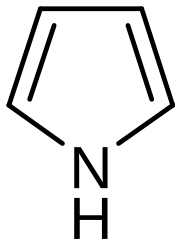
pyridine



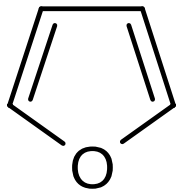
quinoline



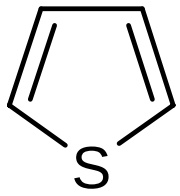
isoquinoline



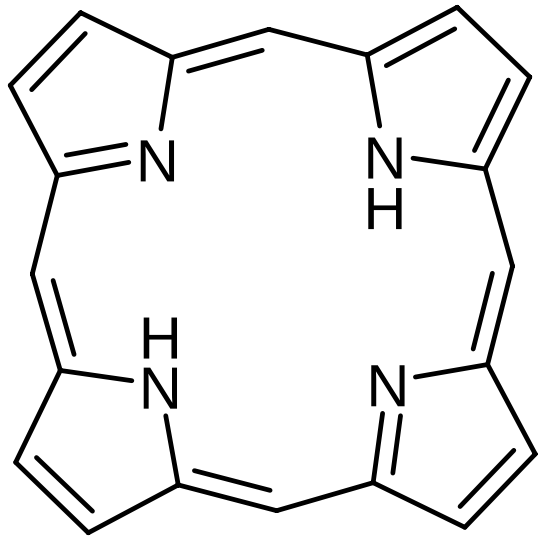
pyrrole



furane



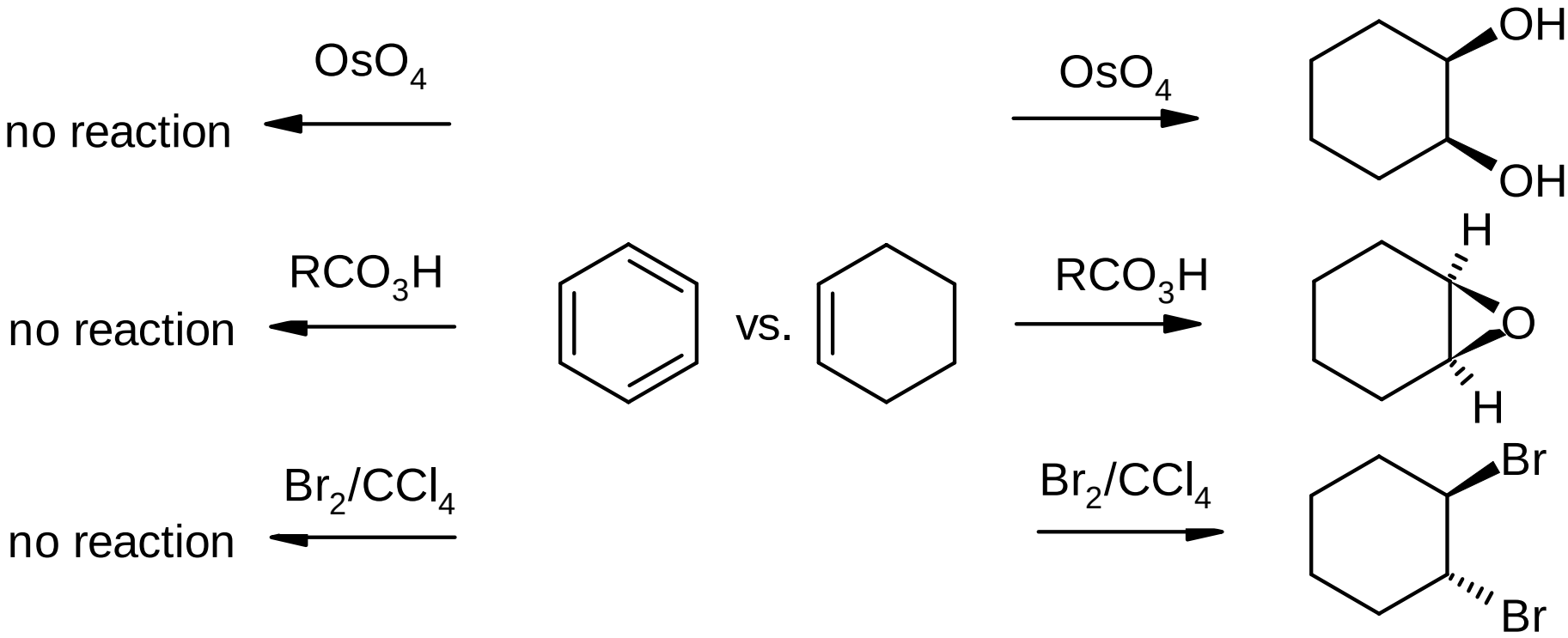
thiophene



porfyrine

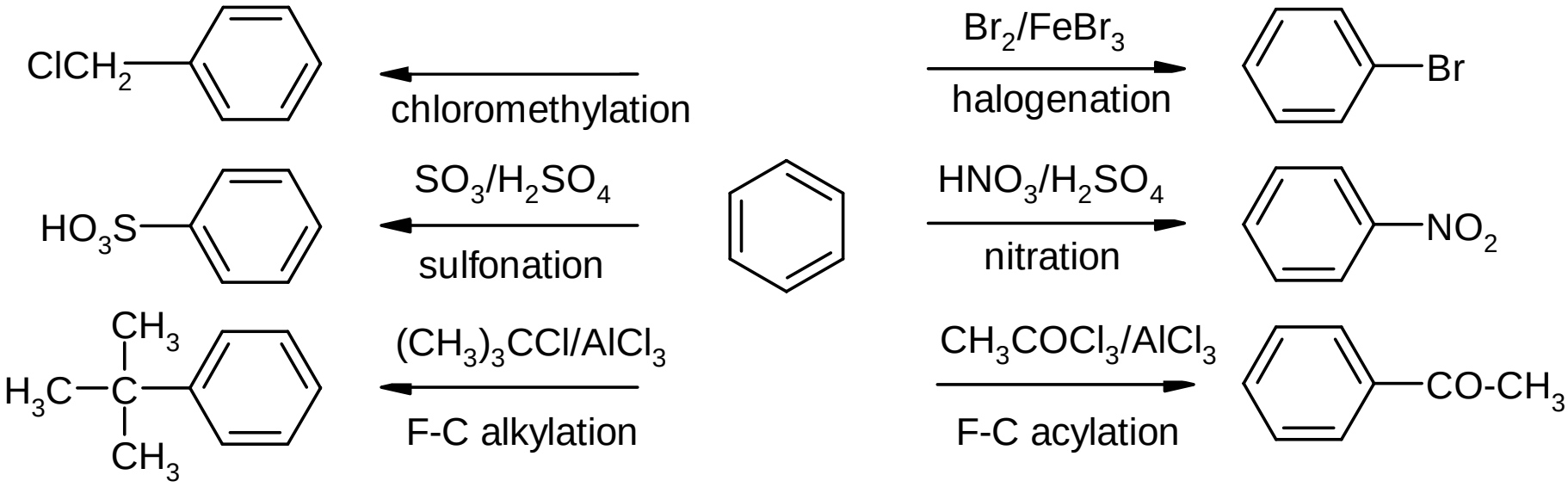
Organic Chemistry – chemistry of aromatics

Aromatic compounds - reactivity



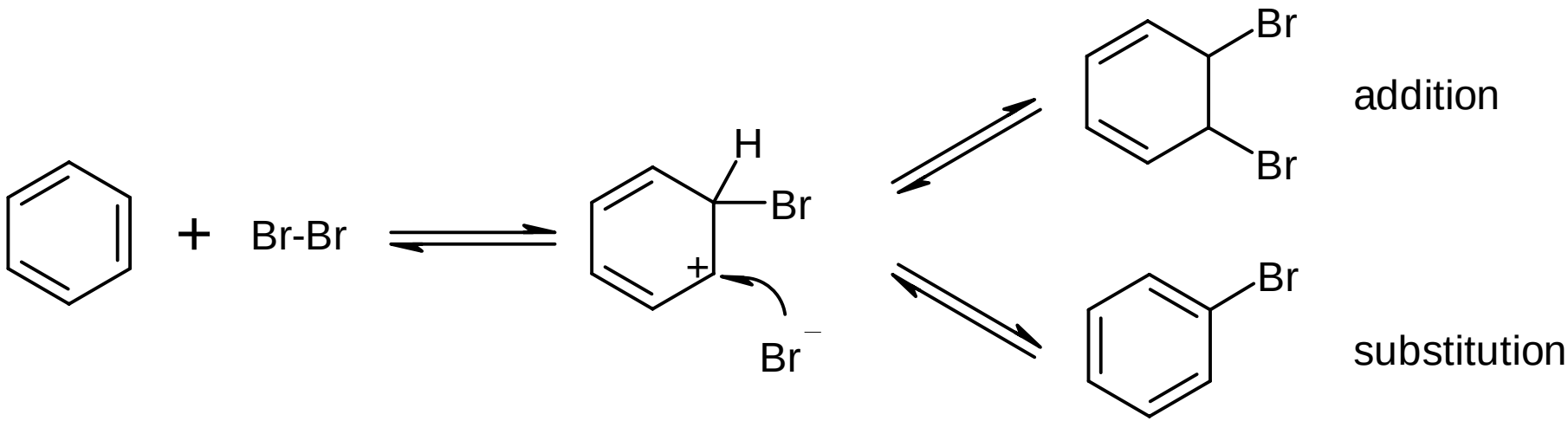
Organic Chemistry – chemistry of aromatics

Aromatic compounds – reactivity – S_E aromatic



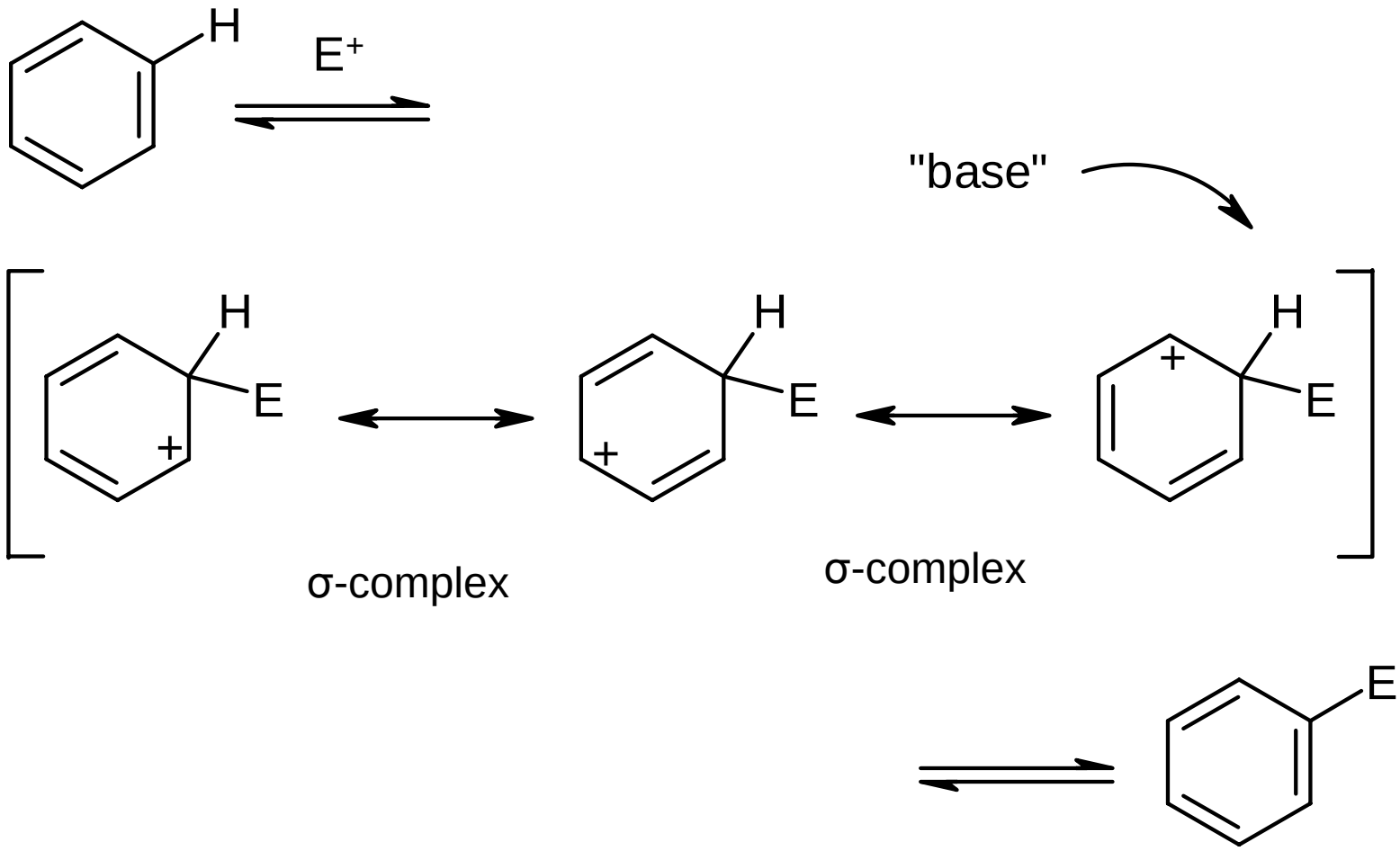
Organic Chemistry – chemistry of aromatics

Aromatic compounds – retention of aromatic character



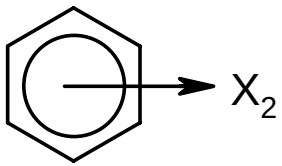
Organic Chemistry – chemistry of aromatics

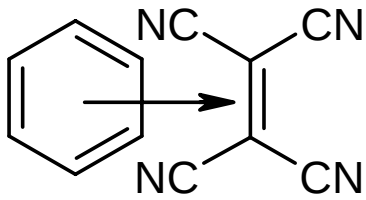
Aromatic compounds – reactivity – S_E aromatic

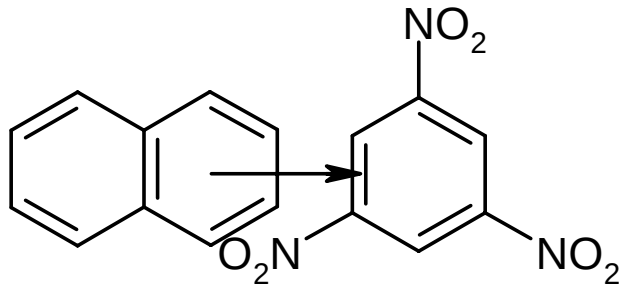


Organic Chemistry – chemistry of aromatics

Aromatic compounds – reactivity – S_E aromatic





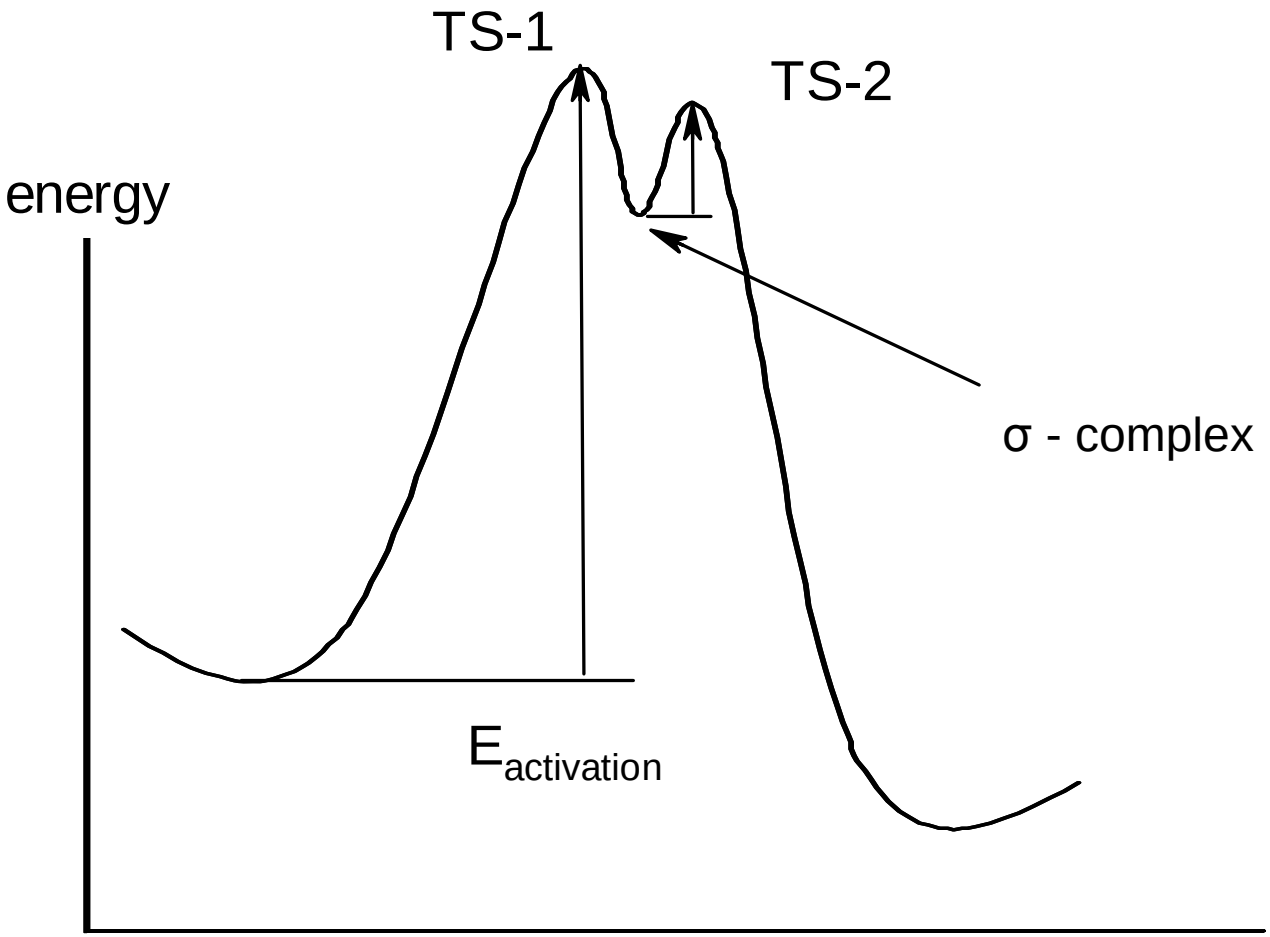


π – complexes

C-T (charge-transfer) complexes

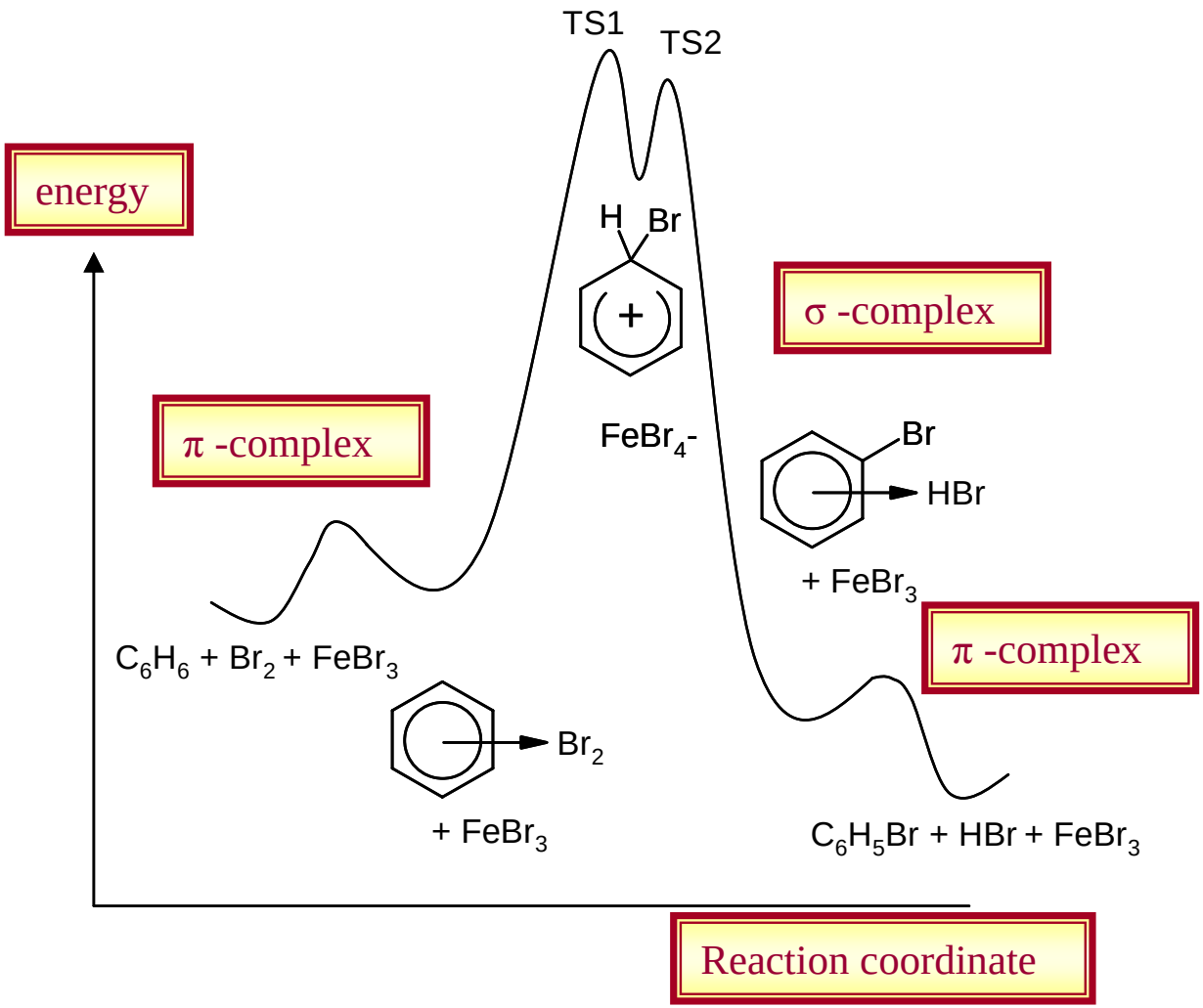
Organic Chemistry – chemistry of aromatics

Aromatic compounds – reactivity – S_E aromatic



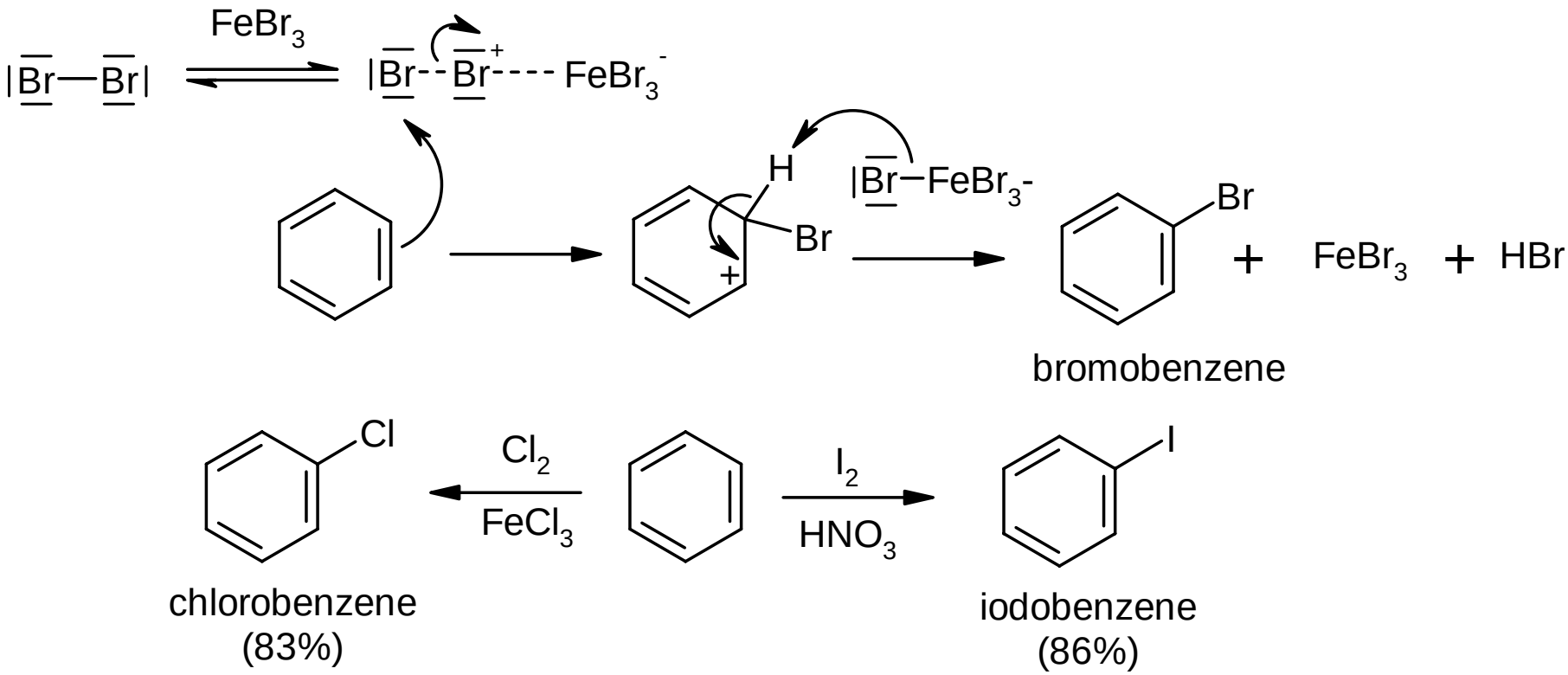
Organic Chemistry – chemistry of aromatics

Aromatic compounds – reactivity – S_E aromatic



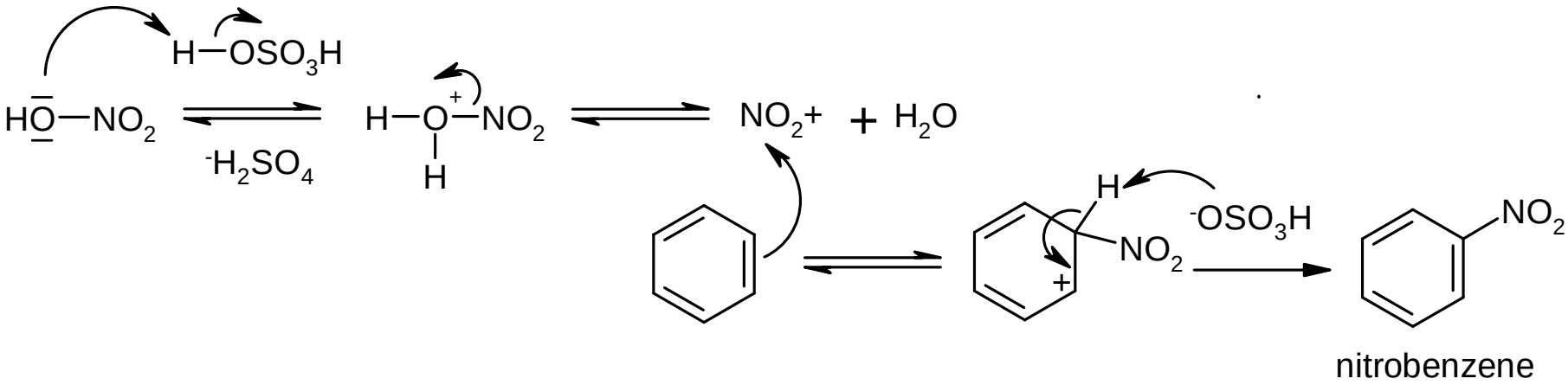
Organic Chemistry – chemistry of aromatics

Aromatic compounds – S_E aromatic - halogenation



Organic Chemistry – chemistry of aromatics

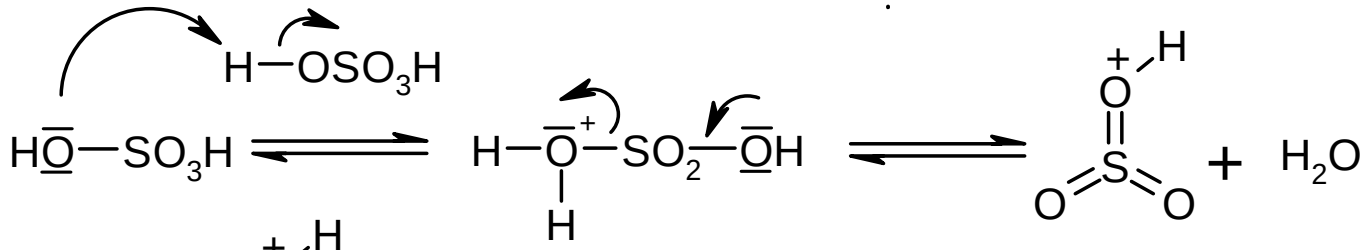
Aromatic compounds – S_E aromatic - nitration

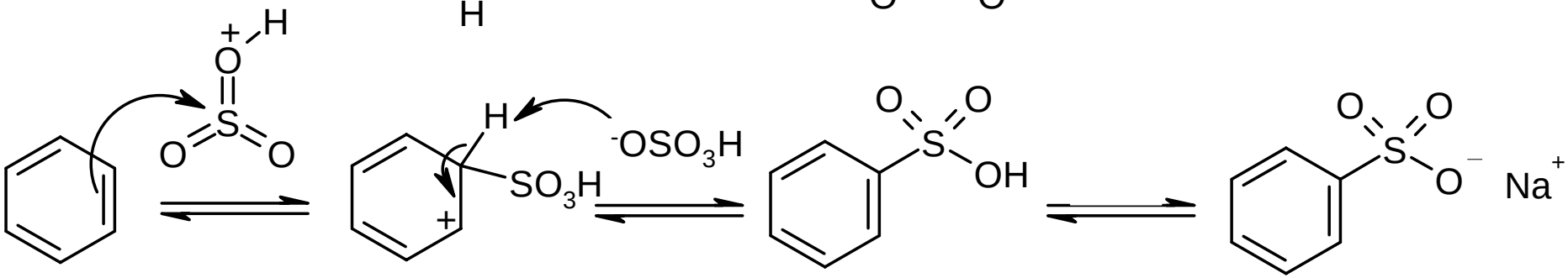


stable salts $NO_2^+ X^-$ (X = BF_4, ClO_4, PF_6)

Organic Chemistry – chemistry of aromatics

Aromatic compounds – S_E aromatic - sulfonation



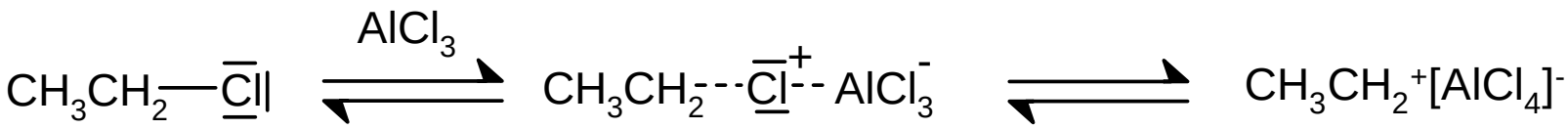


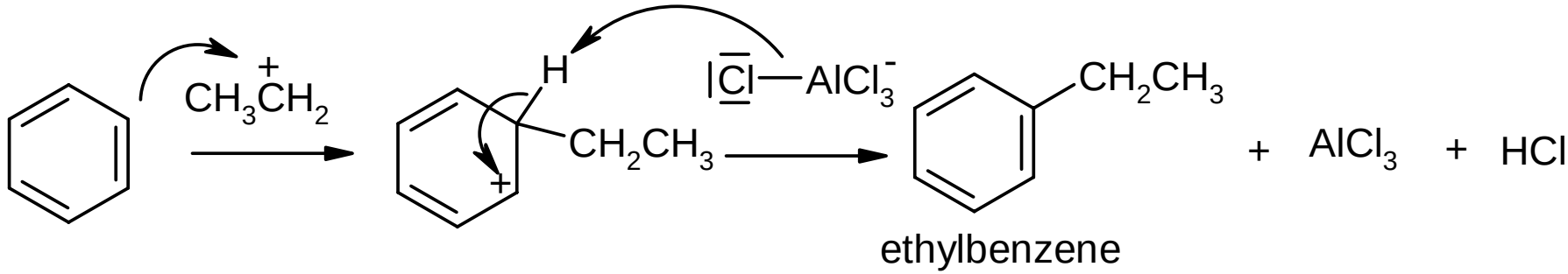
benzenesulfonic acid

natrium-benzenesulfonate

Organic Chemistry – chemistry of aromatics

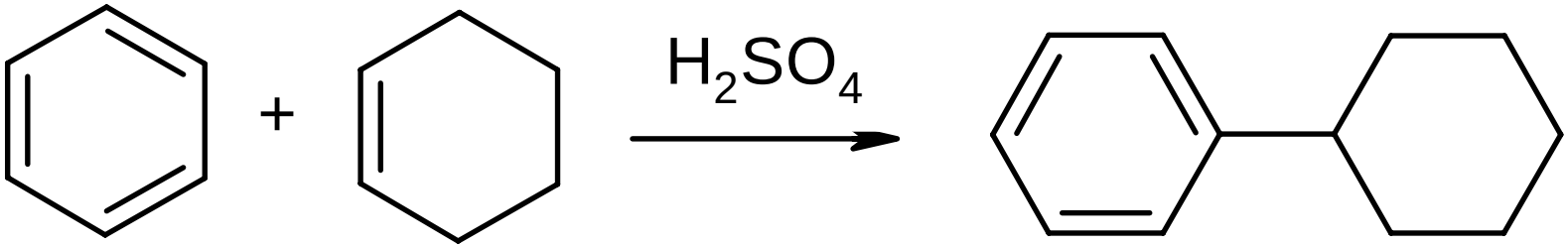
Aromatic compounds – S_E aromatic – F-C alkylation



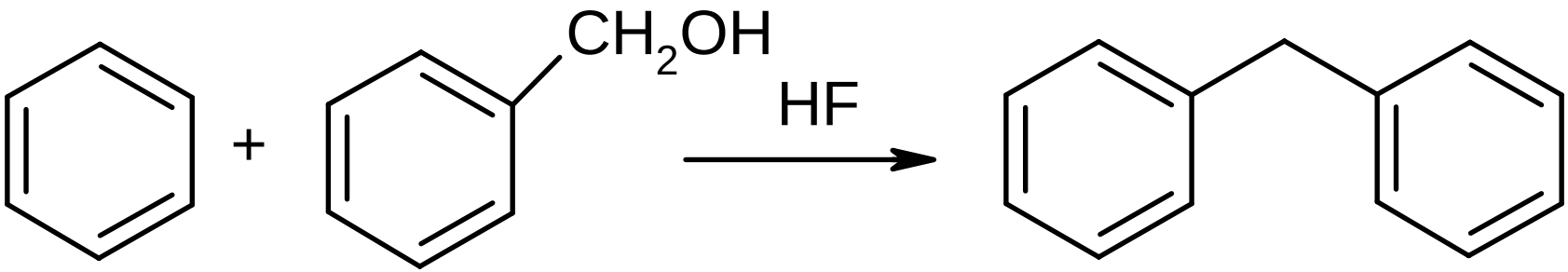


Organic Chemistry – chemistry of aromatics

Aromatic compounds – S_E aromatic – F-C alkylation



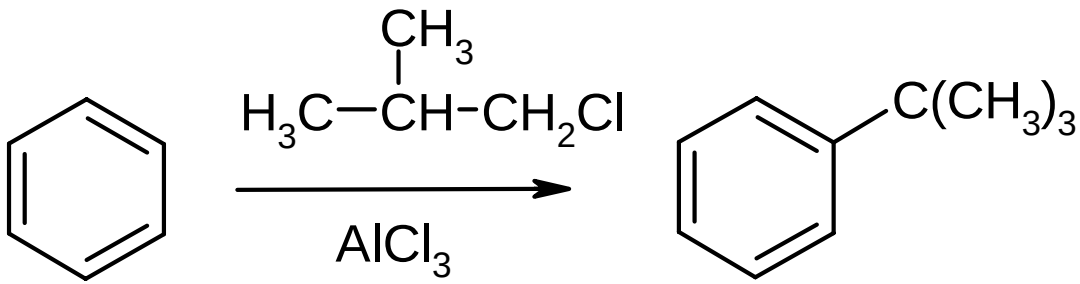
cyclohexylbenzene



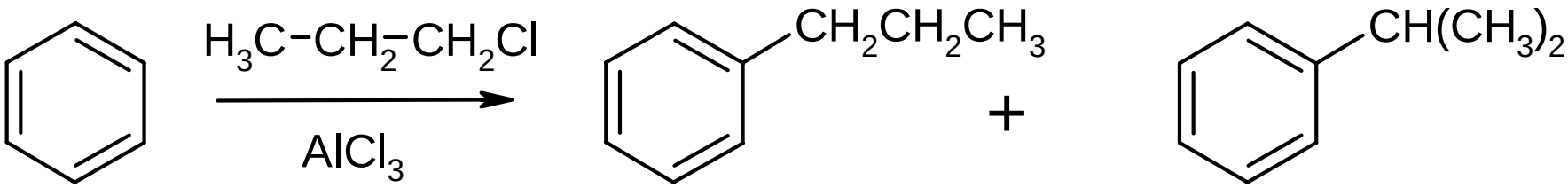
diphenylmethane

Organic Chemistry – chemistry of aromatics

Aromatic compounds – S_E aromatic – F-C alkylation



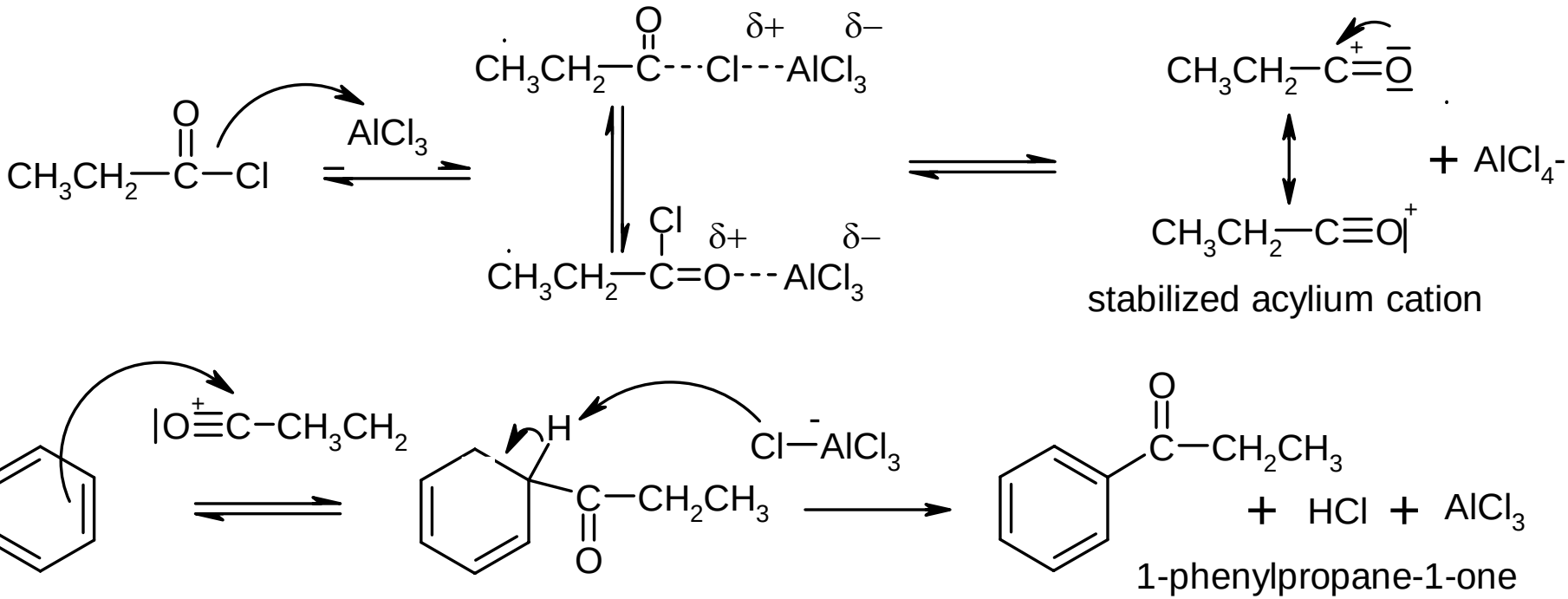
tert-butylbenzene



propylbenzene isopropylbenzene

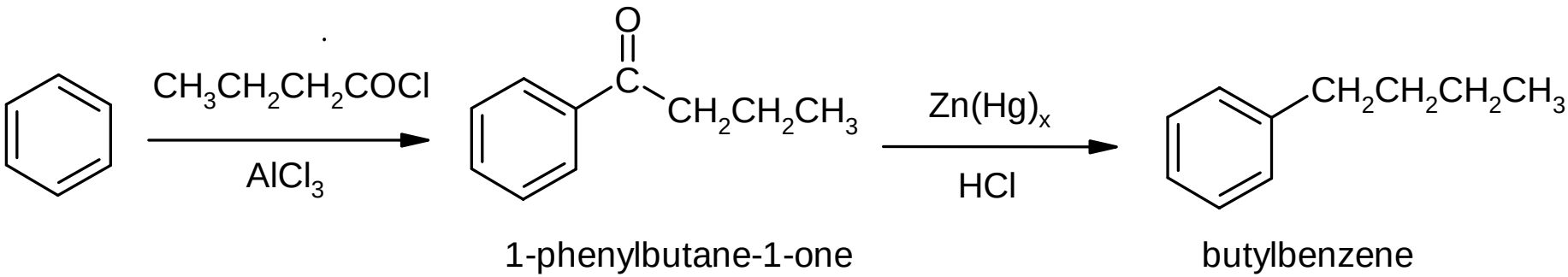
Organic Chemistry – chemistry of aromatics

Aromatic compounds – S_E aromatic – F-C acylation



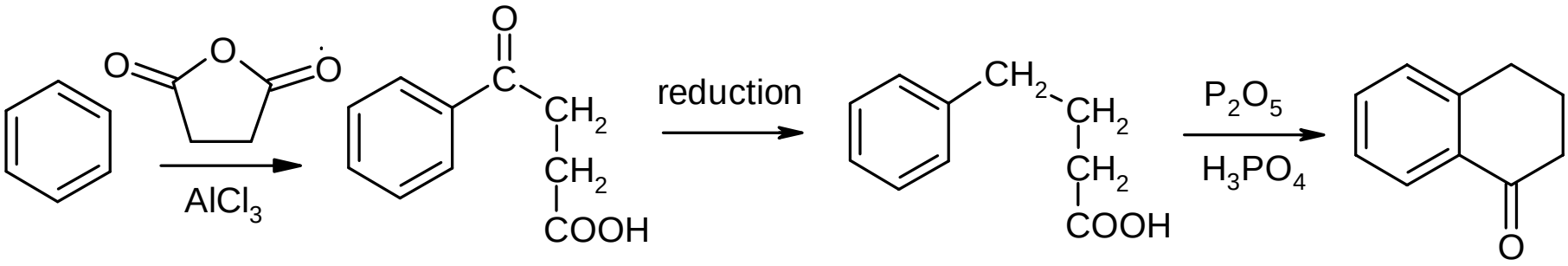
Organic Chemistry – chemistry of aromatics

Aromatic compounds – S_E aromatic – F-C acylation



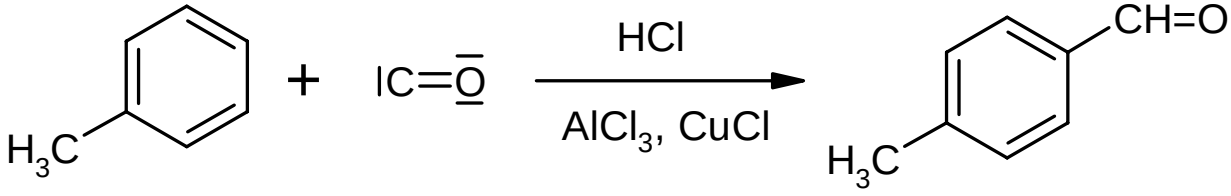
1-phenylbutane-1-one

butylbenzene



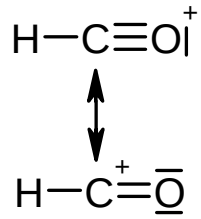
Organic Chemistry – chemistry of aromatics

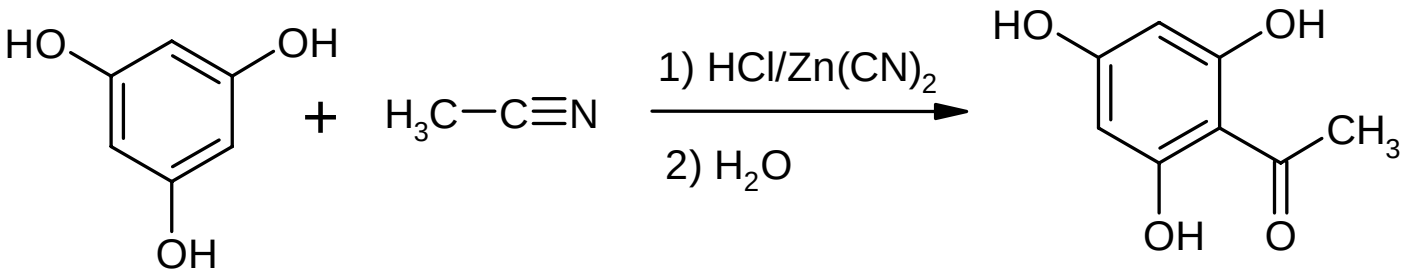
Aromatic compounds – S_E aromatic – varia



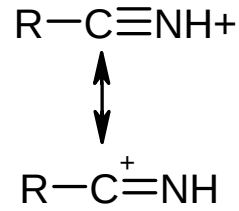
p-methylbenzaldehyde

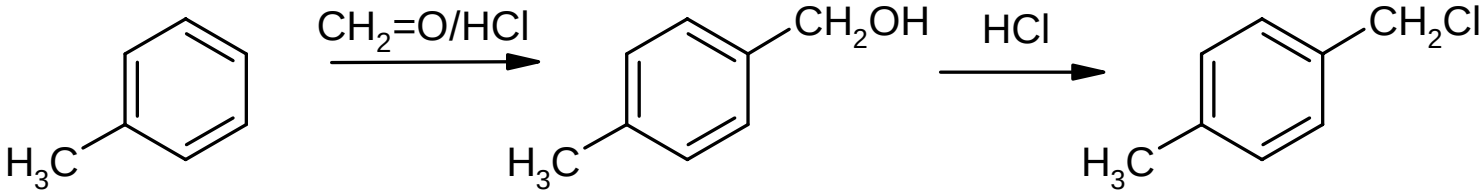
electrophile formed



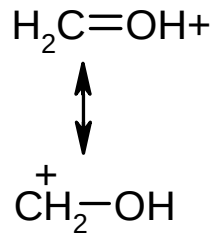


2,4,6-trihydroxyacetophenone



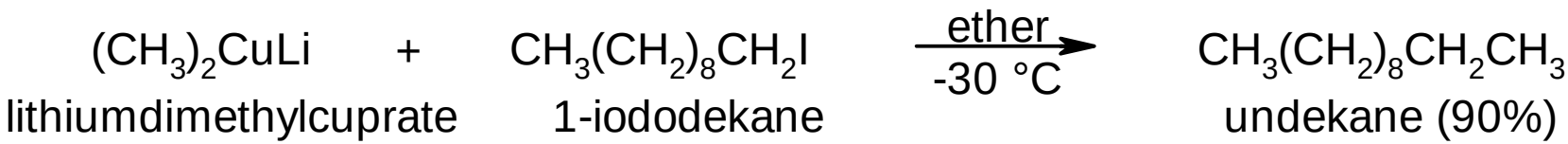


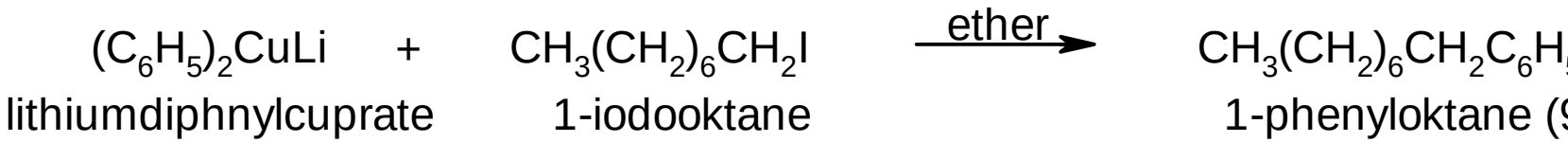
p-methylbenzylchloride

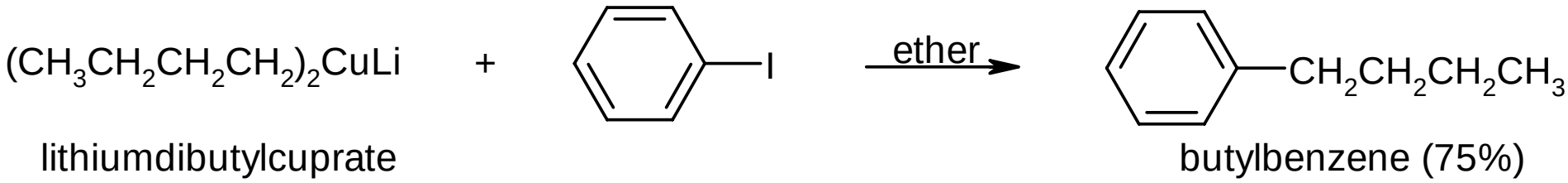


Organic Chemistry – chemistry of aromatics

Aromatic compounds – varia

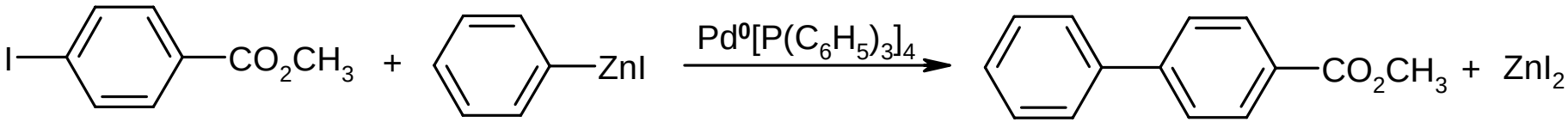






Aromatic compounds – varia

Negishi reaction:

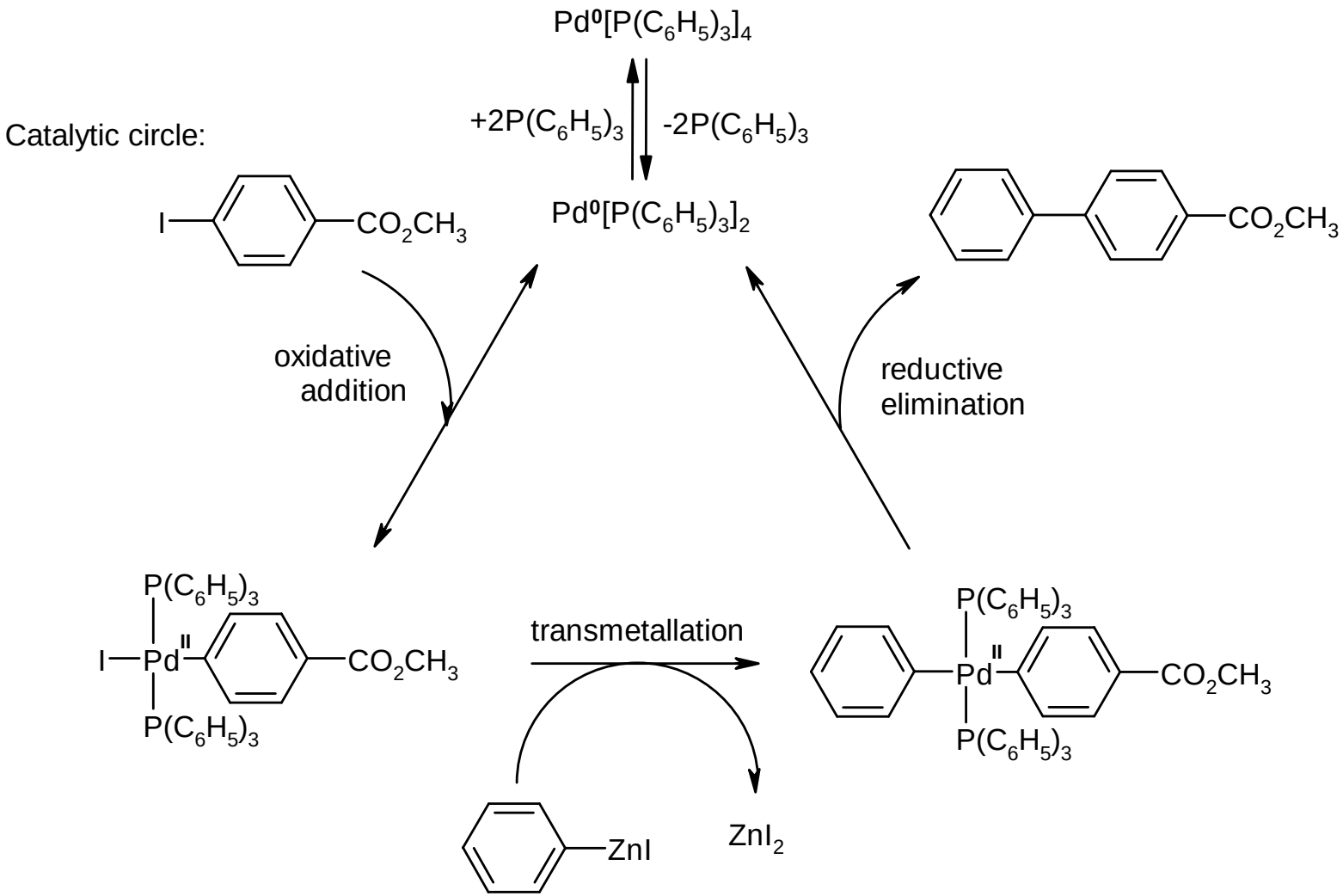


methyl-4-jodobenzoate

phenylzinc iodide

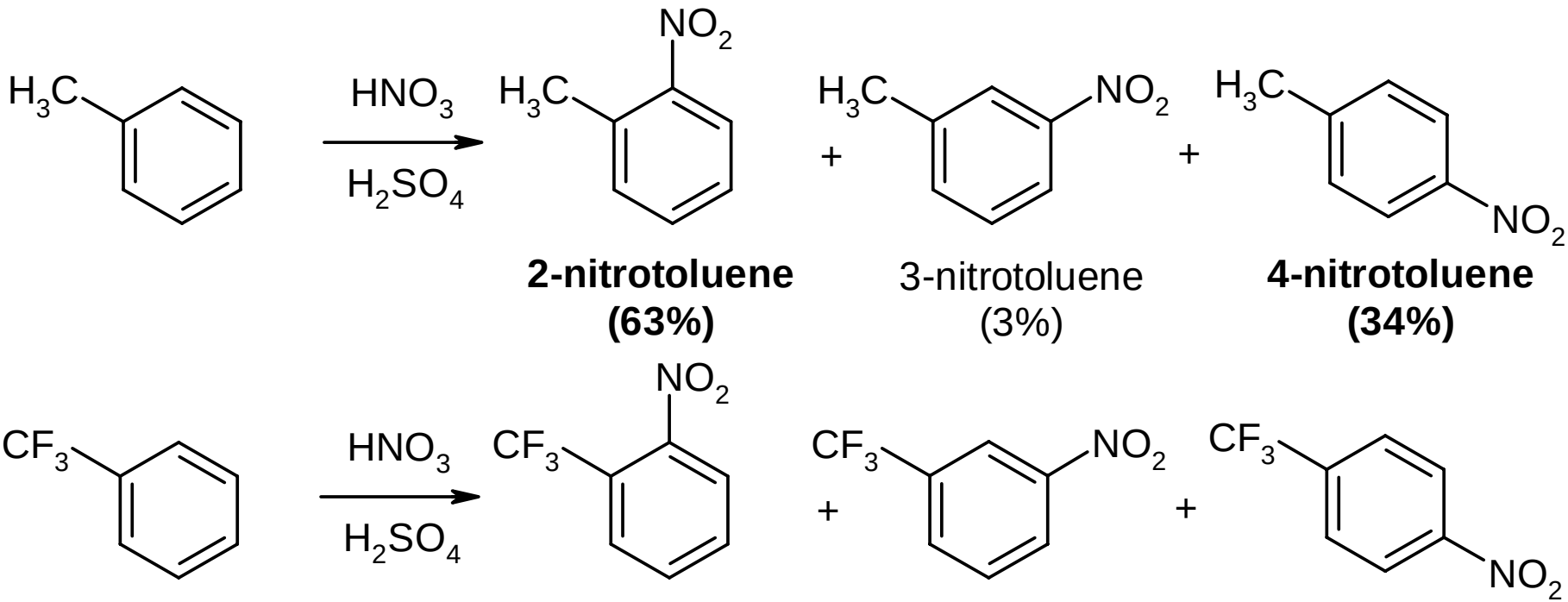
methyl-biphenyl-4-carboxylate

Aromatic compounds – varia



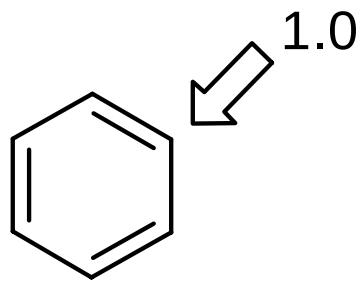
Organic Chemistry – chemistry of aromatics

Aromatic compounds – S_E aromatic – directive effect

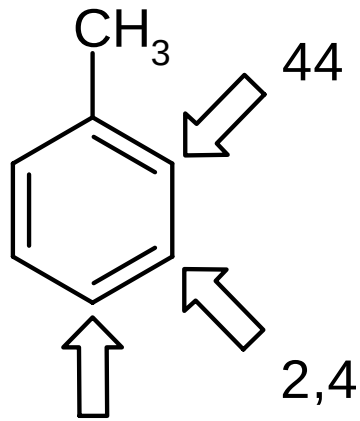


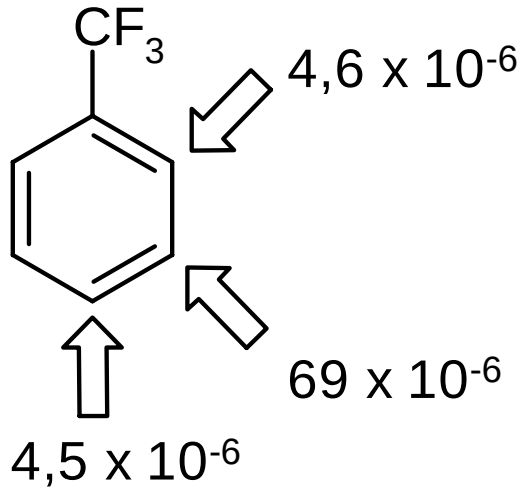
Organic Chemistry – chemistry of aromatics

Aromatic compounds – S_E aromatic – directive effect



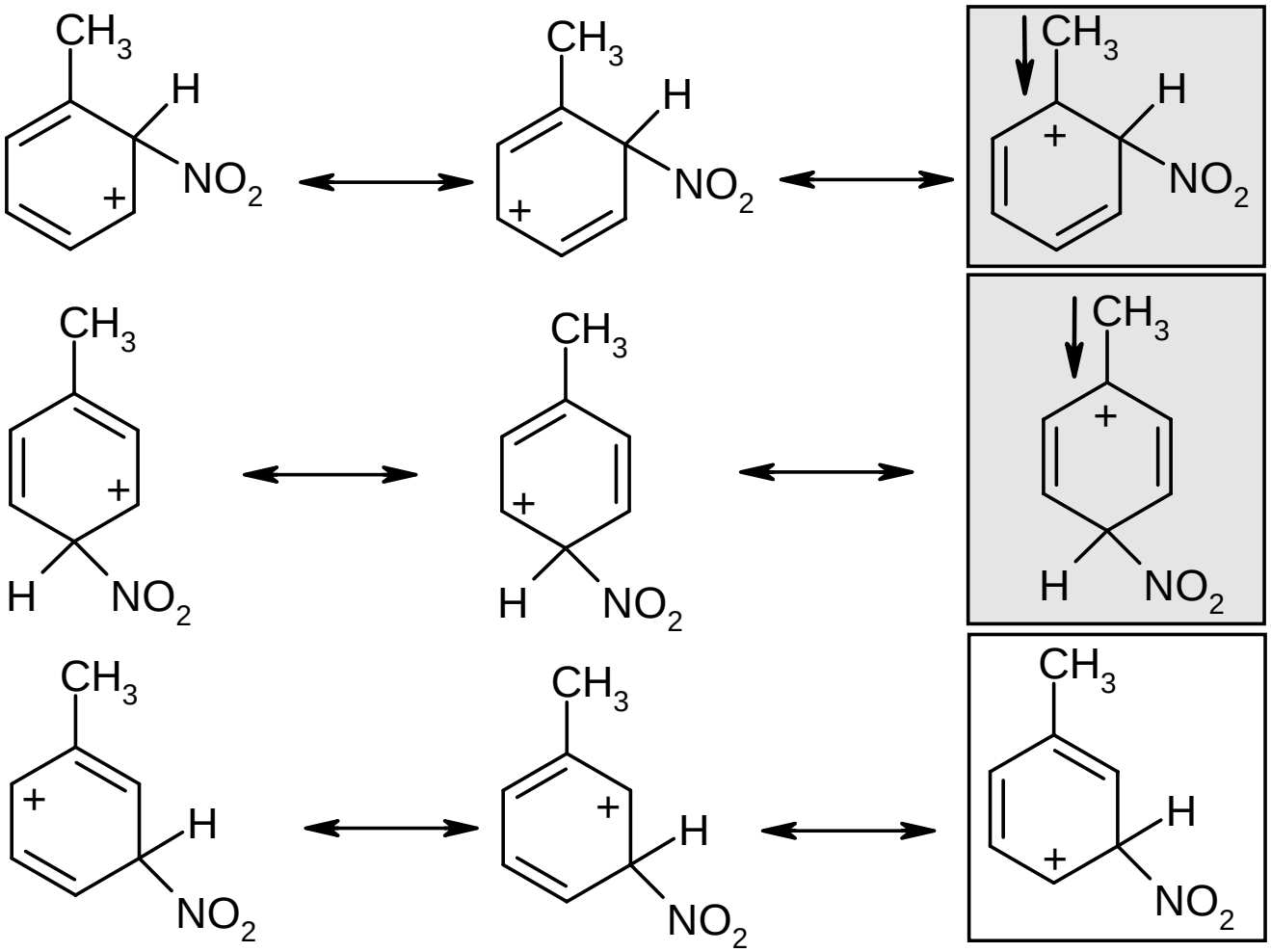
relative velocity of nitration





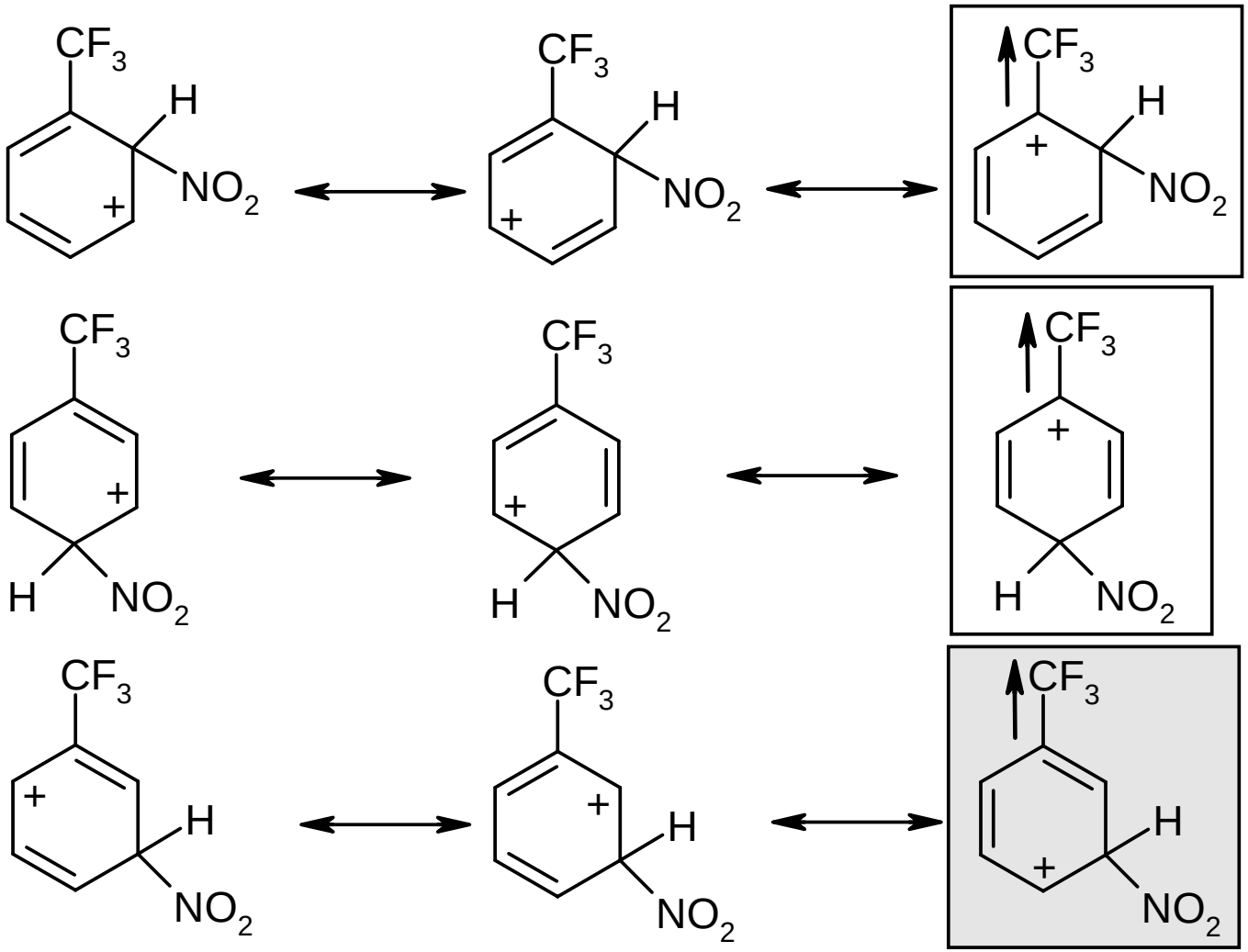
Organic Chemistry – chemistry of aromatics

Aromatic compounds – S_E aromatic – directive effect



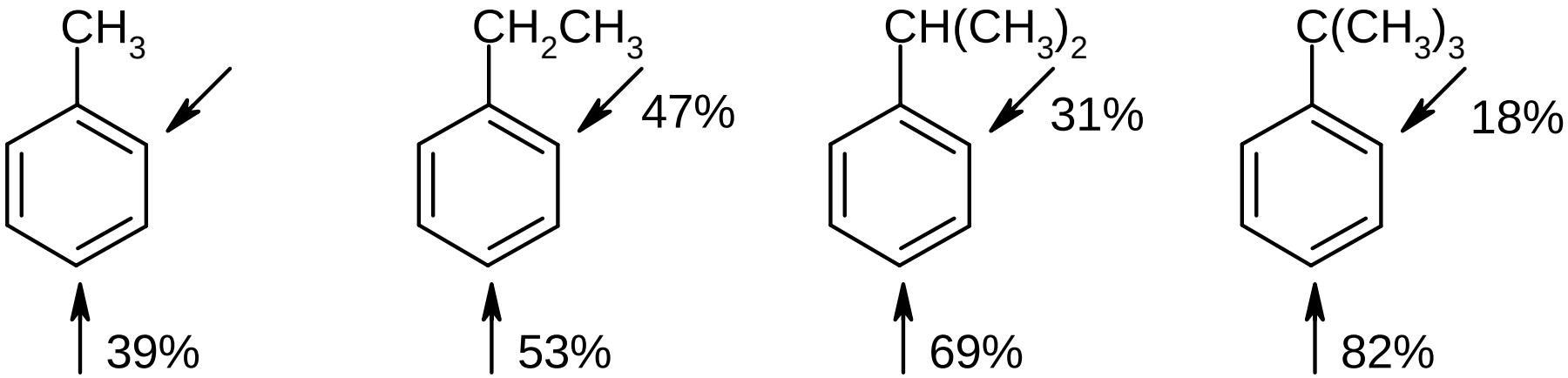
Organic Chemistry – chemistry of aromatics

Aromatic compounds – S_E aromatic – directive effect



Organic Chemistry – chemistry of aromatics

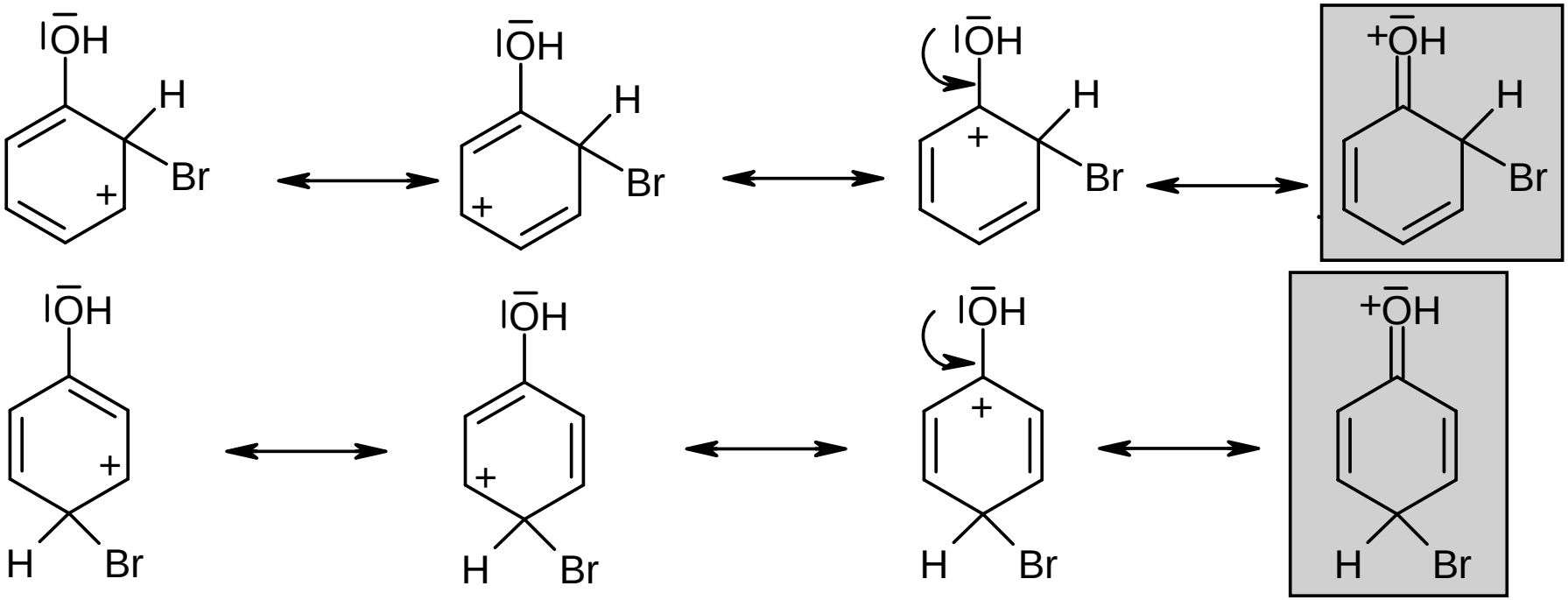
Aromatic compounds – S_E aromatic – directive effect



Steric effect

Organic Chemistry – chemistry of aromatics

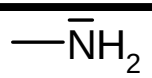
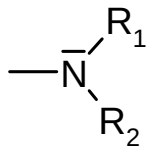
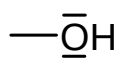
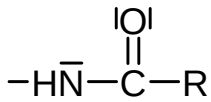
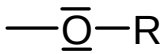
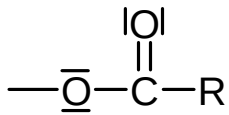
Aromatic compounds – S_E aromatic – directive effect



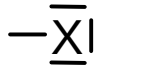
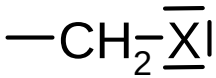
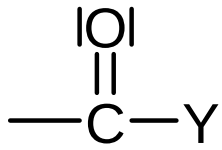
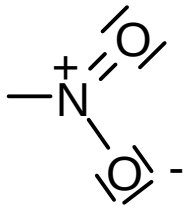
- I $_{+M}$ substituents

Organic Chemistry – chemistry of aromatics

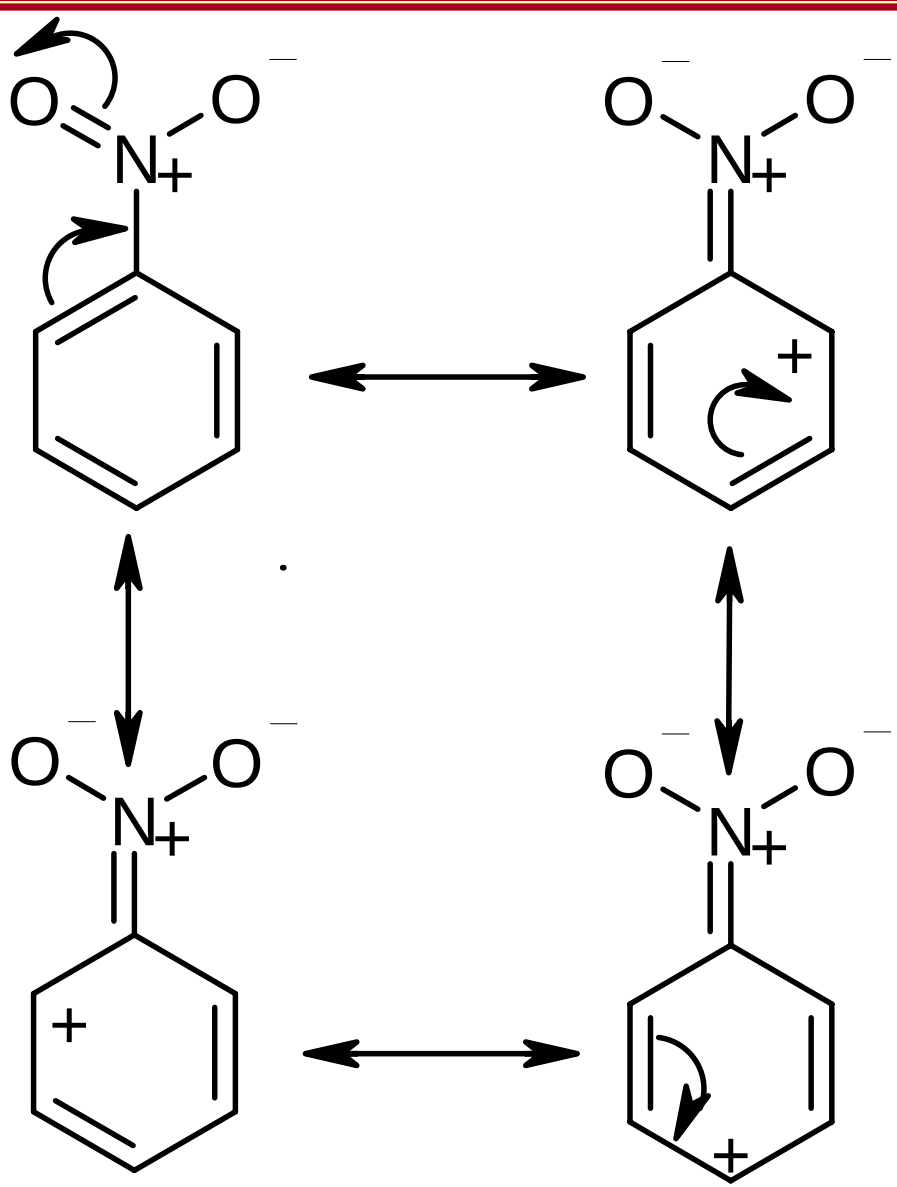
Aromatic compounds – S_E aromatic – directive effect

Velocity of S_EAr	Substituent	Name	Orientation
super activating		amino	*ortho*/*para*
Strongly activating		alkylamino (R_1=H) dialkylamino (R_1,R_2≠H)	*ortho*/*para*
		hydroxy	*ortho*/*para*
		acylamino	*ortho*/*para*
		alkoxy	*ortho*/*para*
		acyloxy	*ortho*/*para*
activating	-R, -Ar	alkyl, aryl	*ortho*/*para*
	-CH=CR_2	alkenyl	*ortho*/*para*
reference	H		

Organic Chemistry – chemistry of aromatics

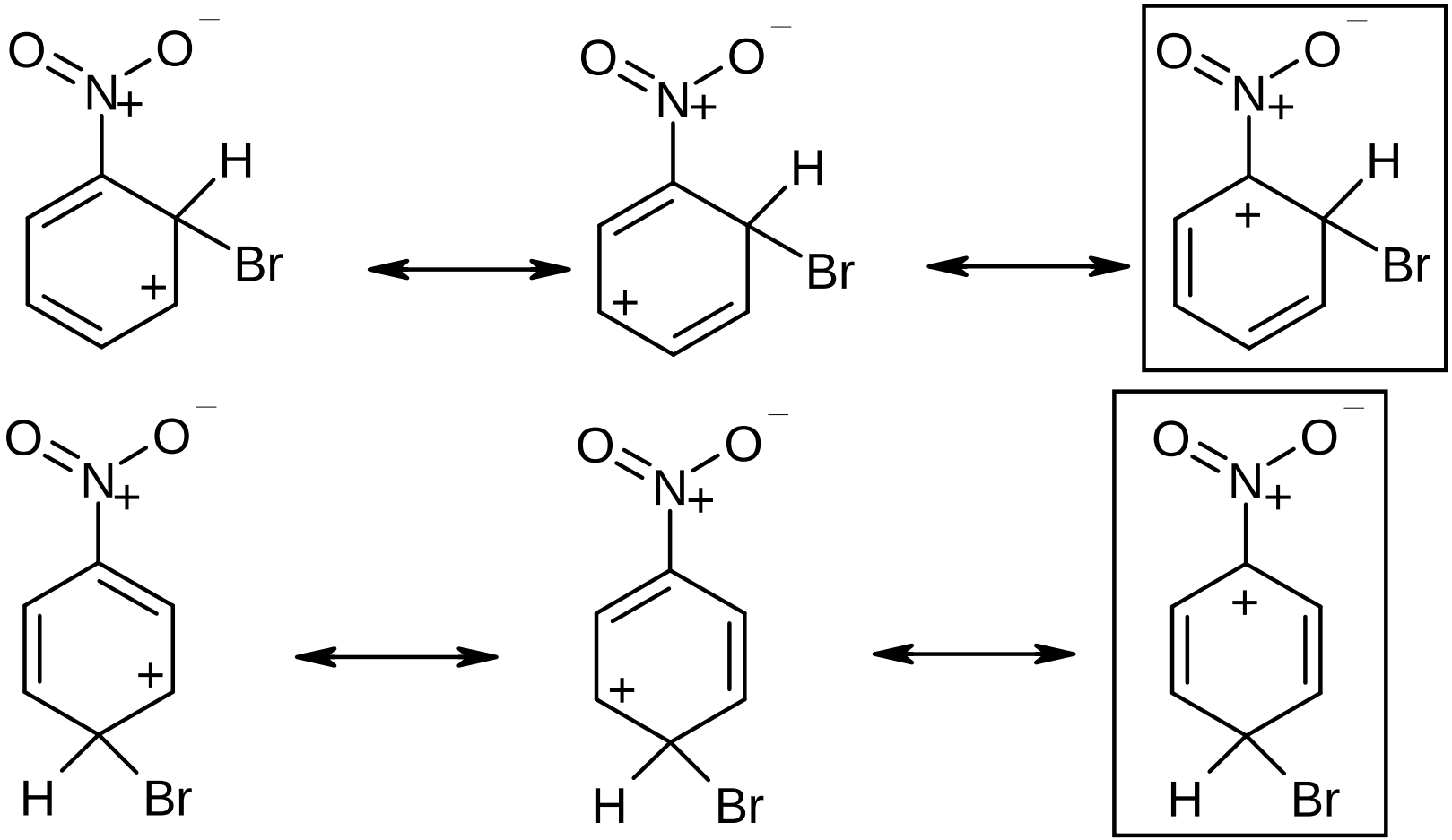
Velocity S_EAr	Substituent	Name	Orientation
reference			
weakly deactivating		halogen	*ortho*/*para*
	(X=F, Cl, Br, I)		
		halogenmethyl	*ortho*/*para*
strongly deactivating		acyl (Y=R) acylchloride (Y=Cl) carboxylic acid (Y=OH) ester (Y=OR)	*meta*
H			
		cyano	*meta*
		sulfonic acid	*meta*
Very strongly deactivating		trifluormethyl	*meta*
		nitro	*meta*

Organic Chemistry – chemistry of aromatics



Organic Chemistry – chemistry of aromatics

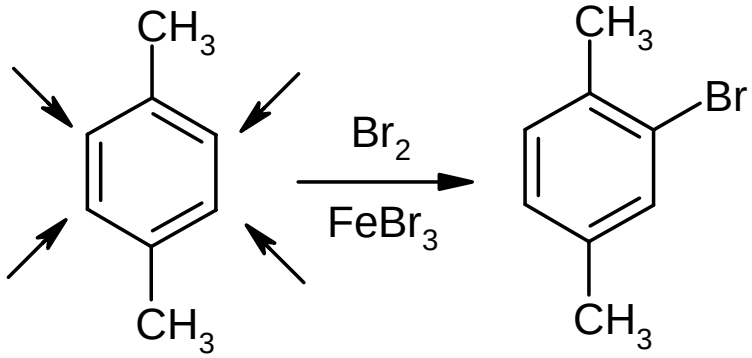
Aromatic compounds – S_E aromatic – directive effect



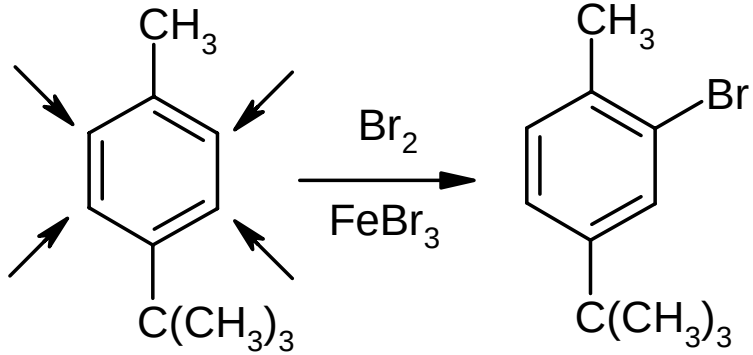
Organic Chemistry – chemistry of aromatics

Aromatic compounds – S_E aromatic – multiple effect

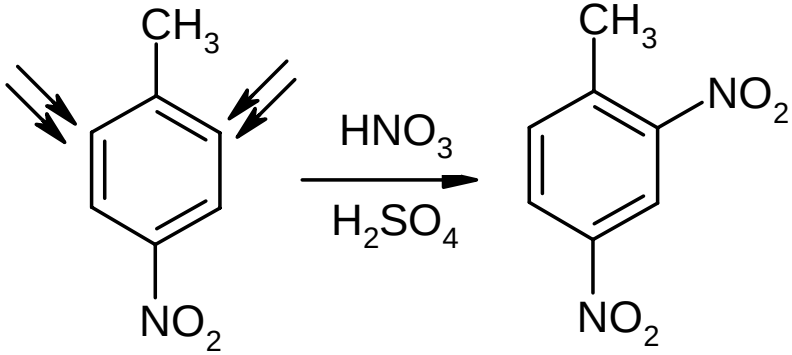
a)



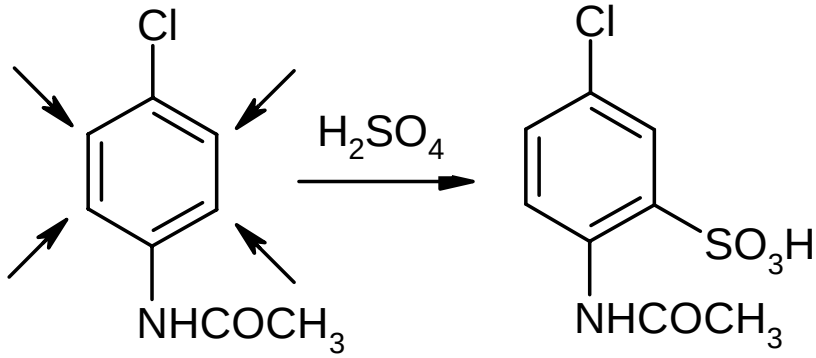
b)



c)

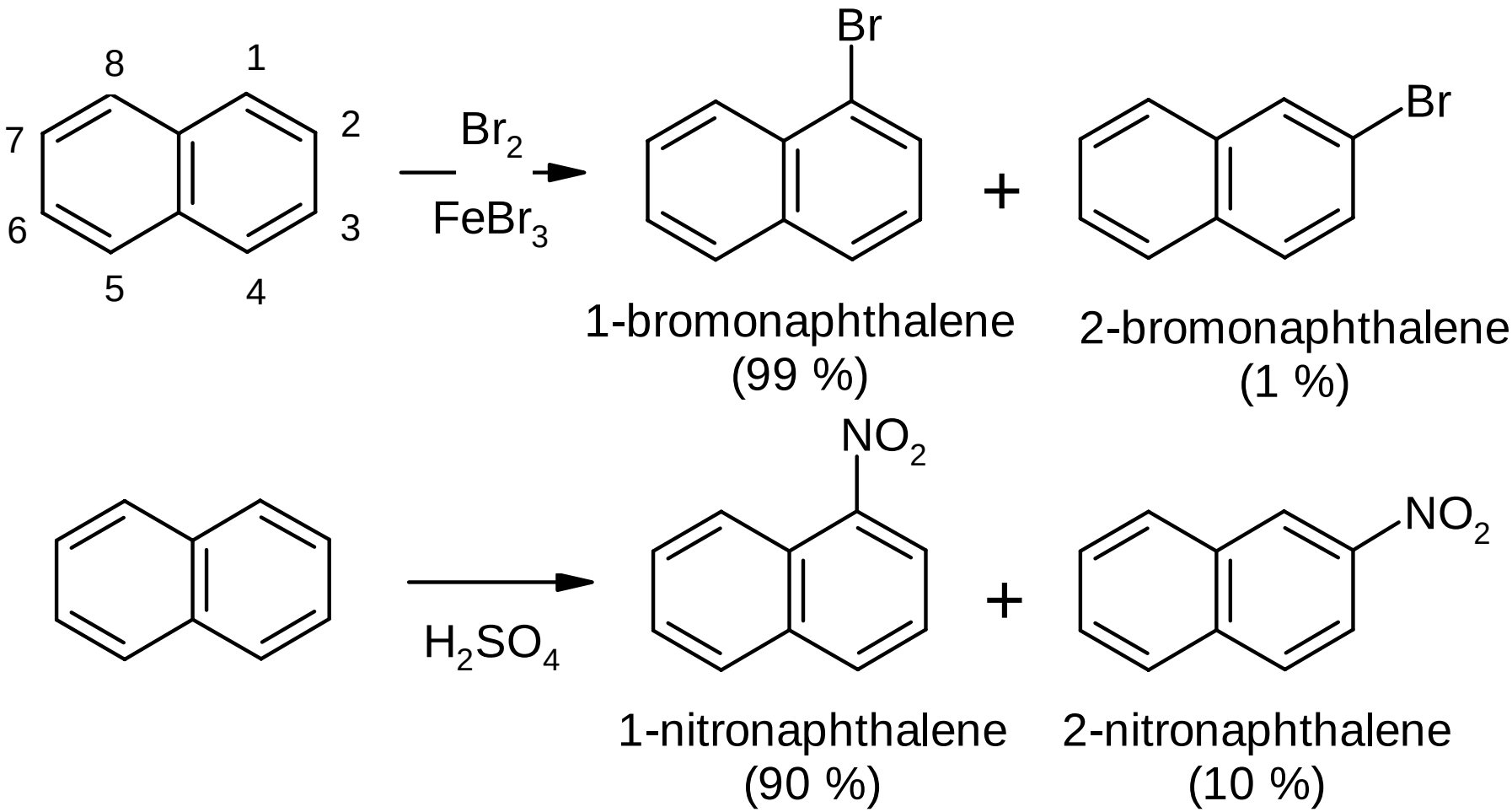


d)



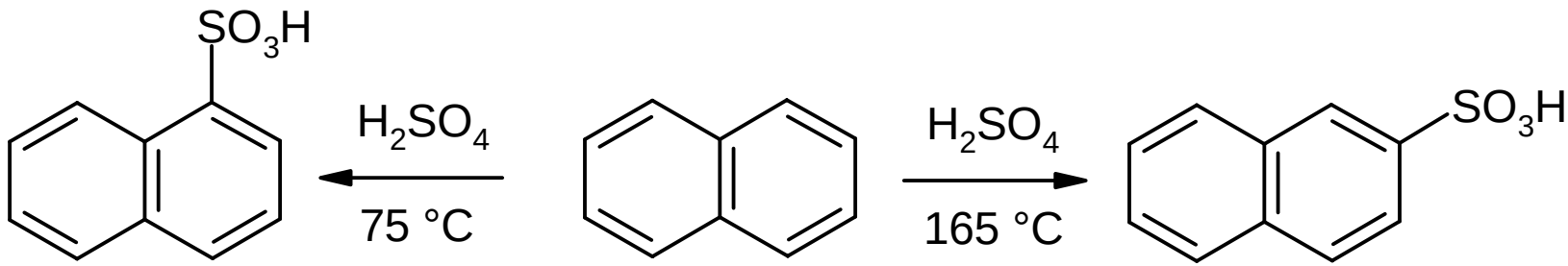
Organic Chemistry – chemistry of aromatics

Aromatic compounds – S_E aromatic – naphthalene



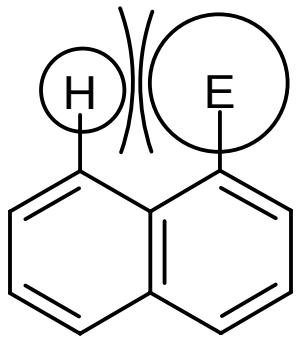
Organic Chemistry – chemistry of aromatics

Aromatic compounds – S_E aromatic – naphthalene



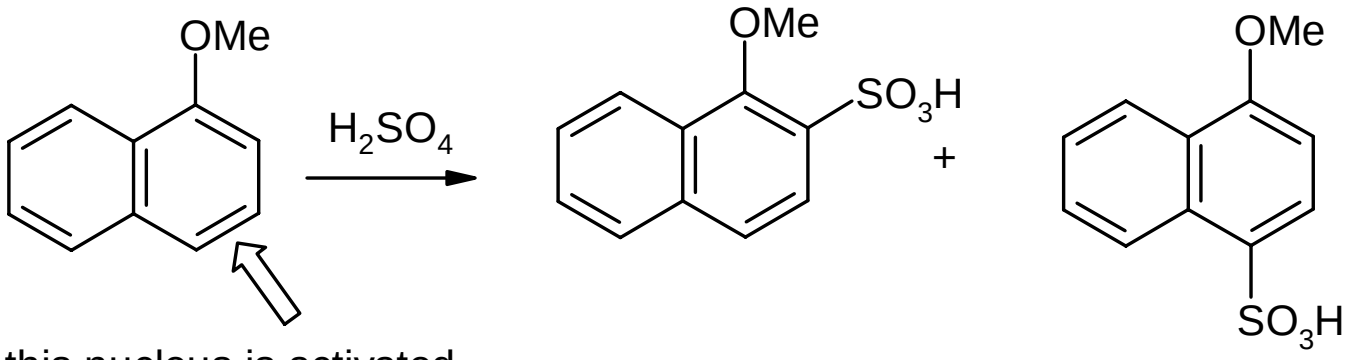
naphthalene-1-sulfonic acid acid (98 %)

naphthalene-2-sulfonic acid (88 %)



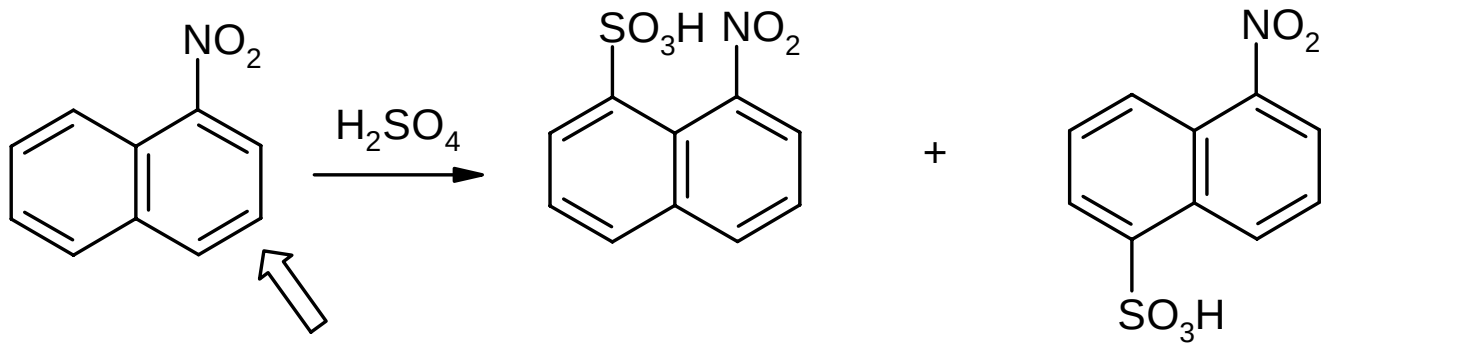
Organic Chemistry – chemistry of aromatics

Aromatic compounds – S_E aromatic – naphthalene



this nucleus is activated

Me = CH_3



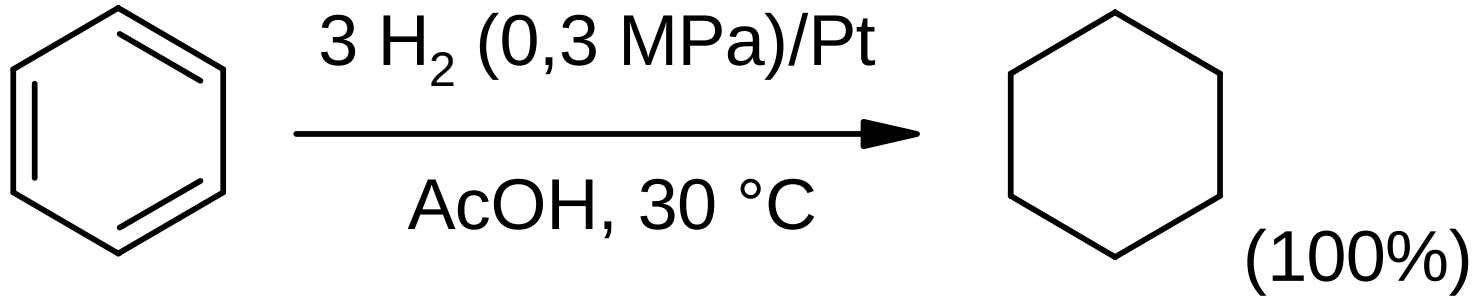
this nucleus is deactivated

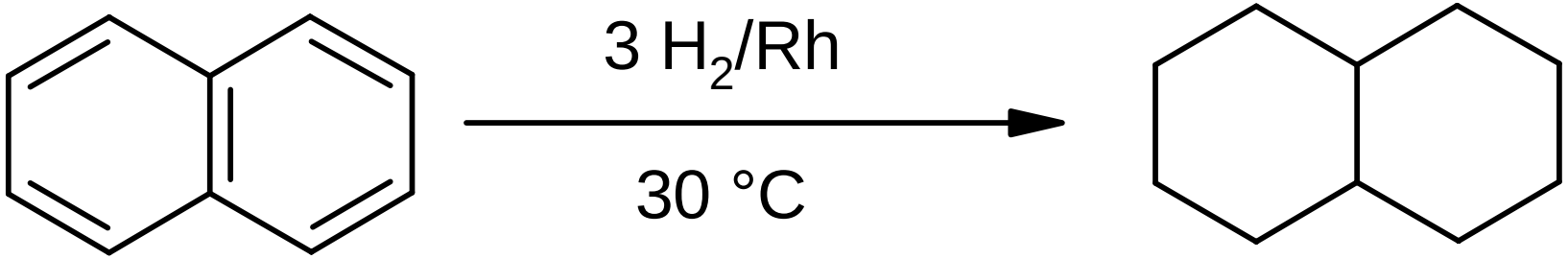
8-nitronaphthalene-1-sulfonic acid

5-nitronaphthalene-1-sulfonic acid

Organic Chemistry – chemistry of aromatics

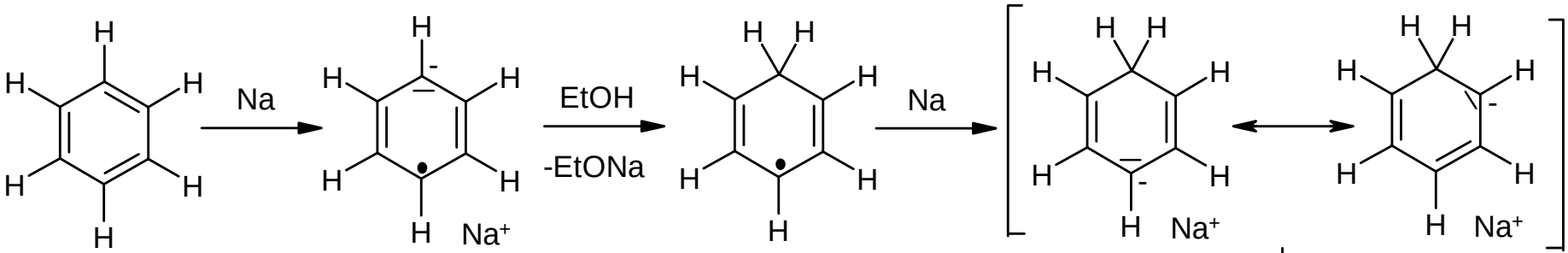
Aromatic compounds – S_E aromatic – reduction

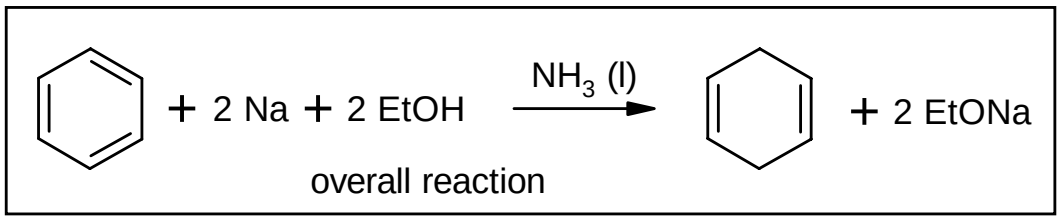


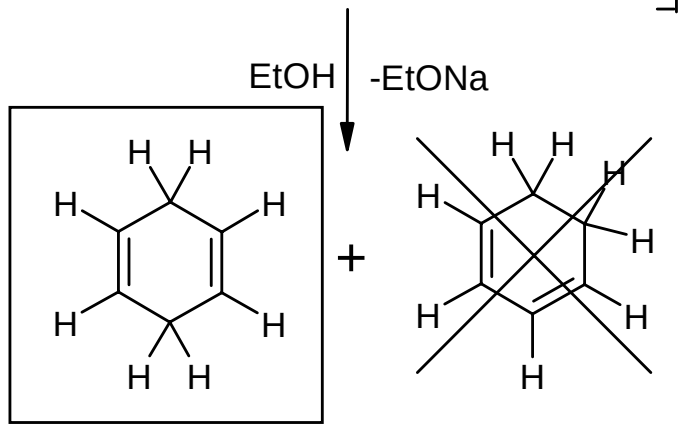


Organic Chemistry – chemistry of aromatics

Aromatic compounds – S_E aromatic – reduction



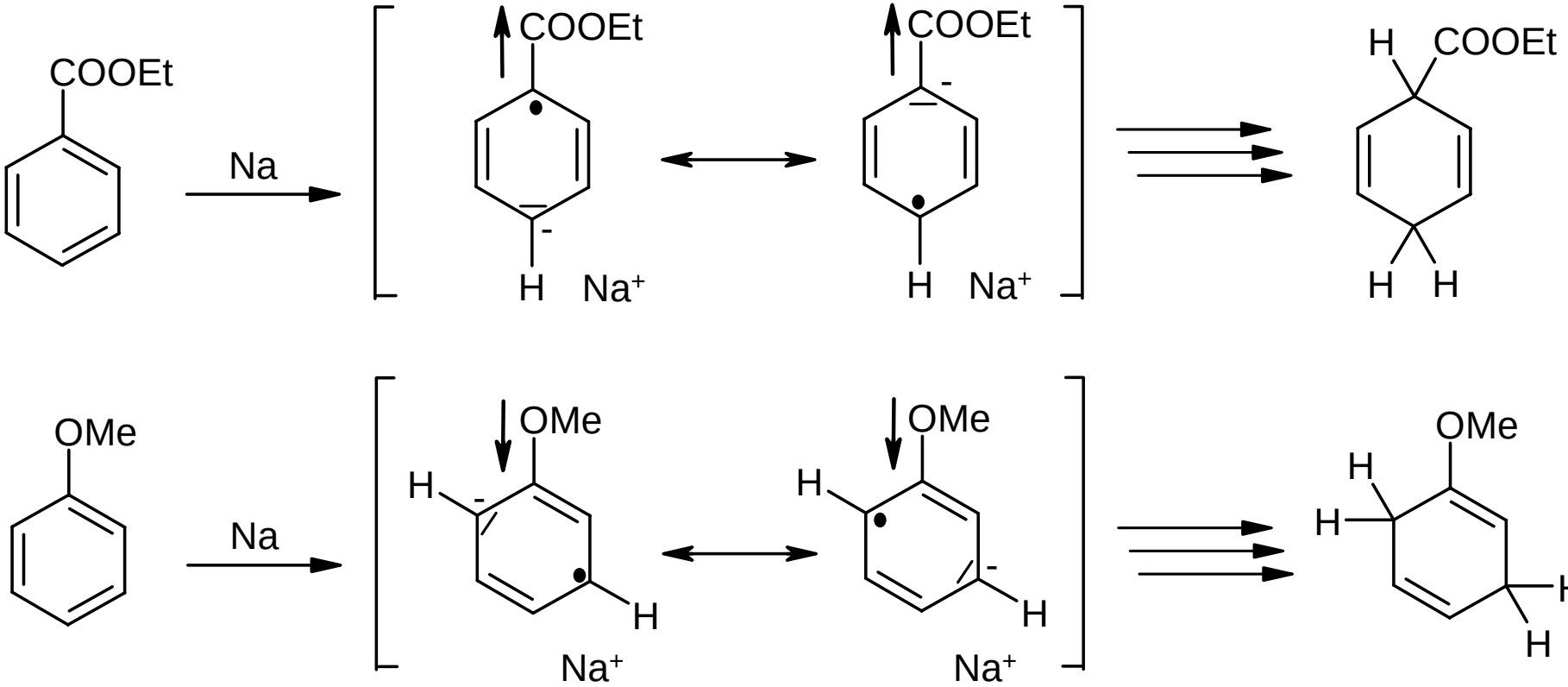




Et = C_2H_5

Organic Chemistry – chemistry of aromatics

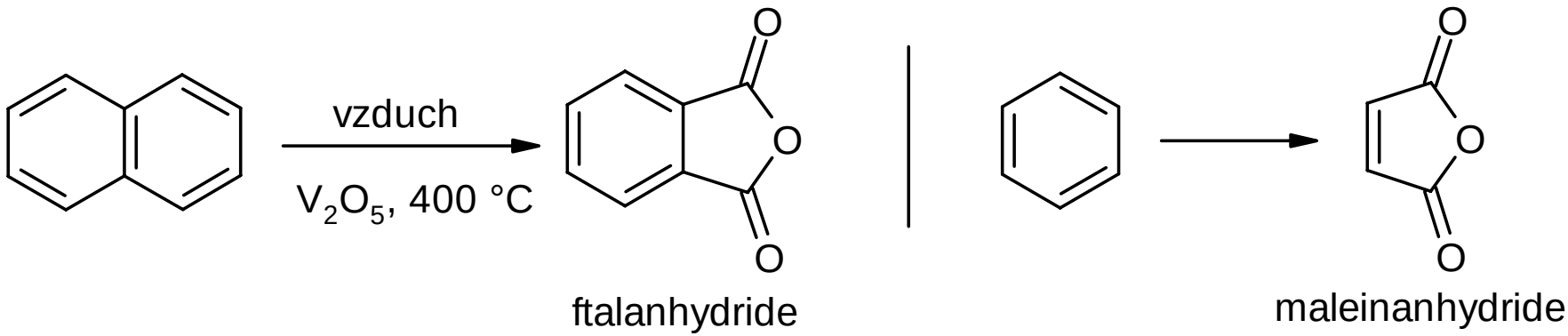
Aromatic compounds – S_E aromatic – reduction



Me = CH_3, Et = C_2H_5

Organic Chemistry – chemistry of aromatics

Aromatic compounds – S_E aromatic – oxidation

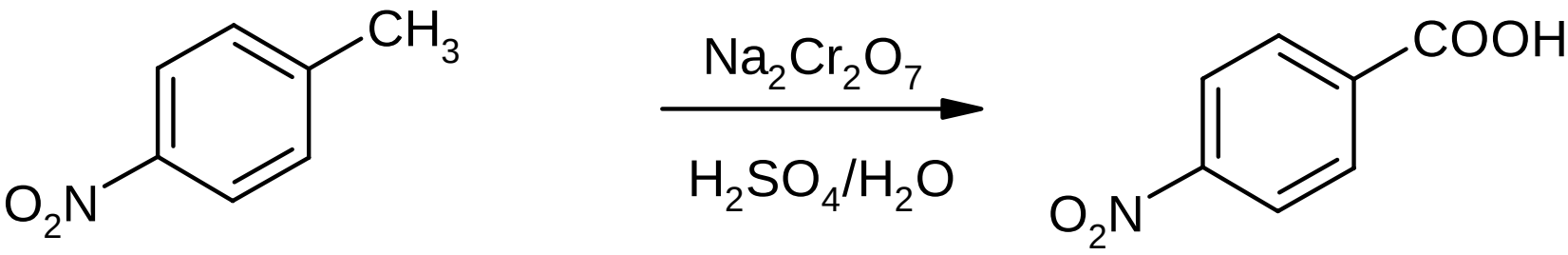


ftalanhydride

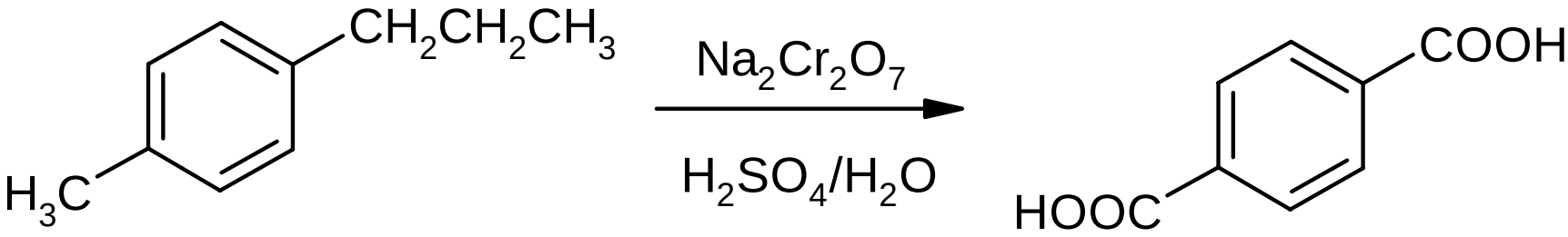
maleinanhydride

Organic Chemistry – chemistry of aromatics

Aromatic compounds – S_E aromatic – oxidation



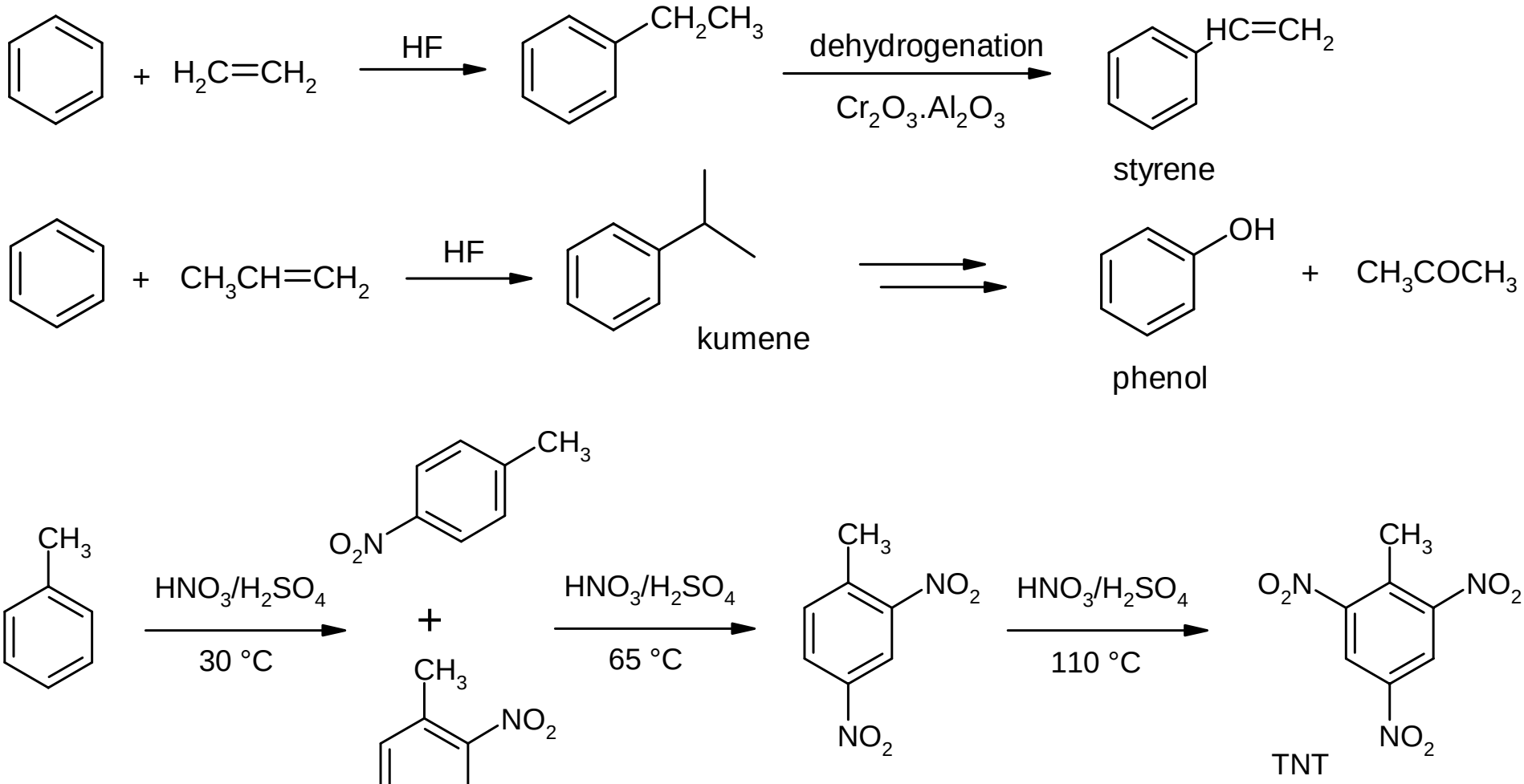
p-nitrobenzoic acid



benzene-1,4-dicarboxylic acid
(tereftaphthalic acid)

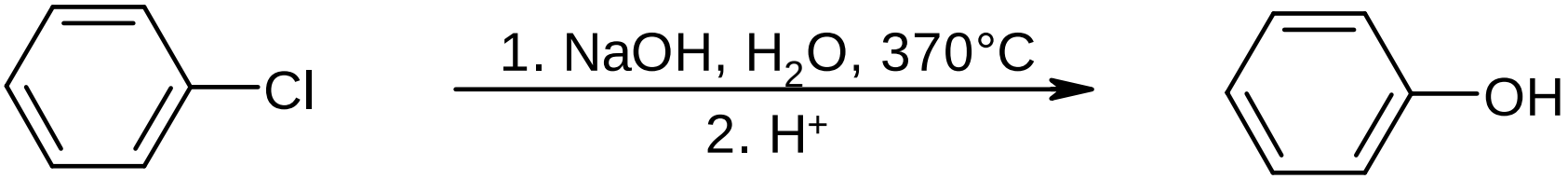
Organic Chemistry – chemistry of aromatics

Aromatic compounds – technically important



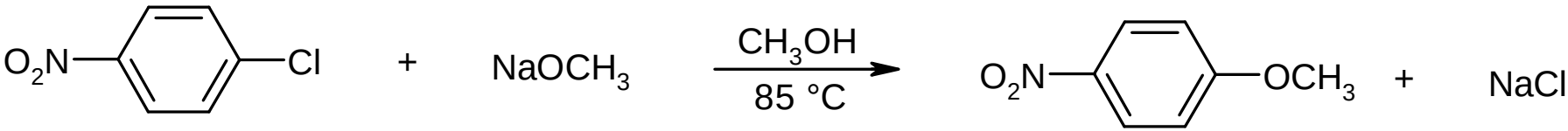
Organic Chemistry – chemistry of aromatics

Phenols - S_N on aromatic halogen



chlorobenzene

phenol (97%)



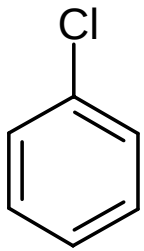
4-chloronitrobenzene

methyl(4-nitrophenyl)ether (92%)

Organic Chemistry – chemistry of aromatics

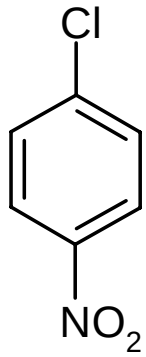
Phenols - S_N on aromatic skeleton

Relative velocity reaction with $NaOCH_3$:



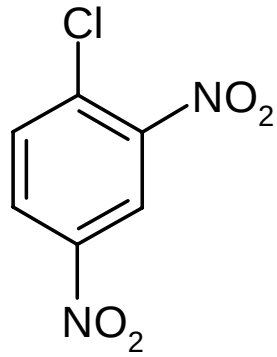
chlorobenzene

1,0



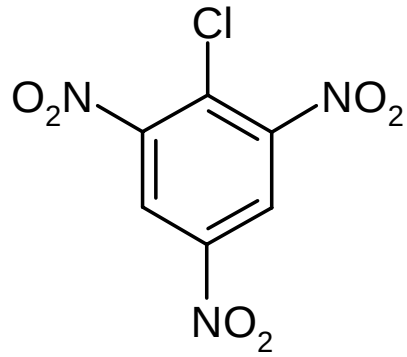
1-chloro-
4-nitrobenzene

$7x10^{10}$



1-chloro-
2,4-dinitrobenzene

$2,4x10^{15}$

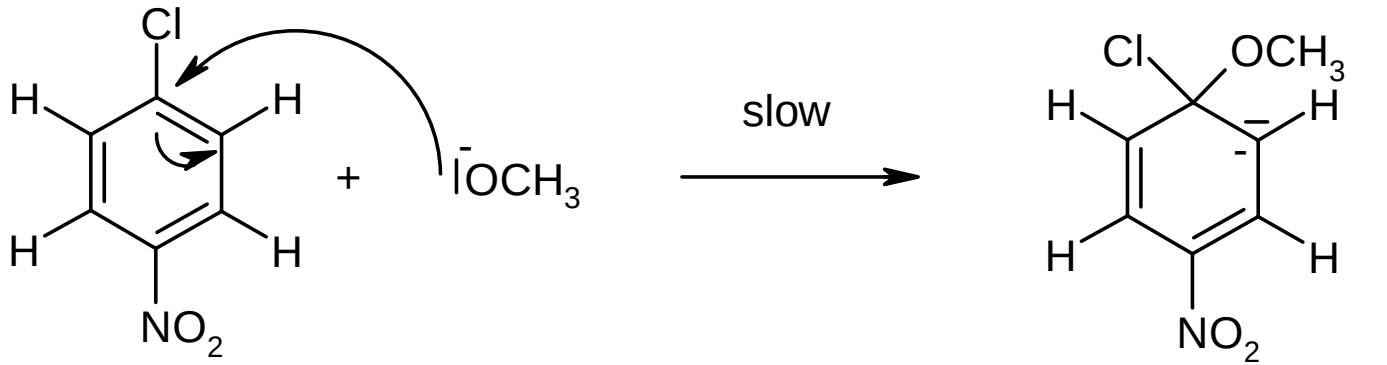


2,4,6-trinitro-
chlorobenzene

too high to be determined

Phenols - S_N on aromatic skeleton - mechanism

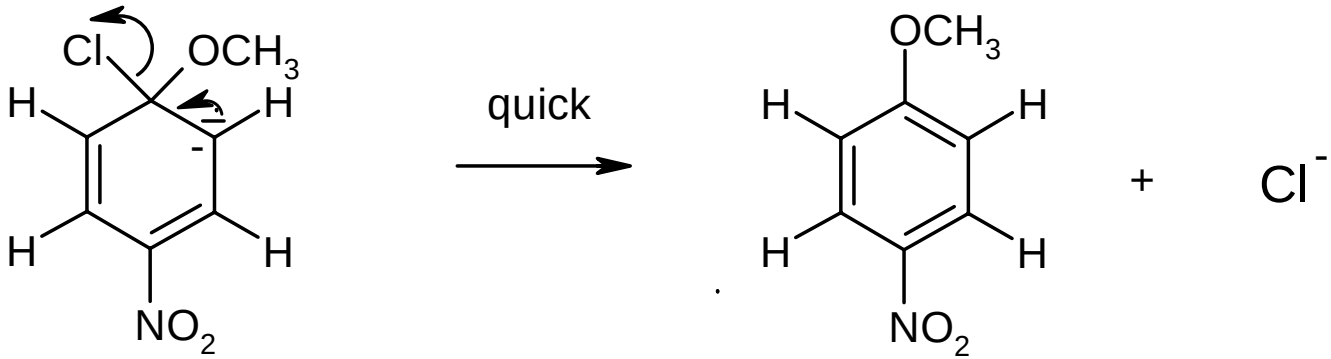
1. step:



4-chloronitrobenzene

cyclohexadienyl anion

2. step:



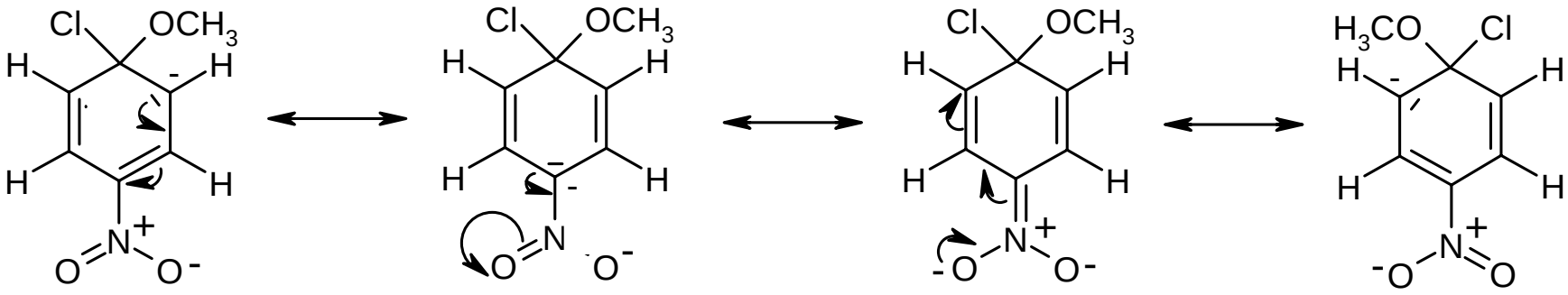
cyclohexadienyl anion

methyl(4-nitrophenyl)ether

Organic Chemistry – chemistry of aromatics

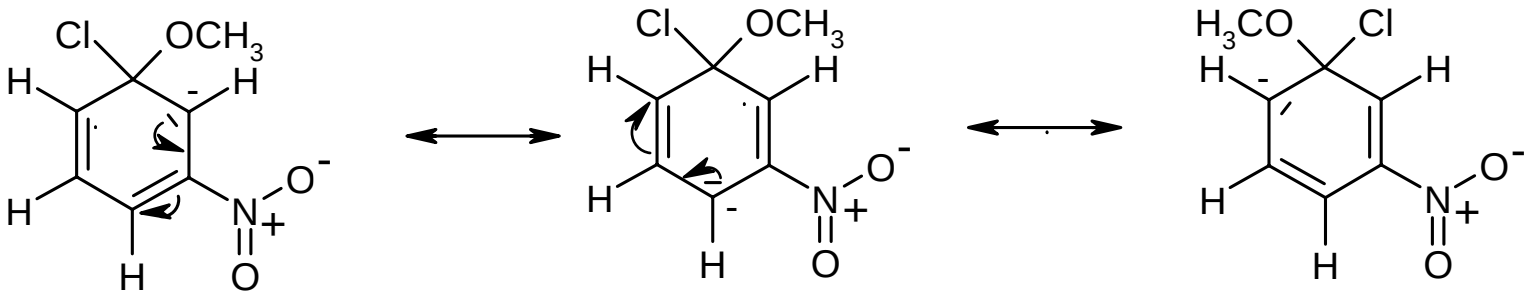
Phenols - S_N on aromatic skeleton - mechanism

4-nitrochlorobenzene:



The most stable mesomeric structure
(negative charge on oxygen)

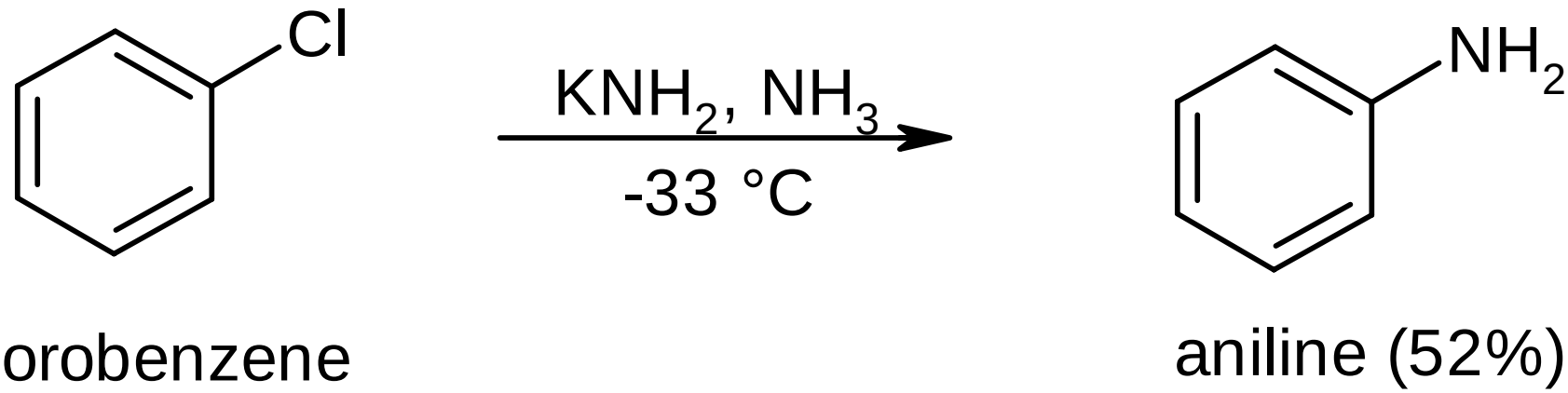
3-nitrochlorobenzene:



Negative charge can be located on carbon atoms only

Organic Chemistry – chemistry of aromatics

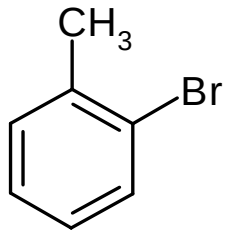
S_N on aromatic skeleton – addition-elimination mechanism



chlorobenzene

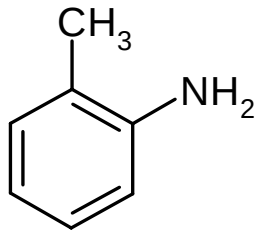
aniline (52%)

Organic Chemistry – chemistry of aromatics

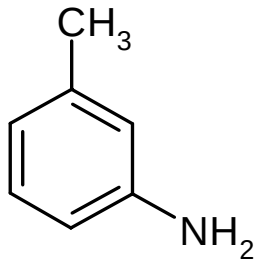


o-bromotoluene

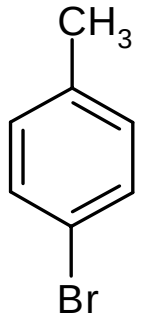
KNH_2, NH_3, -33 °C



o-methylaniline +

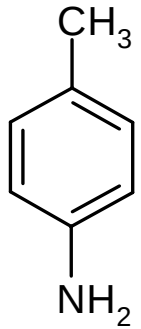


m-methylaniline

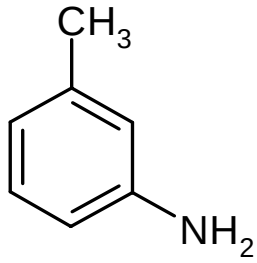


p-bromotoluene

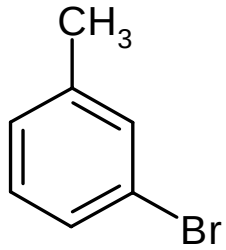
KNH_2, NH_3, -33 °C



p-methylaniline +

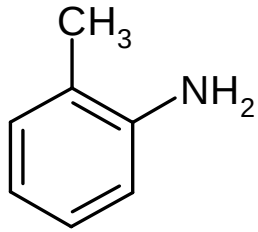


m-methylaniline

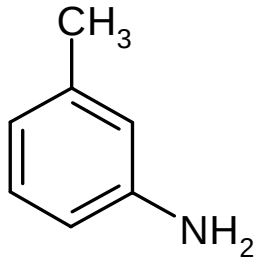


m-bromotoluene

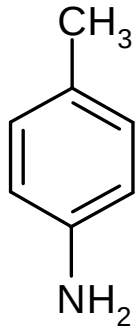
KNH_2, NH_3, -33 °C



o-methylaniline +



m-methylaniline +

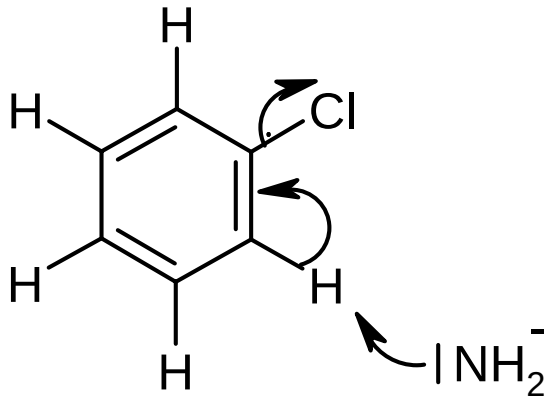


p-methylaniline

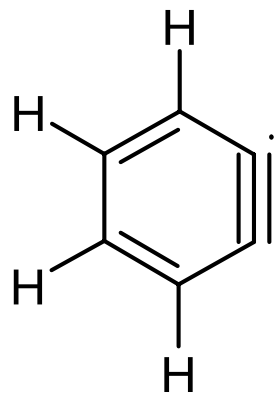
Organic Chemistry – chemistry of aromatics

S_N on aromatic skeleton – addition-elimination mechanism

1. step - elimination:

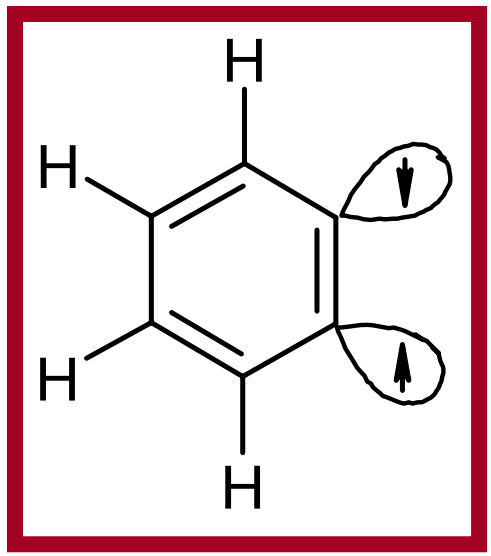


chlorobenzene

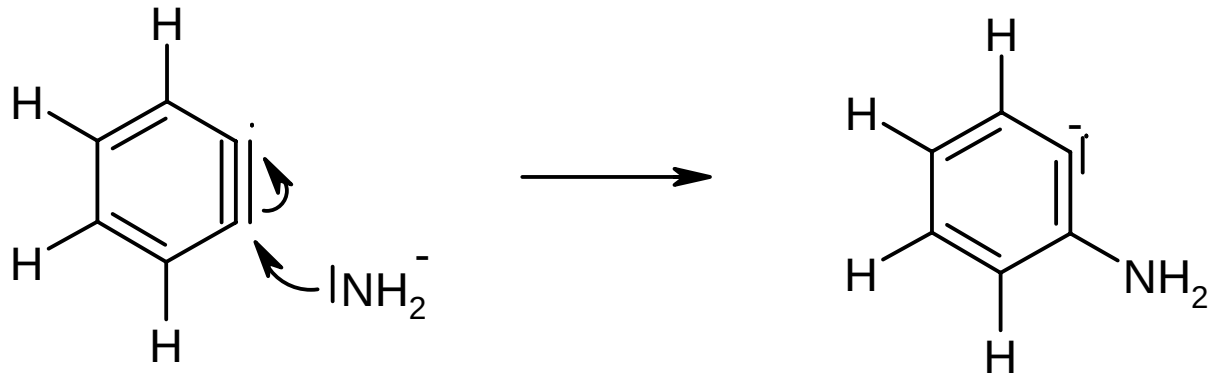


benzyne

+ NH_3 + Cl^-

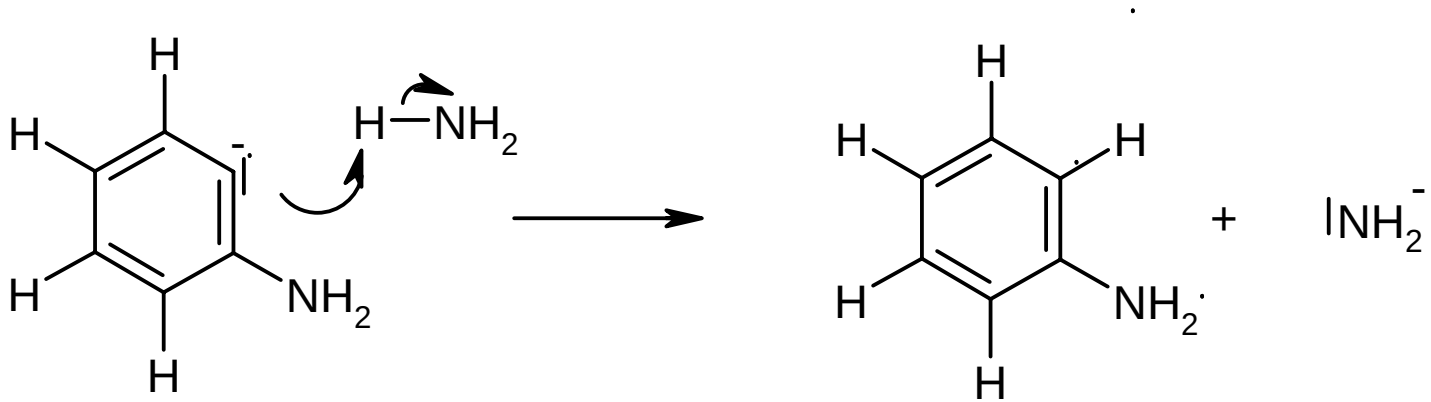


2. step - addition amide anion:



benzyne aryl anion

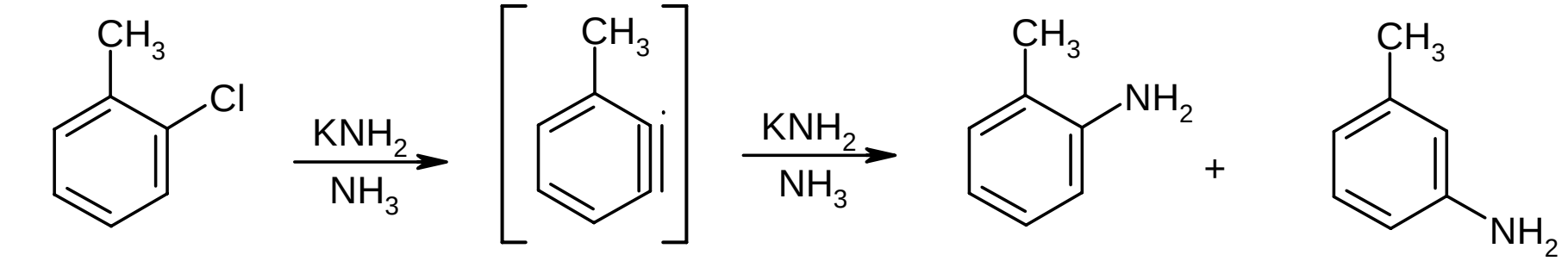
3. step - protonation:



aryl anion aniline

Organic Chemistry – chemistry of aromatics

S_N on aromatic skeleton – addition-elimination mechanism



o-chlorotoluene 3-methylbenzyne *o*-methylaniline *m*-methylaniline