كلية العلوم التطبيقية
Faculty of Applied Sciences

قسم الكيمياء
Department of Chemistry

Polycyclic Aromatic hydrocarbons

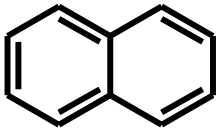
Chapter 9

COURSE NAME: Chemistry of Aromatic Compounds
COURSE CODE: 4022142-3

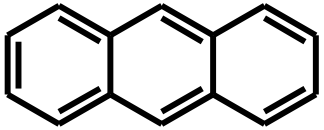
By the end of this chapter, you should understand:

1. The methods of synthesis of the main fused aromatic systems.
2. Electrophilic attack on naphthalene, anthracene and phenanthrene.
3. The oxidation of these polycycles.

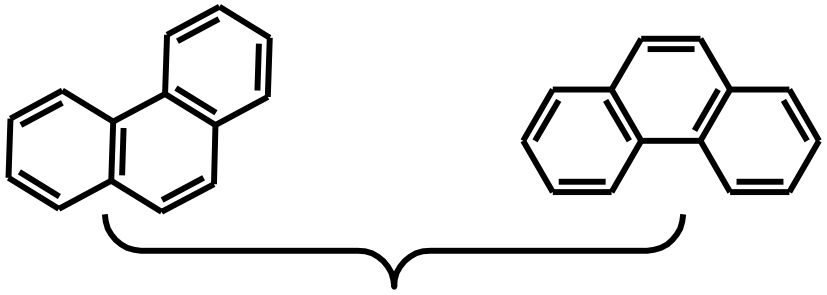
Polynuclear



Naphthalene

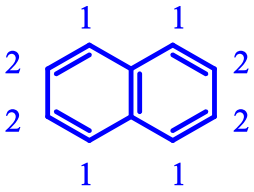


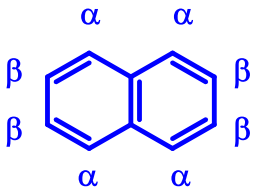
Anthracene



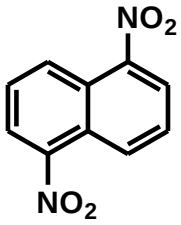
Phenanthrene

Naphthalene

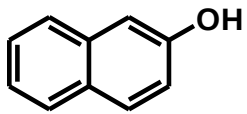




Nomenclature

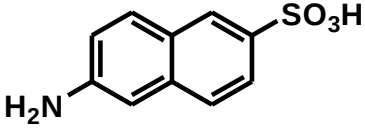


1,5-Dinitronaphthalene

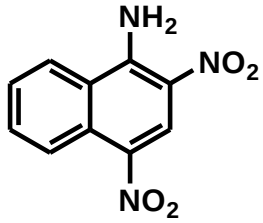


2-Naphthol

β-Naphthol

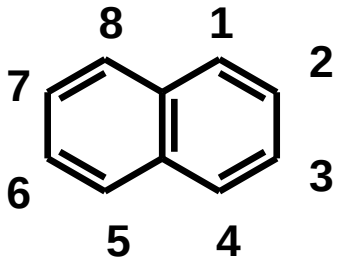


6-Amino-2-naphthalenesulphonic acid



2,4-Dinitro-1-naphthylamine

Structure of naphthalene

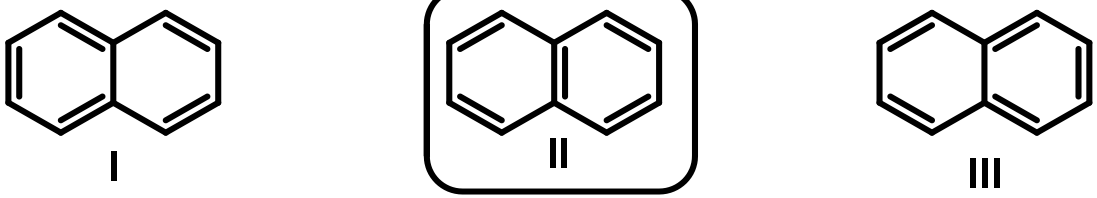


1) MF: $C_{10}H_8$

2) Planer molecule with high degree of unsaturation

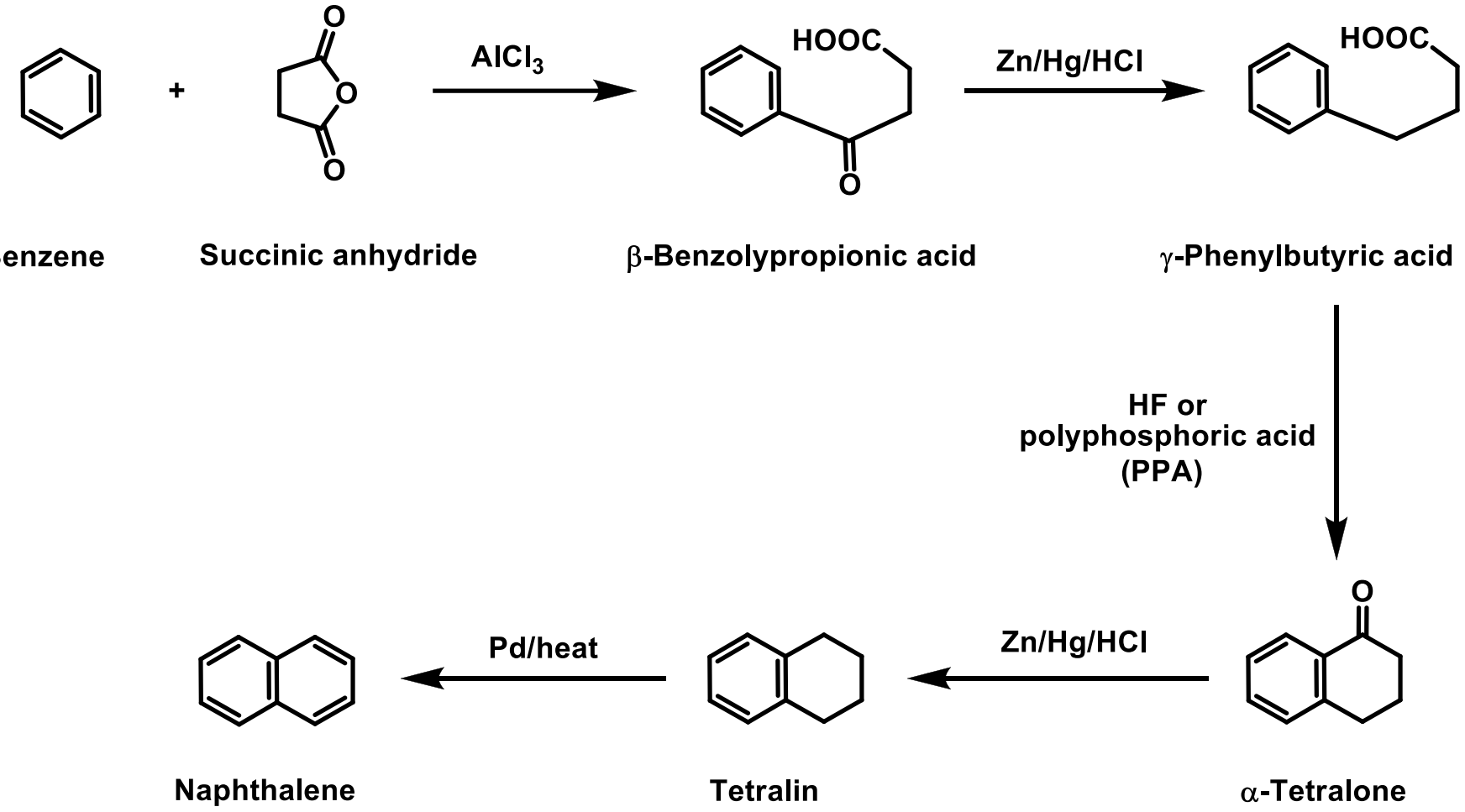
3) It resists the addition reactions and undergoes electrophilic substitution reactions easily.

4) X-ray proved that C1-C2, C3-C4, C5-C6 and C7-C8 are double bonds



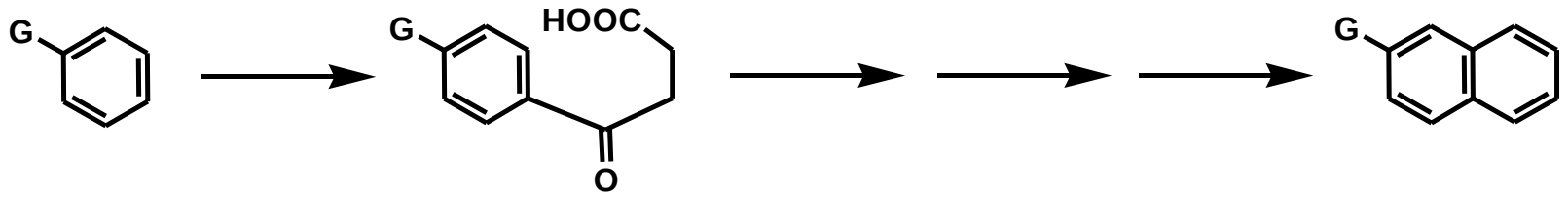
Haworth synthesis of naphthalene derivatives

Haworth synthesis of naphthalene



Synthesis of substituted naphthalene

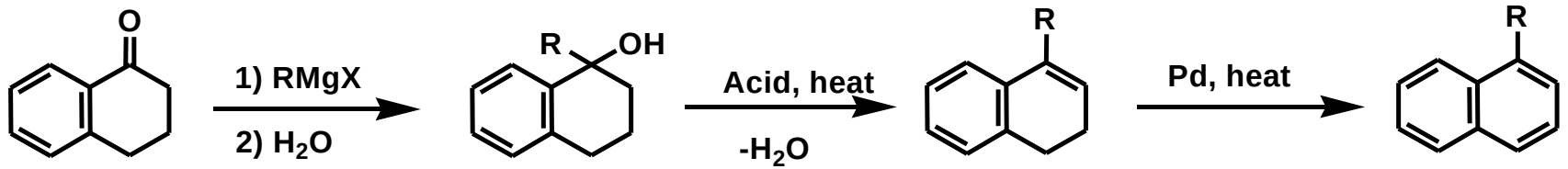
a) Synthesis of β-substituted naphthalene



G = -R, -X, -OCH_3

β-Substituted naphthalene

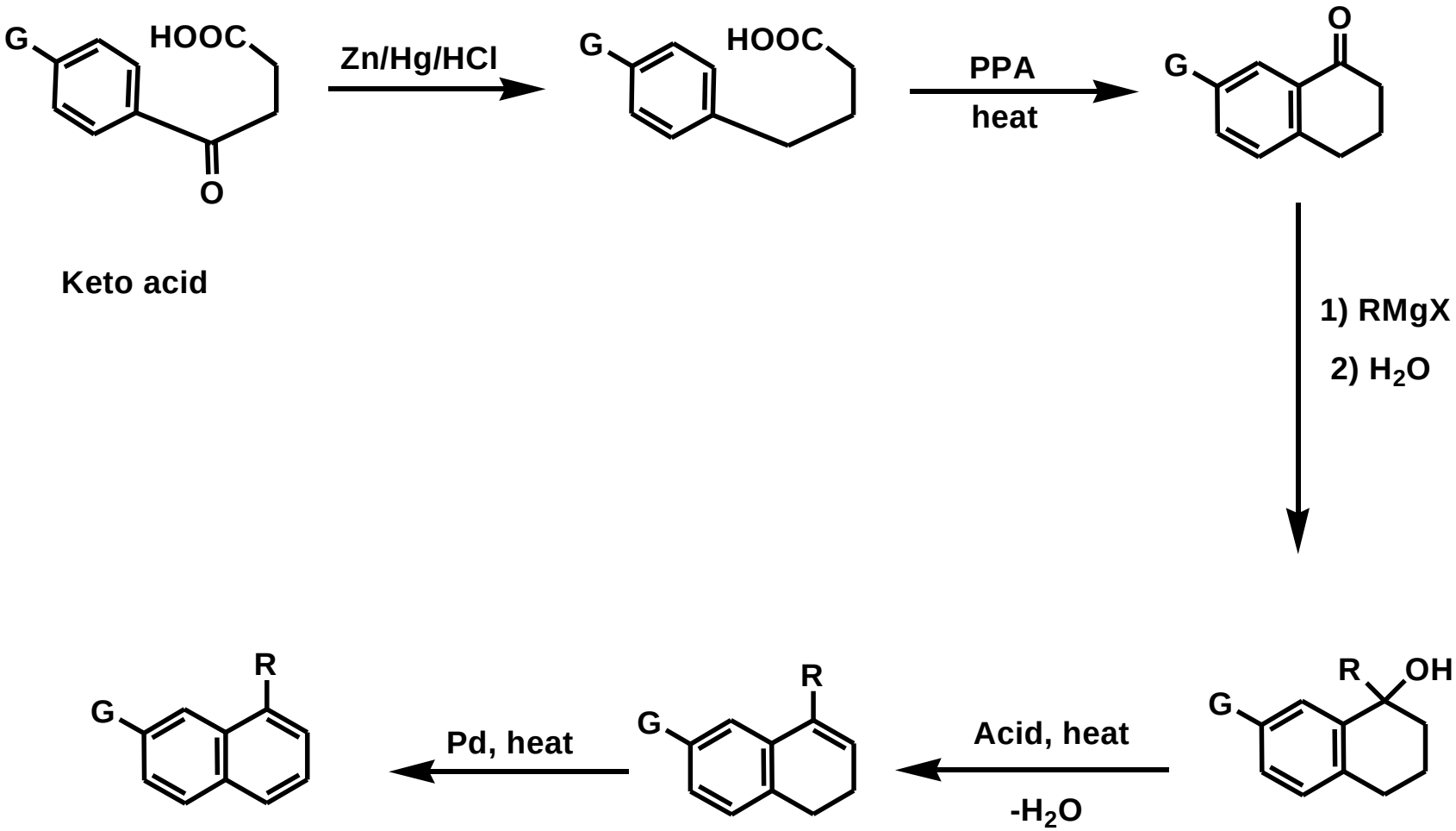
b) Synthesis of α-substituted naphthalene



α-Tetralone

α-Substituted naphthalene

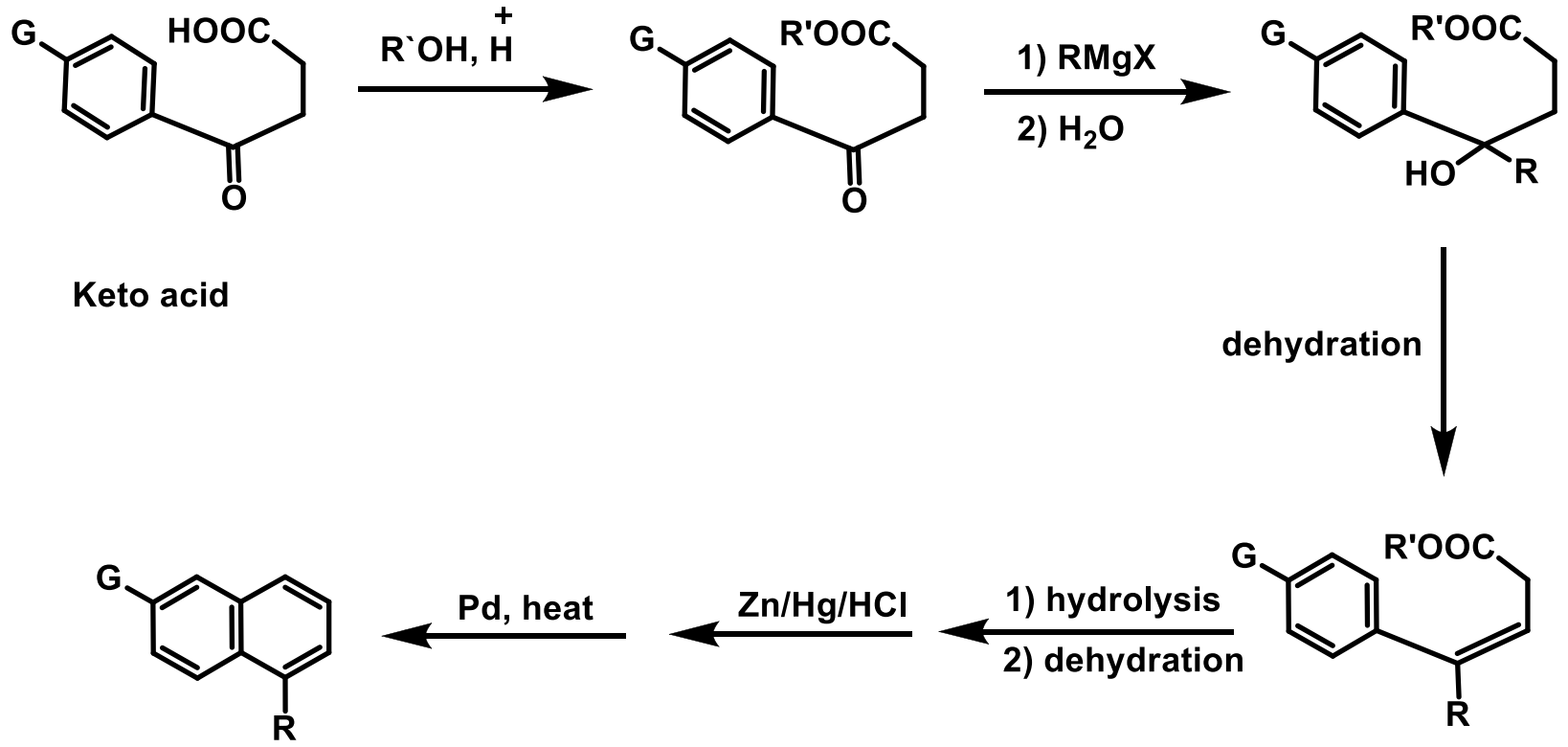
c) Synthesis of 1,7-disubstituted naphthalene



Keto acid

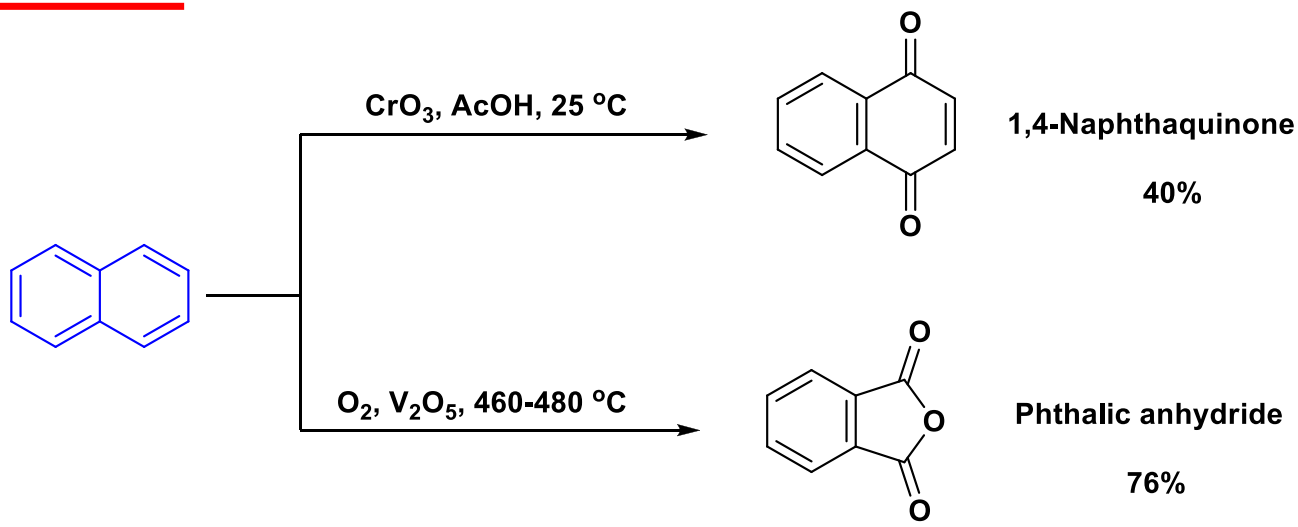
1,7-disubstituted naphthalene

d) Synthesis of 1,6-disubstituted naphthalene

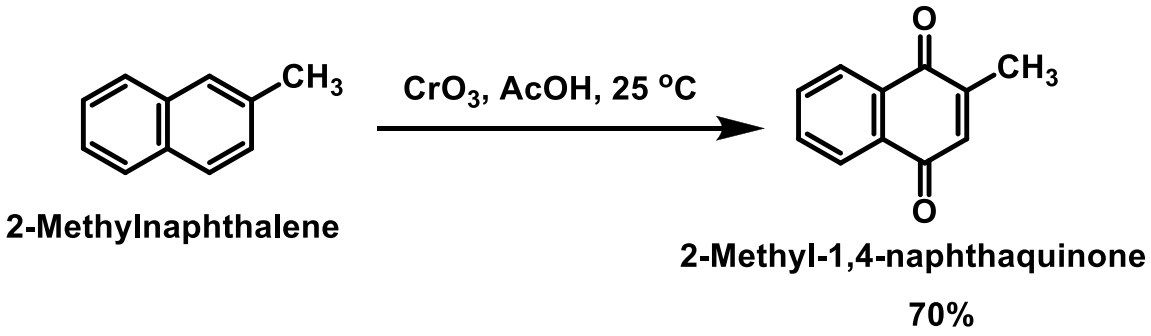


Reactions of naphthalene

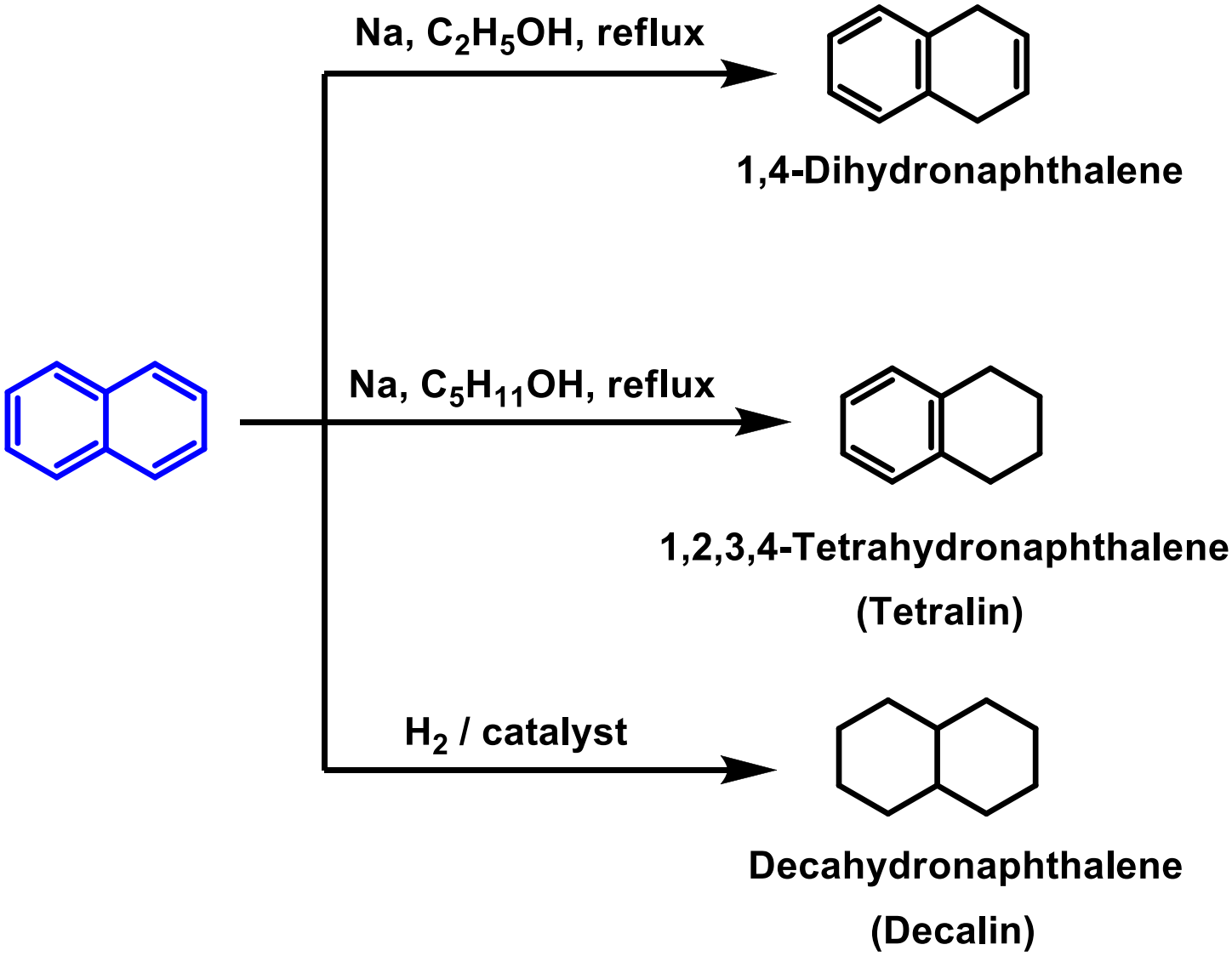
1) Oxidation



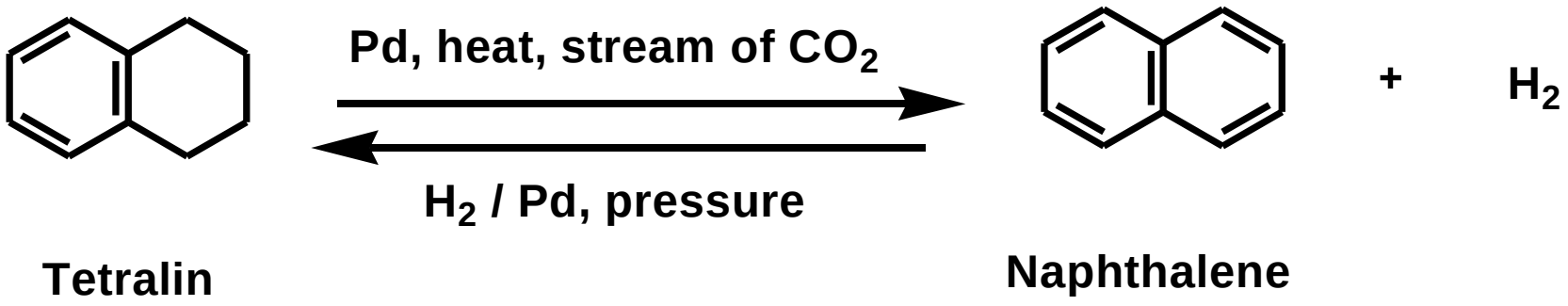
For naphthalene derivatives with electron donating group, the oxidation taking place in the same ring carrying such kind of substituent.



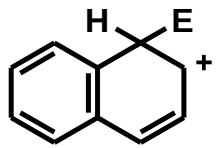
2) Reduction of naphthalene



3) Dehydrogenation of hydroaromatic compounds (Aromatization)

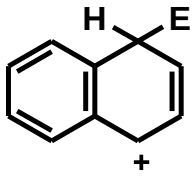


Orientation of electrophilic substitution in naphthalene



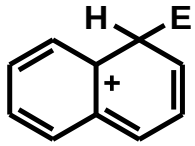
(I)

More stable:
aromatic sixtet
presented



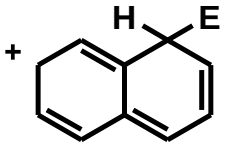
(II)

More stable:
aromatic sixtet
presented



(III)

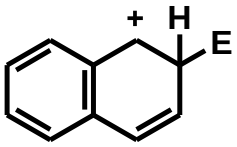
Less stable:
aromatic sisxtet
disrupted



(IV)

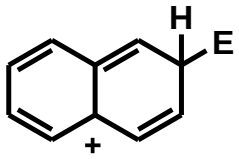
Less stable:
aromatic sisxtet
disrupted

Alpha
attack



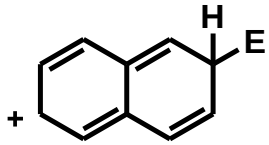
(I)

More stable:
aromatic sixtet
presented



(II)

Less stable:
aromatic sisxtet
disrupted

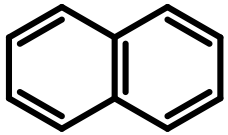


(III)

Less stable:
aromatic sisxtet
disrupted

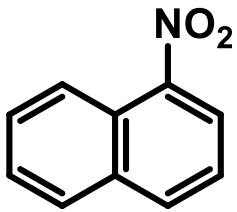
Beta
attack

4) Nitration and halogenation of naphthalene



Naphthalene

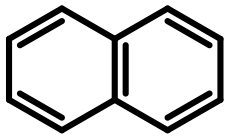
HNO_3, H_2SO_4, 50-60 °C



90-95%

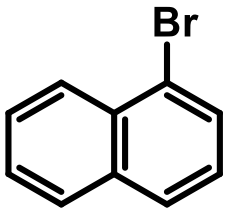
1-Nitronaphthalene

α-Nitronaphthalene



Naphthalene

Br_2, CCl_4, reflux

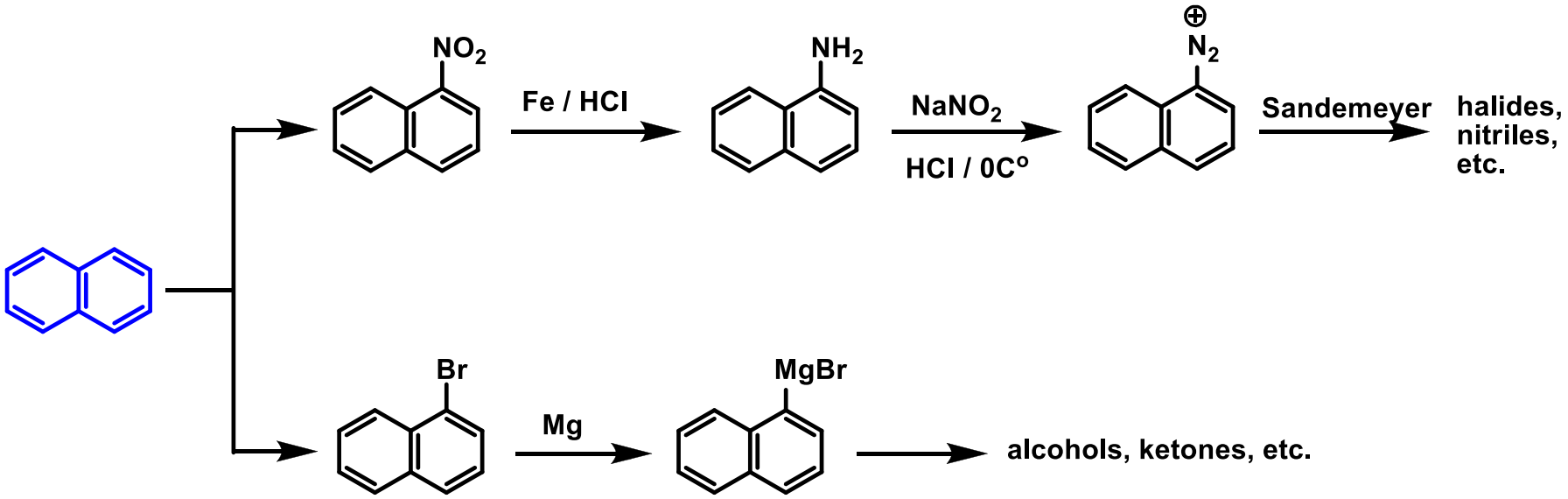


15%

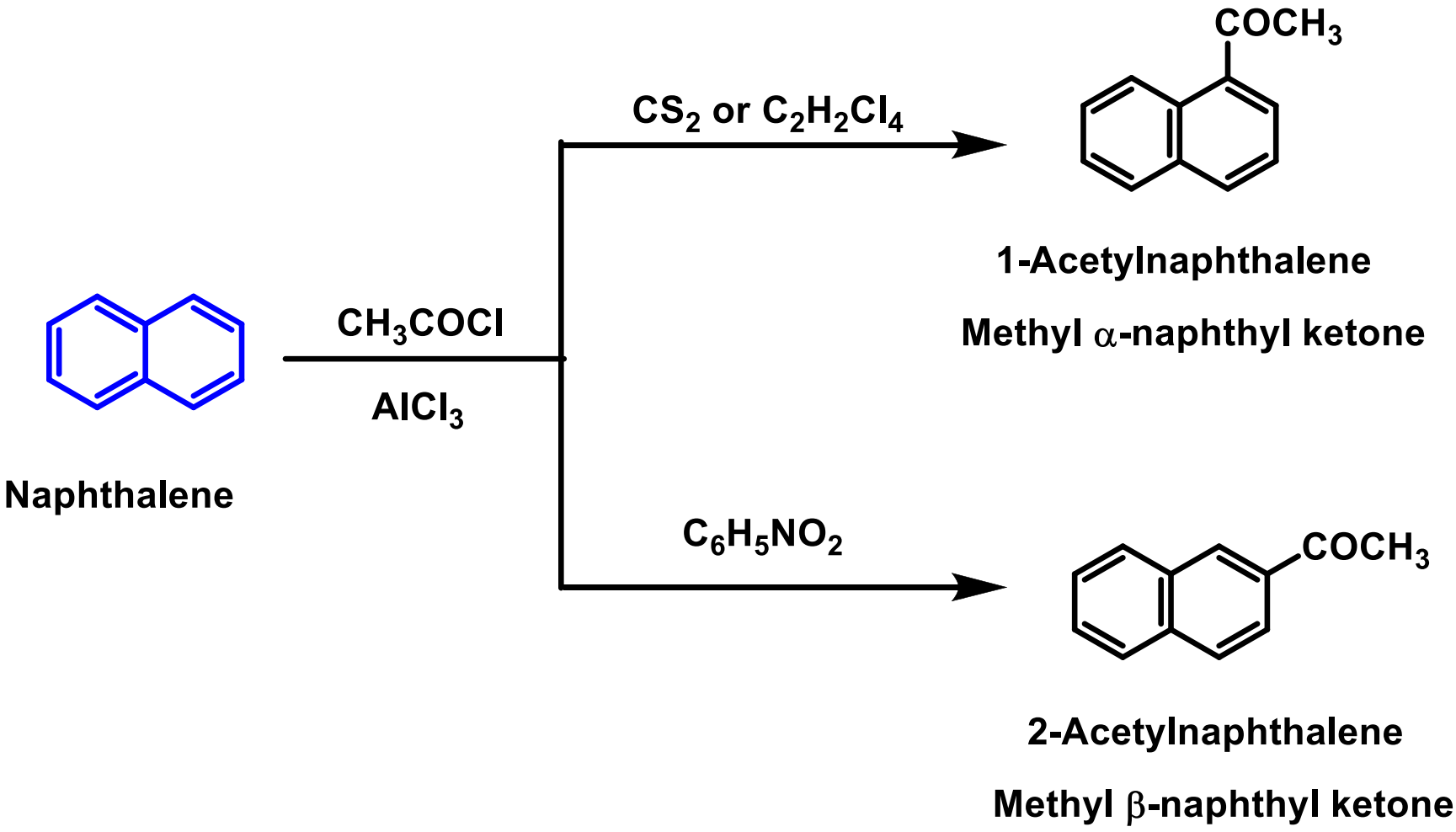
1-Bromonaphthalene

α-Bromonaphthalene

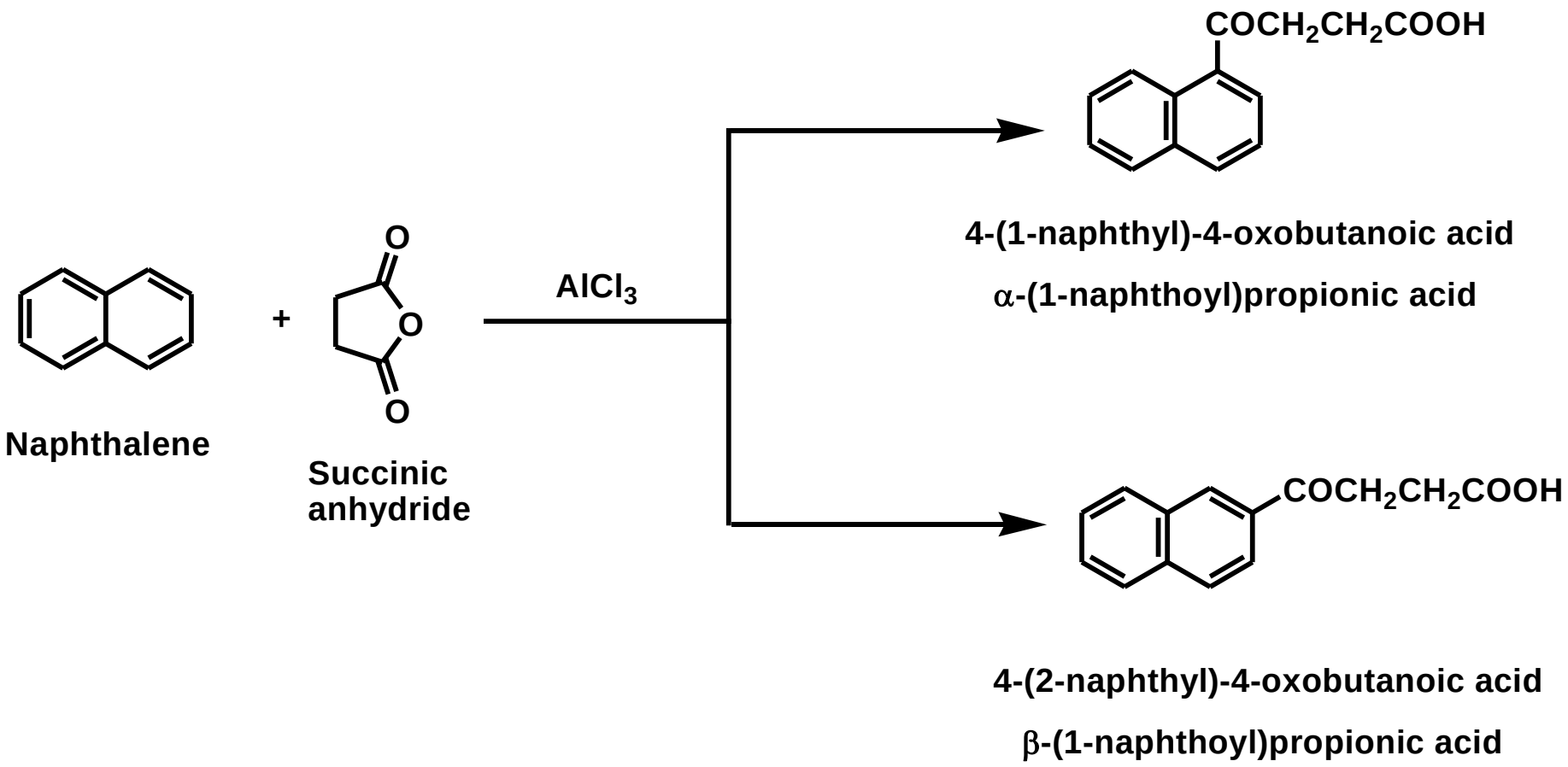
Utilities of nitro- and bromonaphthalene



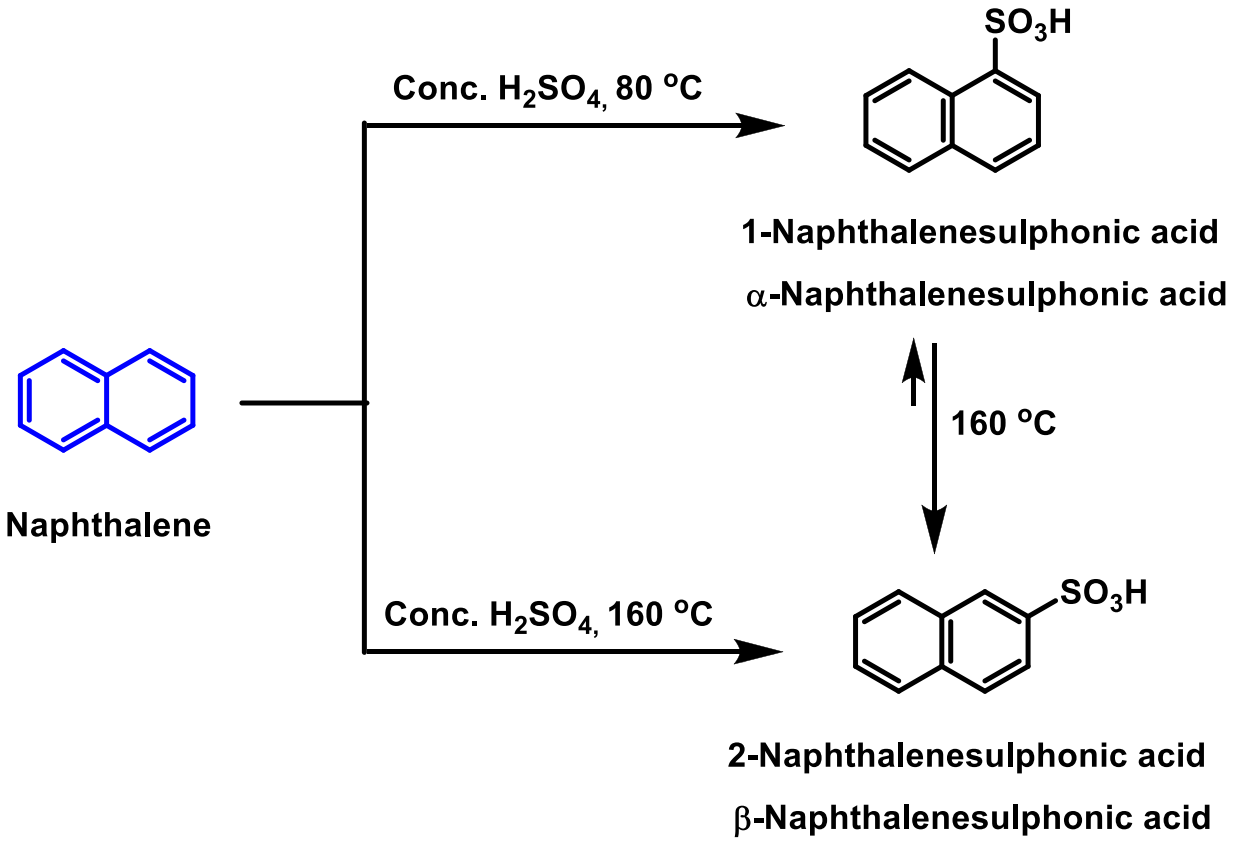
5) Friedel-Crafts acylation of naphthalene

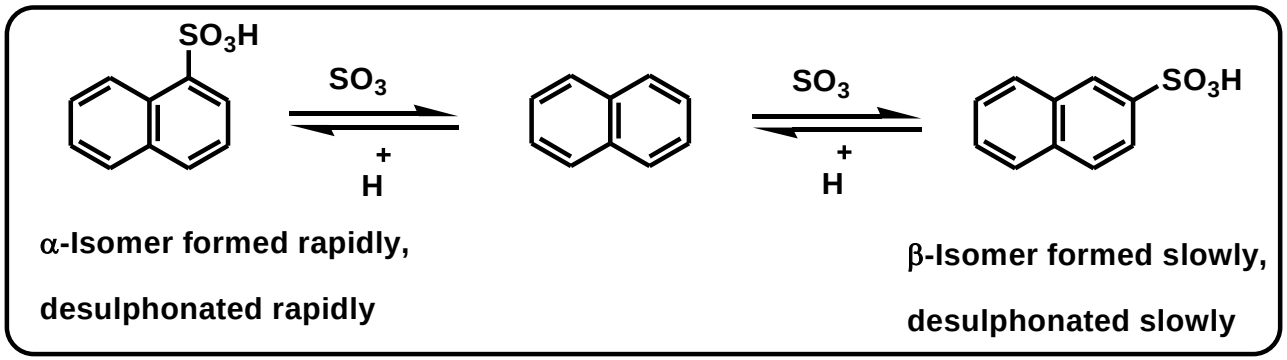


Acylation of naphthalene by succinic anhydride



6) Sulfonation of naphthalene

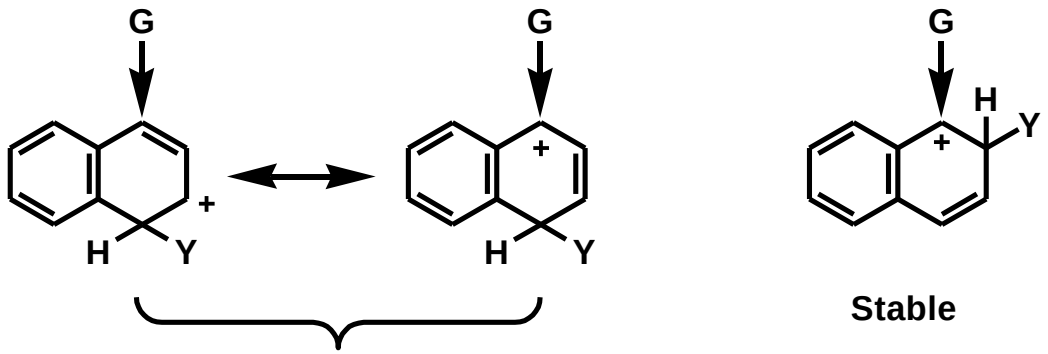




Orientation of electrophilic substitution in naphthalene derivatives

a) Electron releasing group will direct the coming substituent to the same ring (at ortho and para positions with respect to the first group)

i) In case of the electron releasing group is located at position 1 it will direct the second substituent to positions 2 and 4



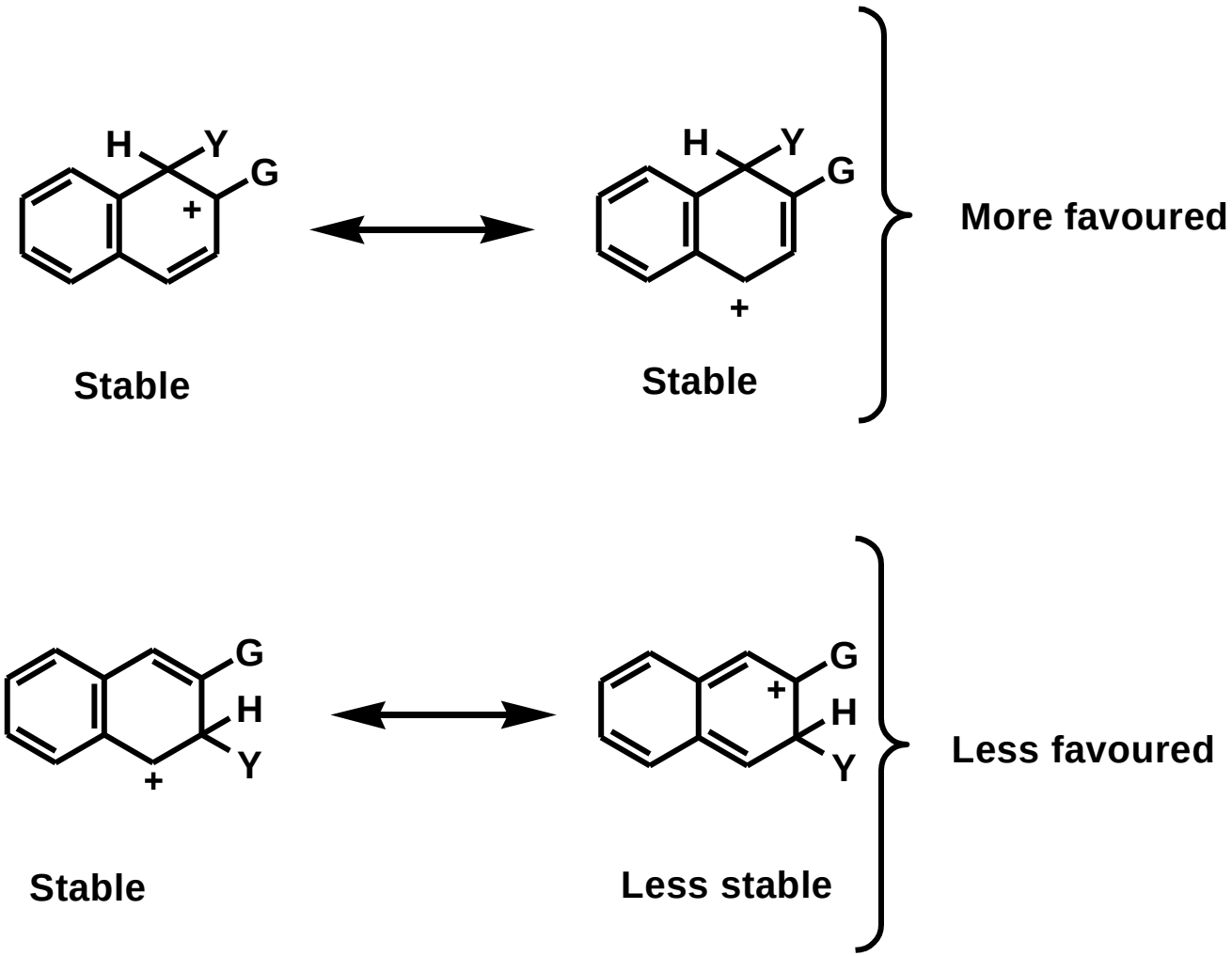
Stable

Y is directed to para (4) position

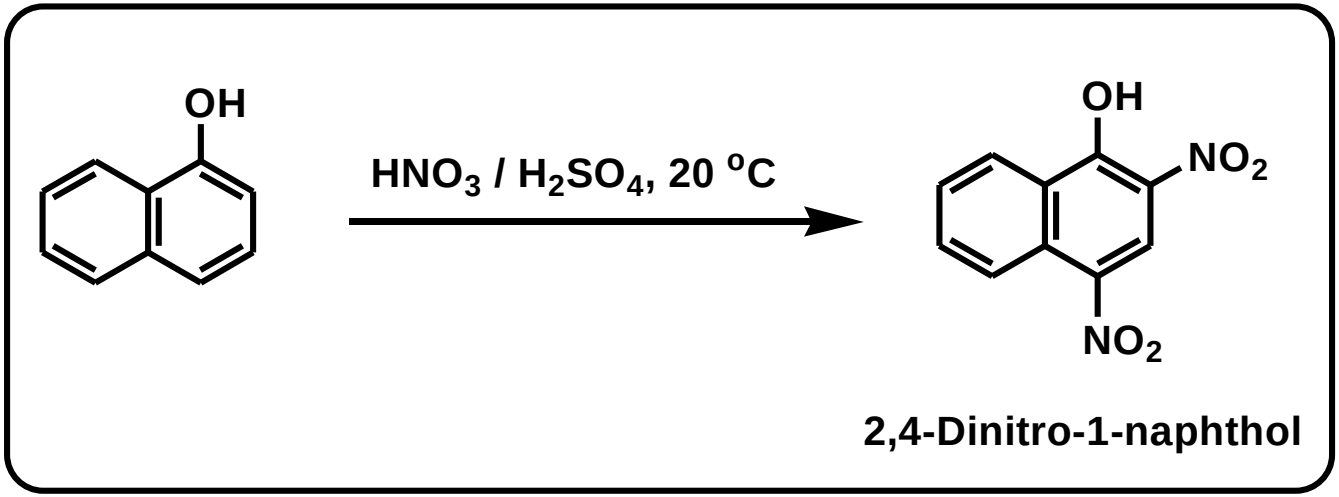
Stable

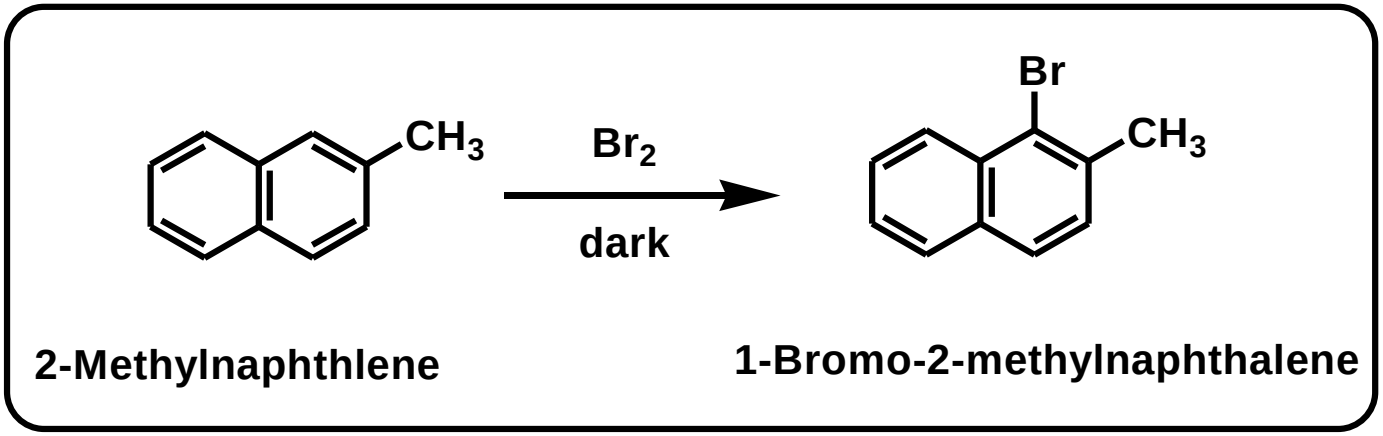
Y is directed to ortho (2) position

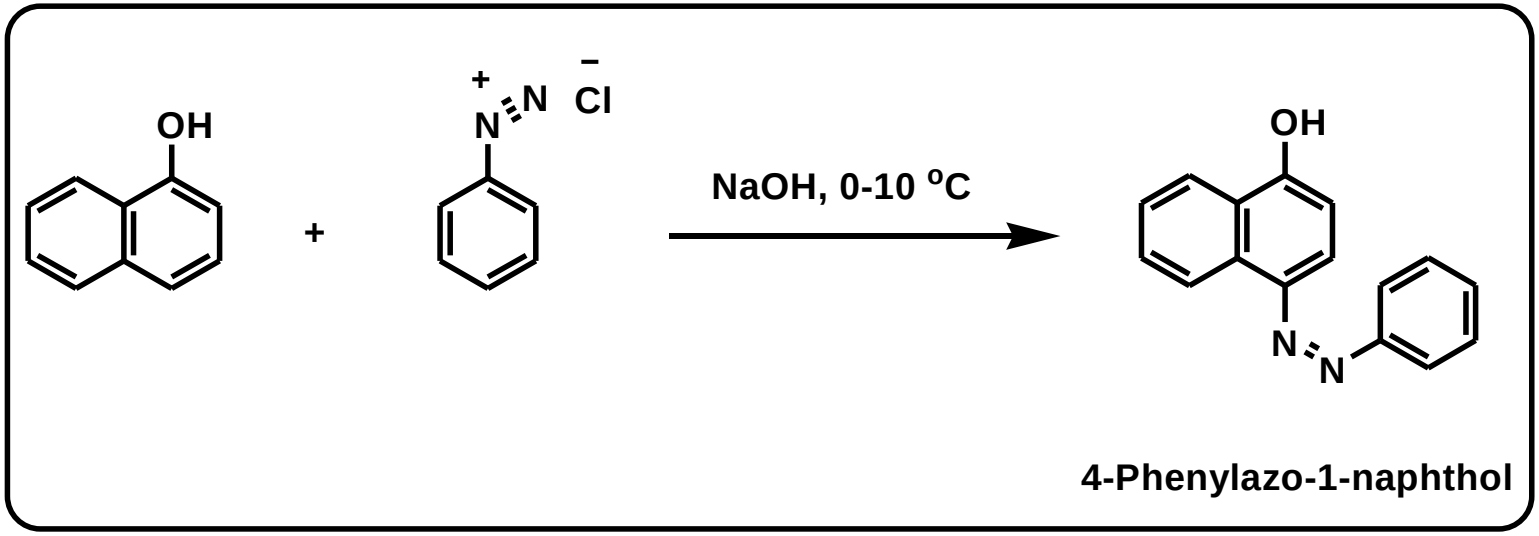
ii) In case of the electron releasing group is located at position 2, it will direct the second substituent to positions 1 only

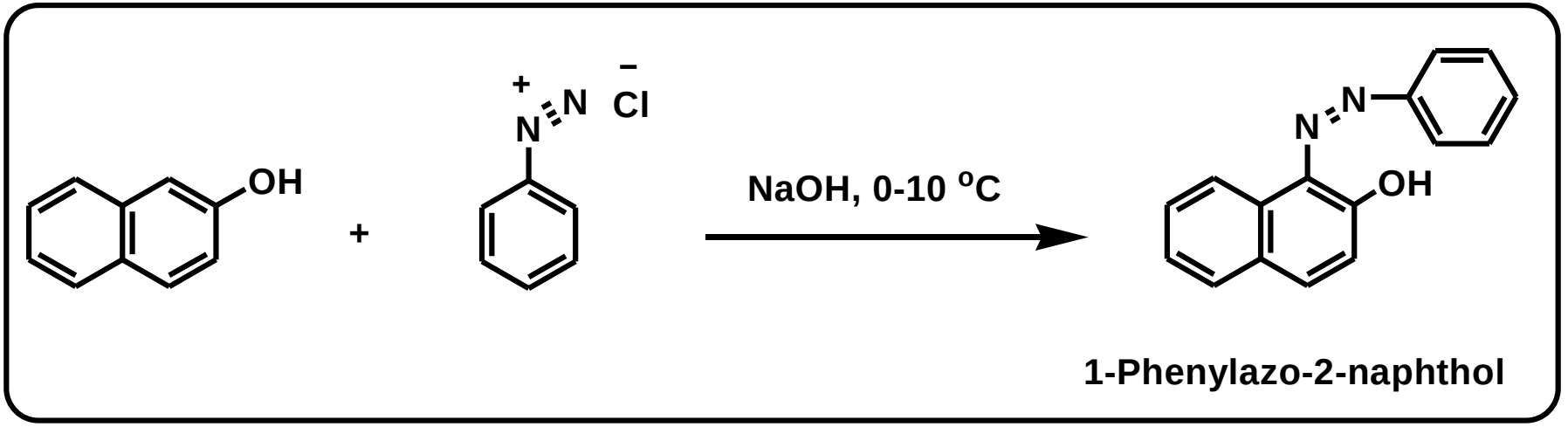


Examples

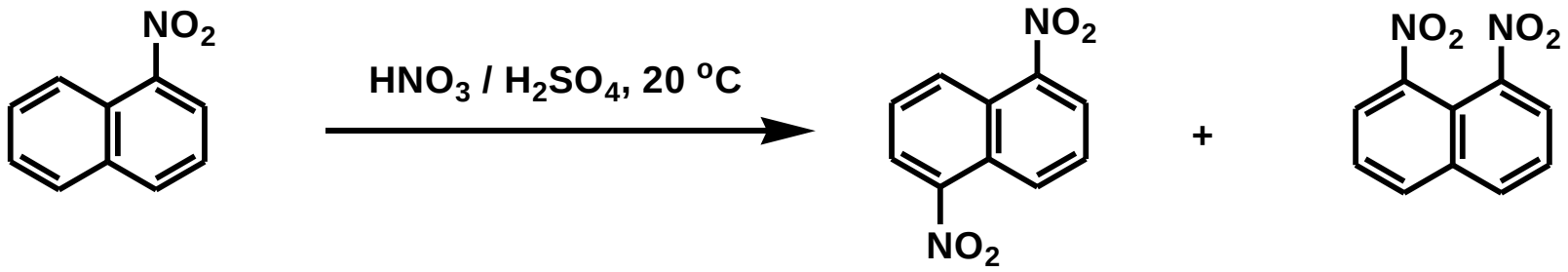

OH
HNO3 / H2SO4, 20 oC
OH
NO2
NO2
2,4-Dinitro-1-naphthol


CH3
Br2
dark
Br
CH3
2-Methylnaphthlene
1-Bromo-2-methylnaphthalene


OH
+
N
N
Cl
NaOH, 0-10 °C
OH
N
N
4-Phenylazo-1-naphthol


OH
+
N
N
Cl
NaOH, 0-10 °C
N
N
OH
1-Phenylazo-2-naphthol

b) Electron with drawing group will direct the coming substituent to the second ring (at C5 and C8 positions)



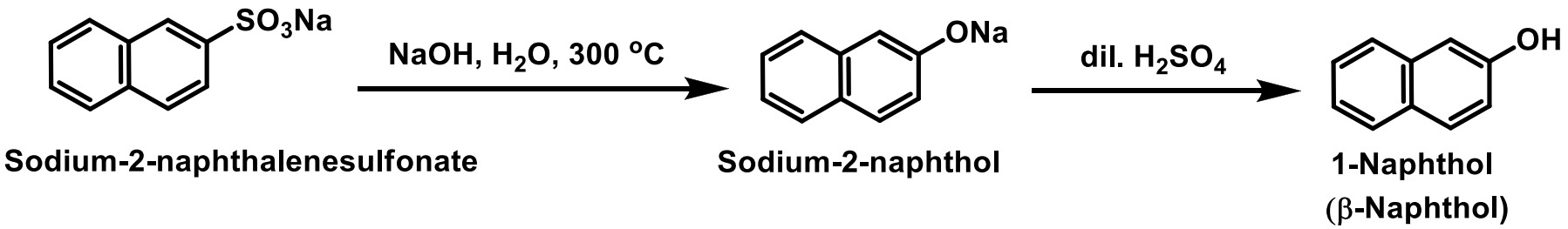
1-Nitronaphthlene

1,5-Dinitronaphthlene

1,8-Dinitronaphthlene

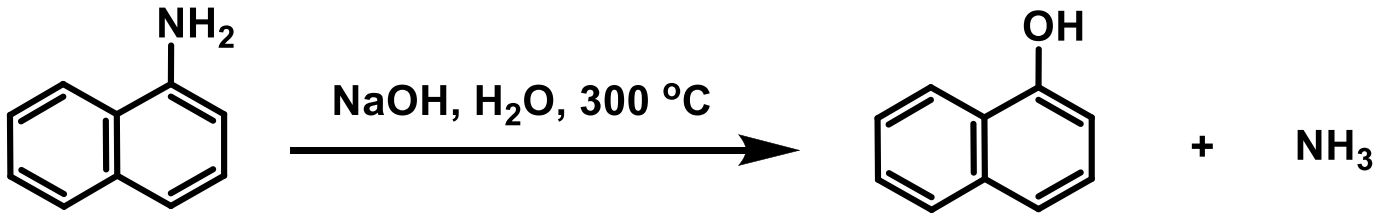
Naphthols

β-Naphthol



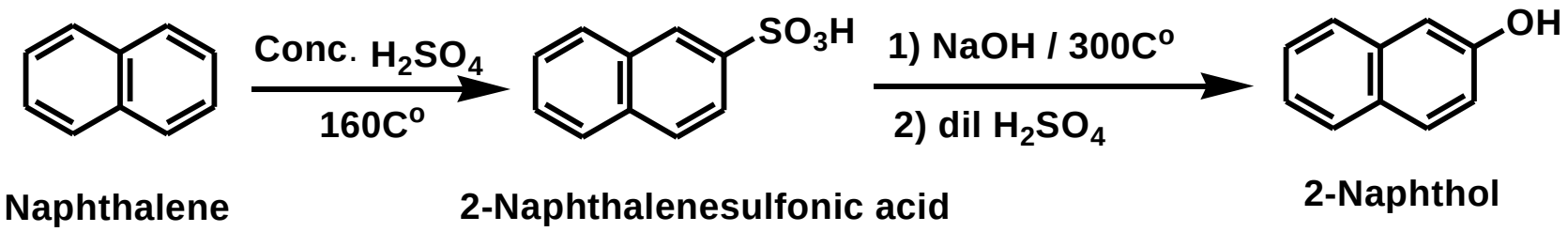
Sodium-2-naphthalenesulfonate → Sodium-2-naphthol → 1-Naphthol (β-Naphthol)

α-Naphthol



1-Naphthylamine → 1-Naphthol (α-Naphthol) + NH_3

Utilities of naphthols



Naphthalene

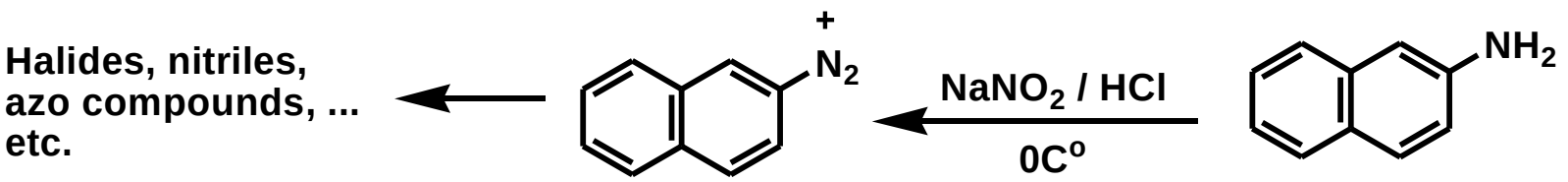
2-Naphthalenesulfonic acid

2-Naphthol

(Bucher reaction)

NH_3, $(NH_4)_2SO_4$

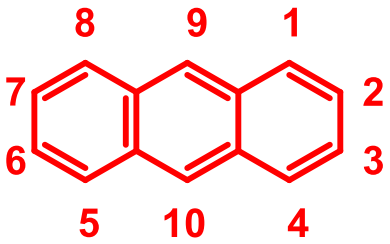
heat, pressure



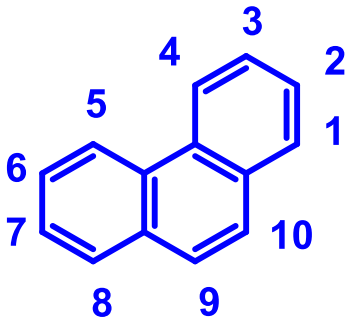
2-Naphthalenediazonium salt

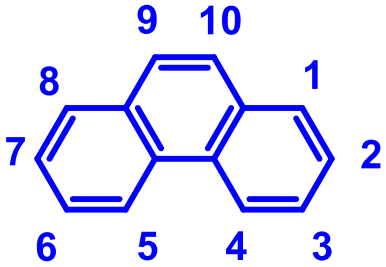
2-Naphthylamine

Anthracene and phenanthrene



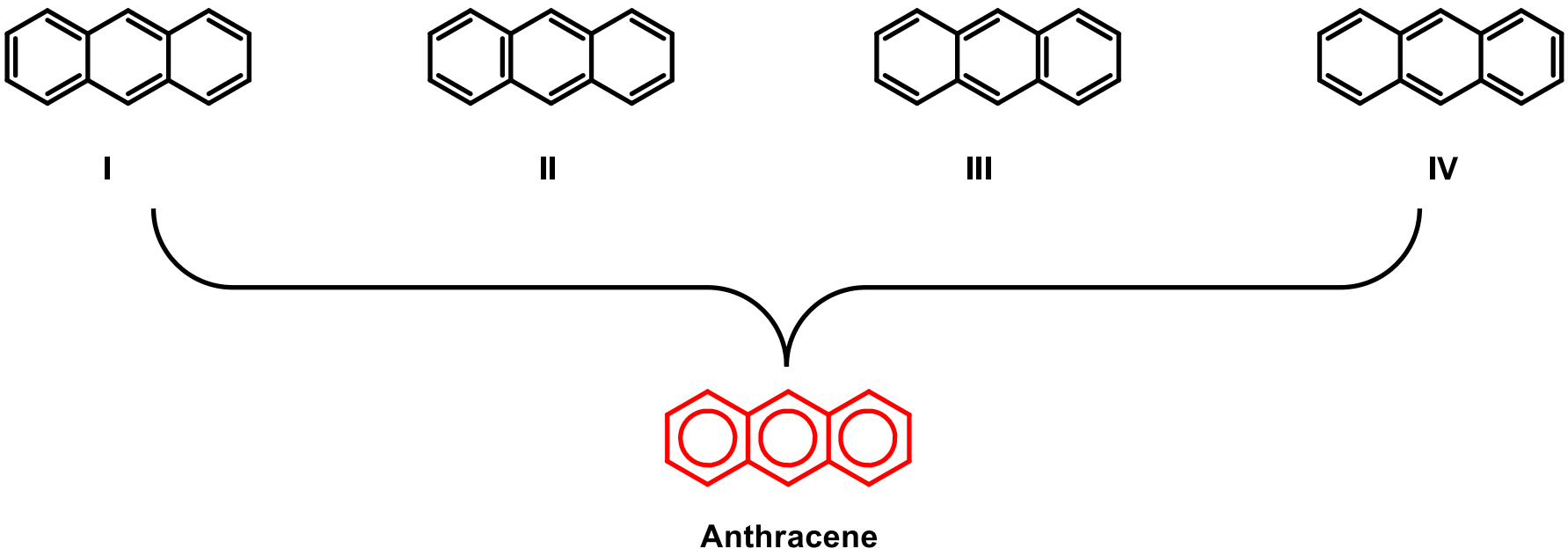
Anthracene



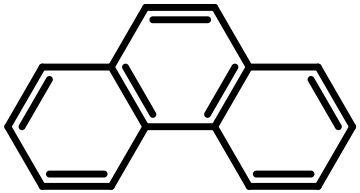


Phenanthrene

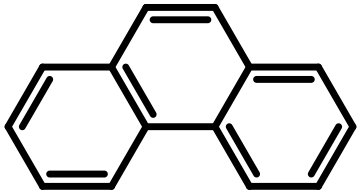
Structure of anthracene



Structure of phenanthrene



I



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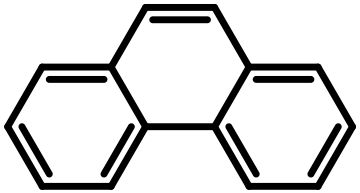

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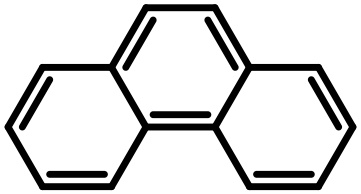

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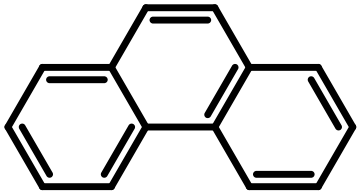

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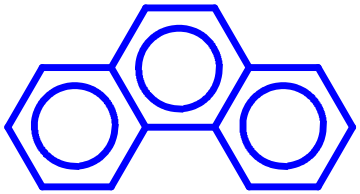
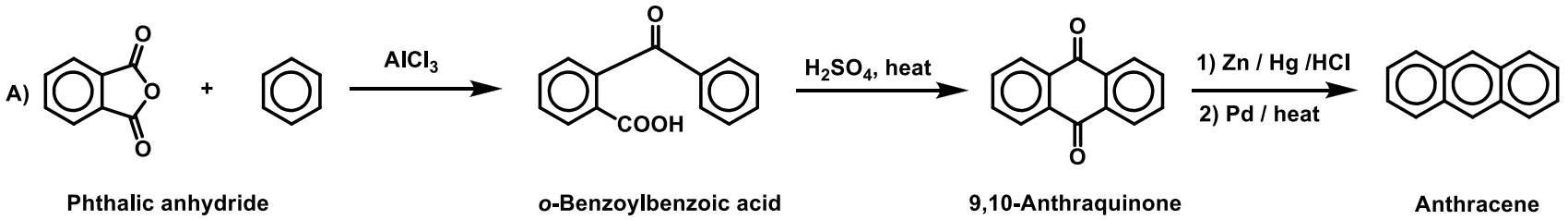
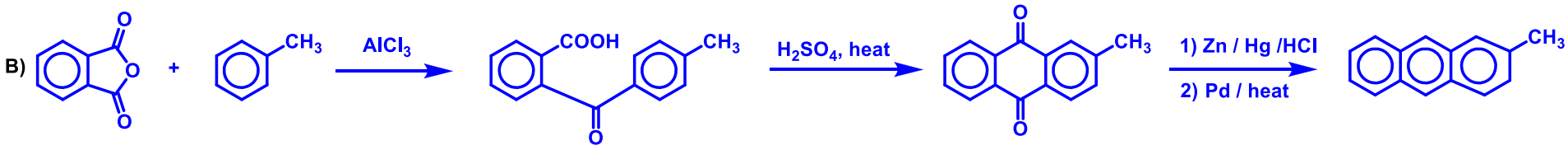


Phenanthrene

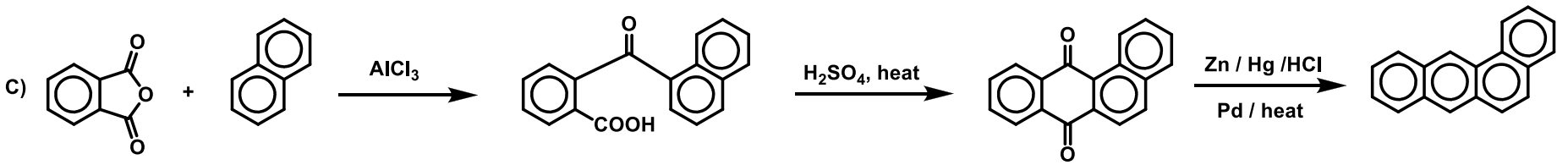
Preparation of anthracene derivatives



Phthalic anhydride | *o*-Benzoylbenzoic acid | 9,10-Anthraquinone | Anthracene

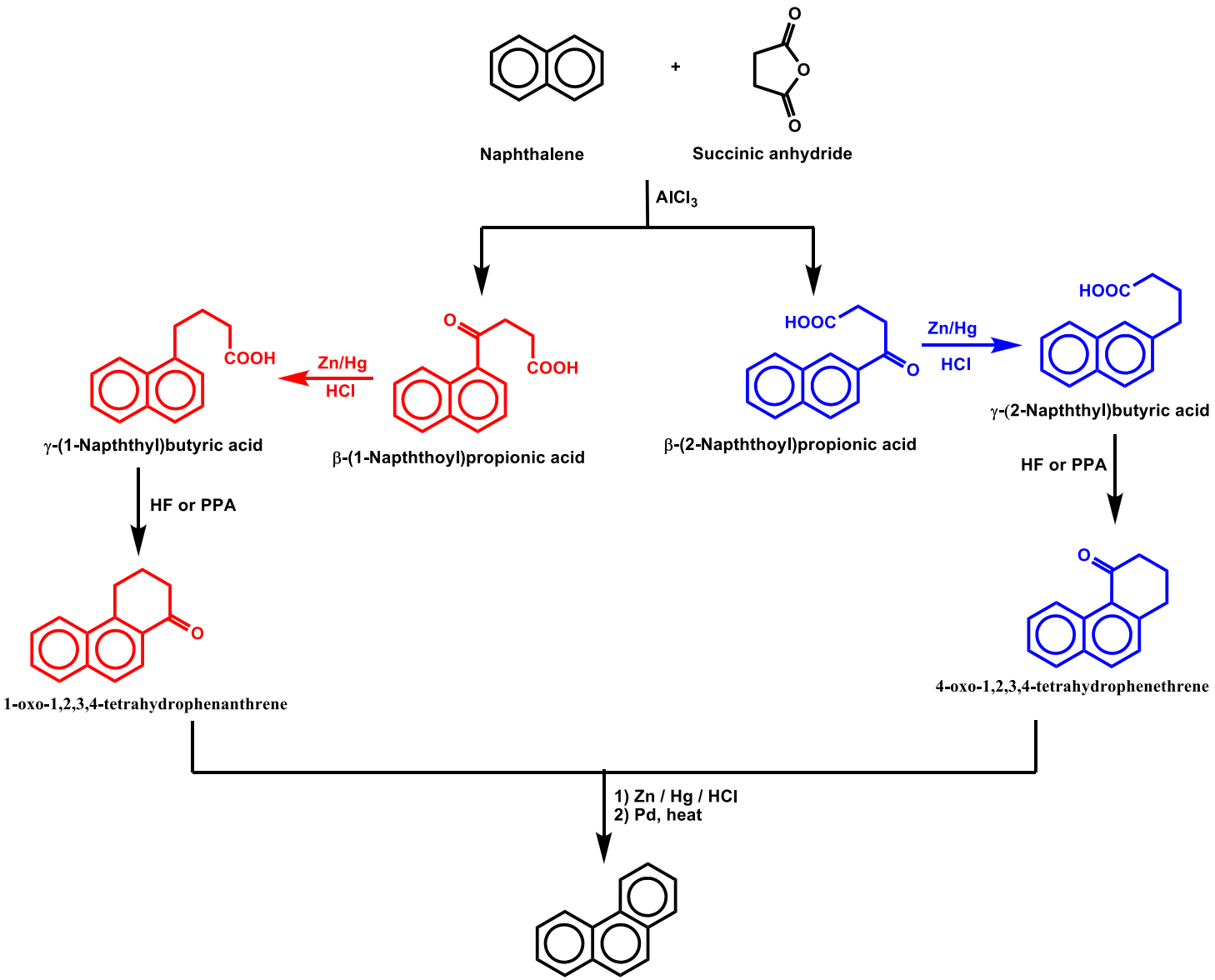


Phthalic anhydride | *o*-(4-methylbenzoyl)benzoic acid | 2-Methyl-9,10-anthraquinone | 2-Methylanthracene



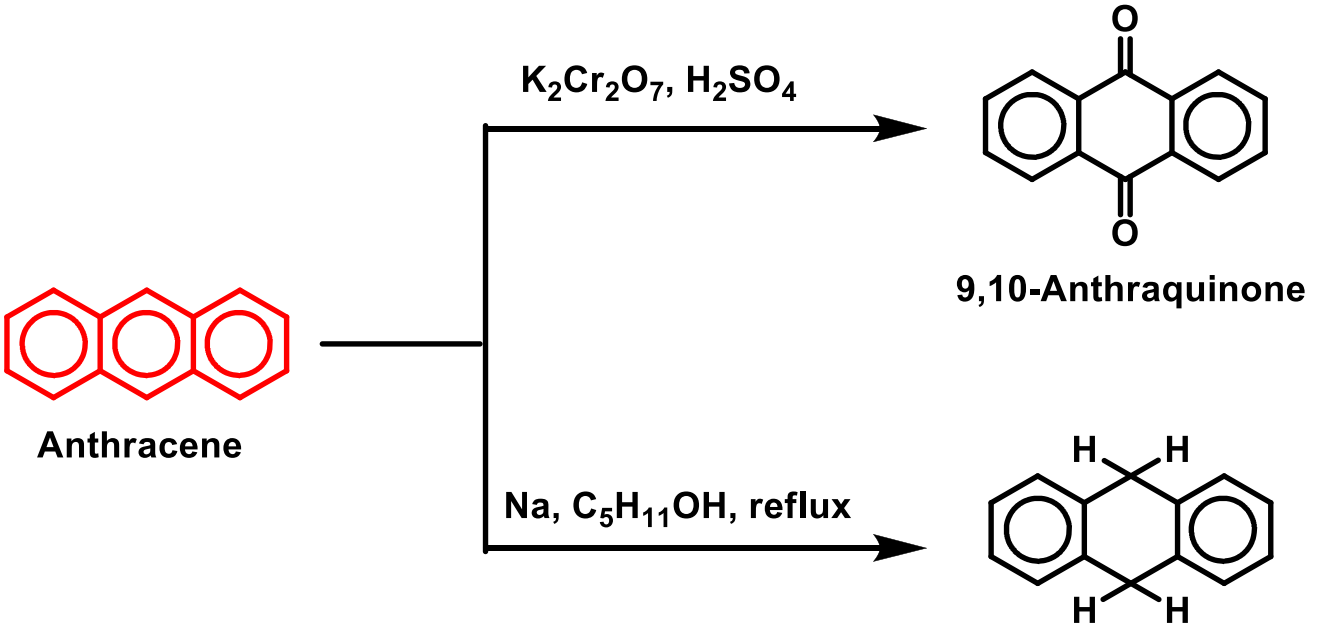
Phthalic anhdride | Naphthalene | *o*-(1-Naphthoyl)benzoic acid | 1,2-Benzo-9,10-anthraquinone | (1,2-Benzoanthracene) Tetraphene

Preparation of phenanthrene

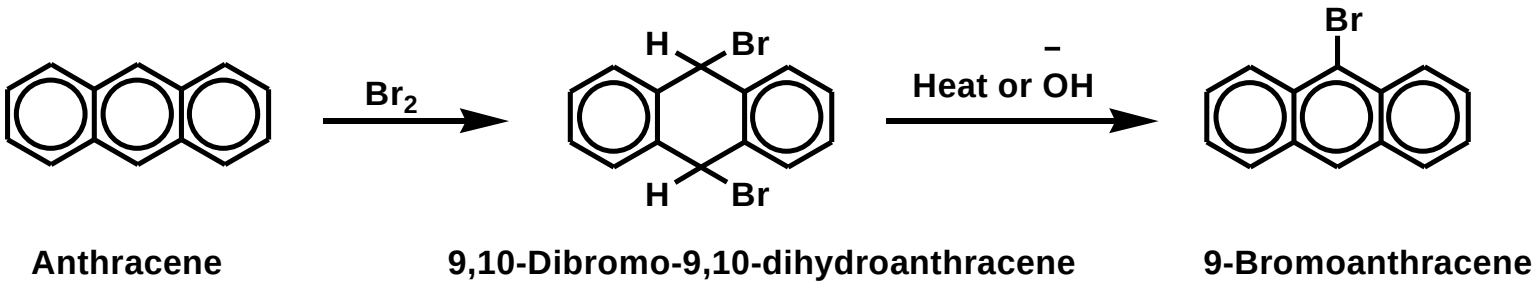


Reactions of anthracene

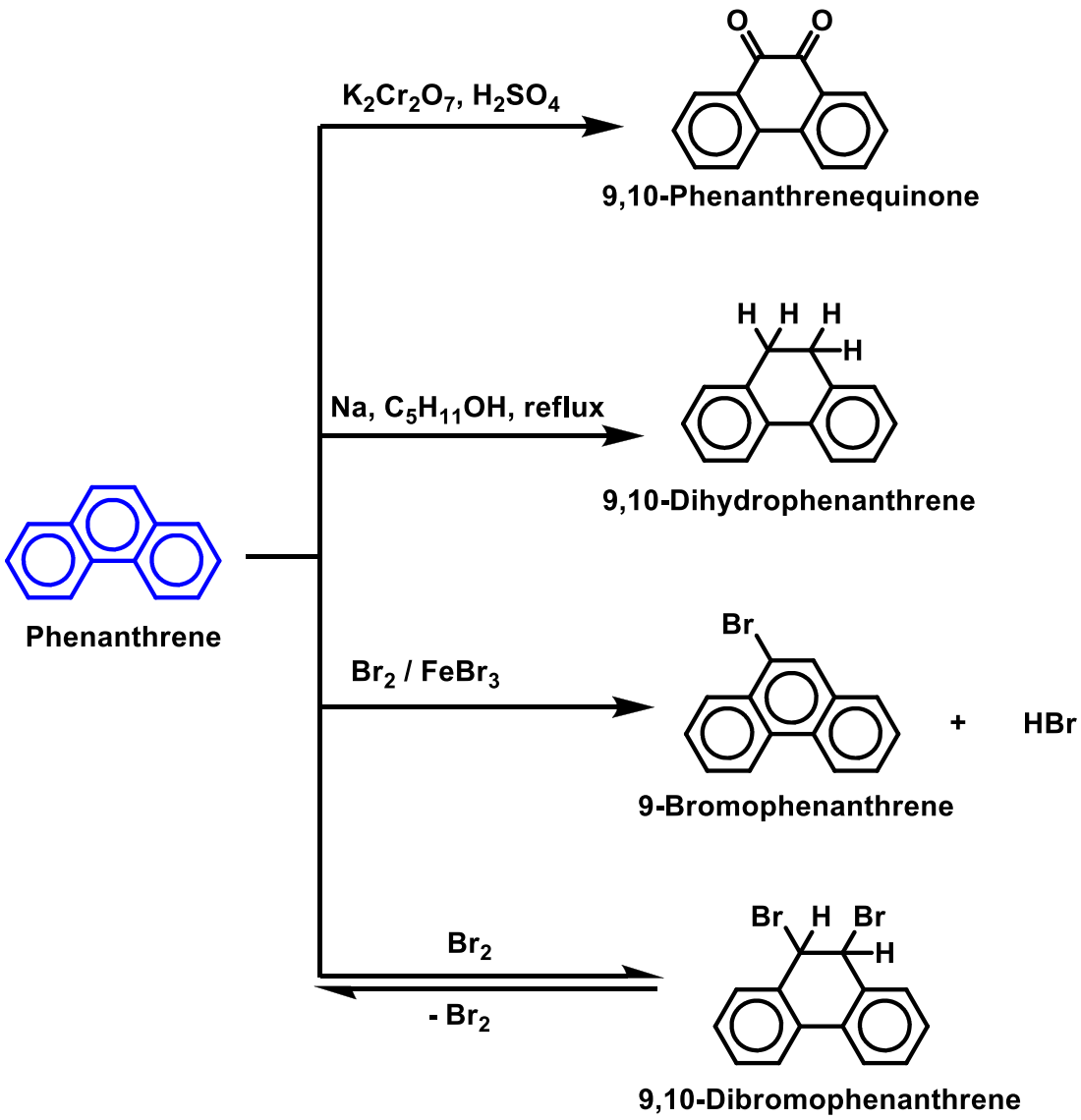
Oxidation



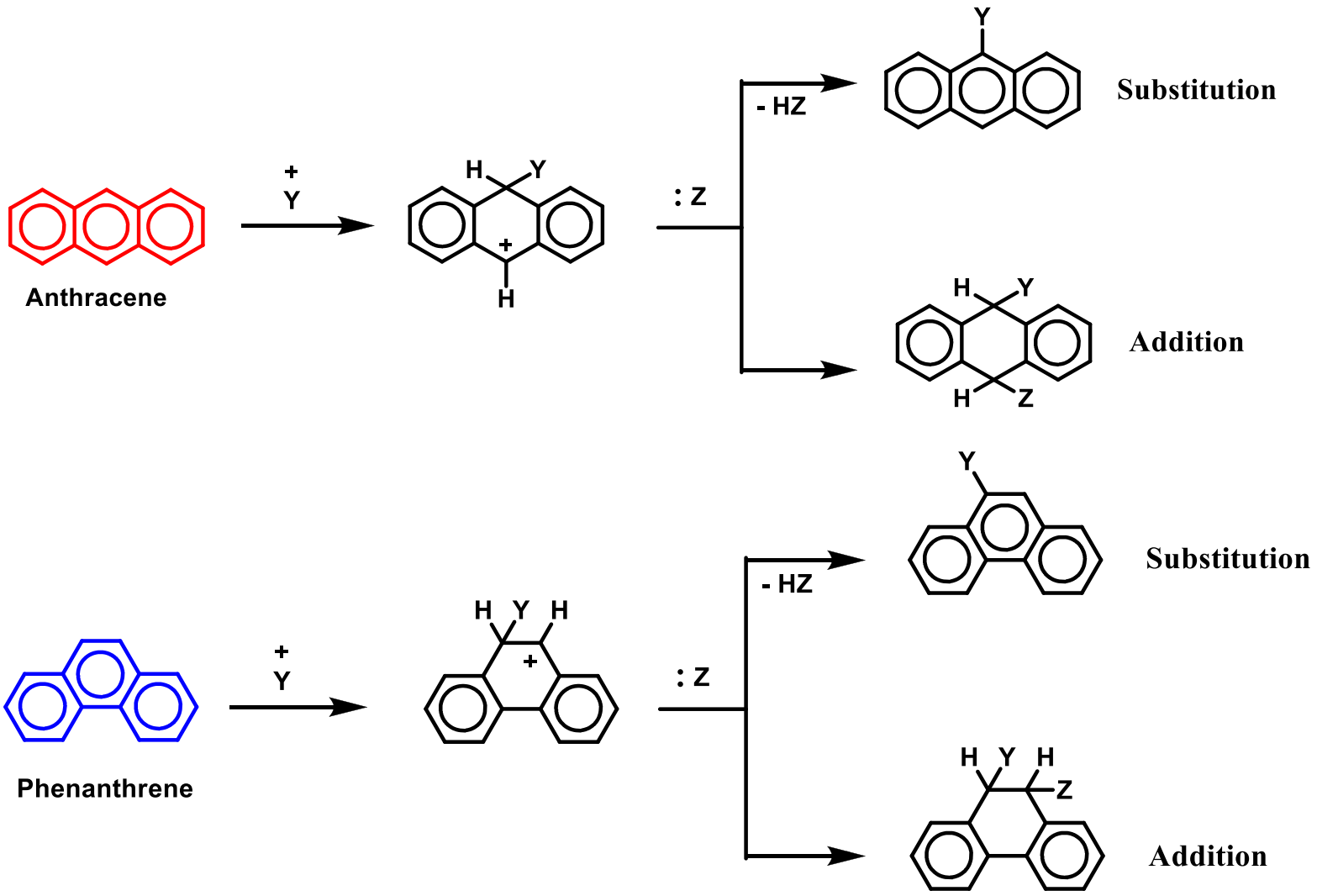
Bromination



Reactions of phenanthrene



The reactivity of 9- and 10-positions towards electrophilic attack



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2. J. McMurry. "*Organic Chemistry*", 9th Edition, Cengage Learning, 2015.