

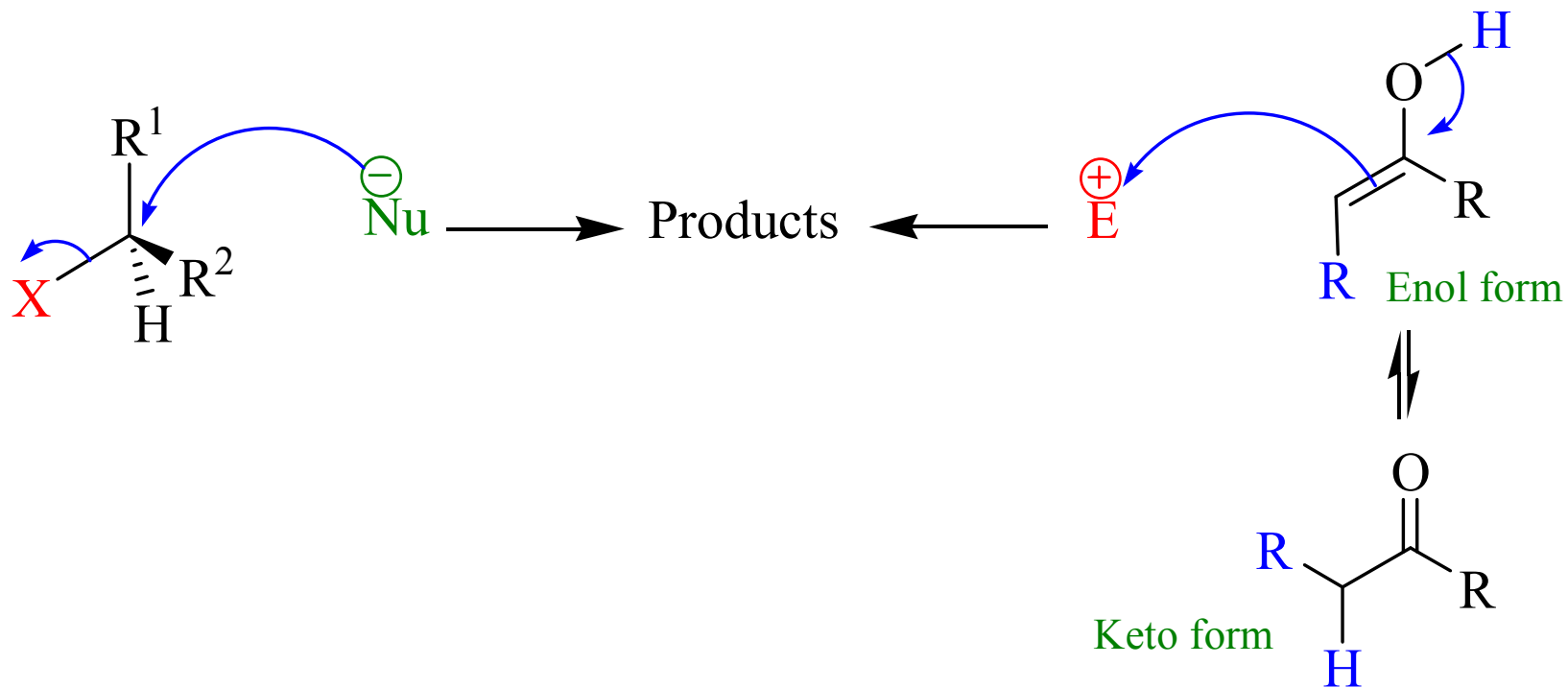
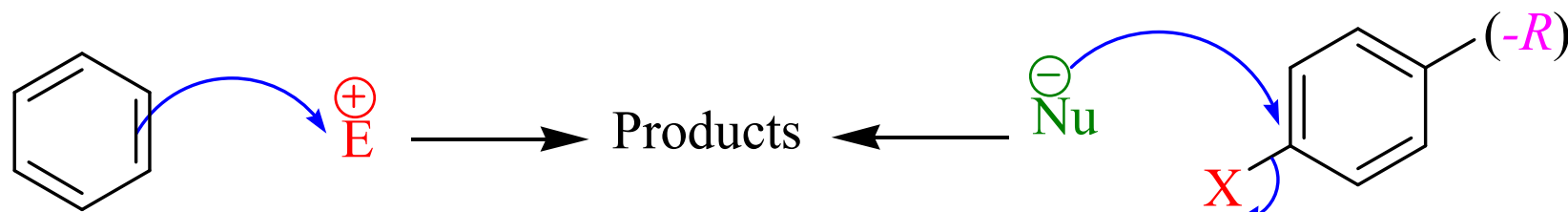
Reaction Mechanism

(CHEM-563)

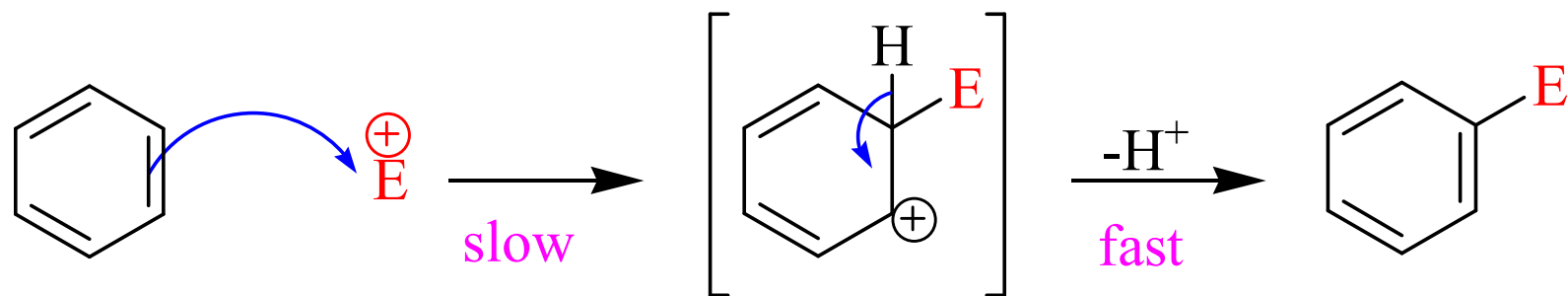
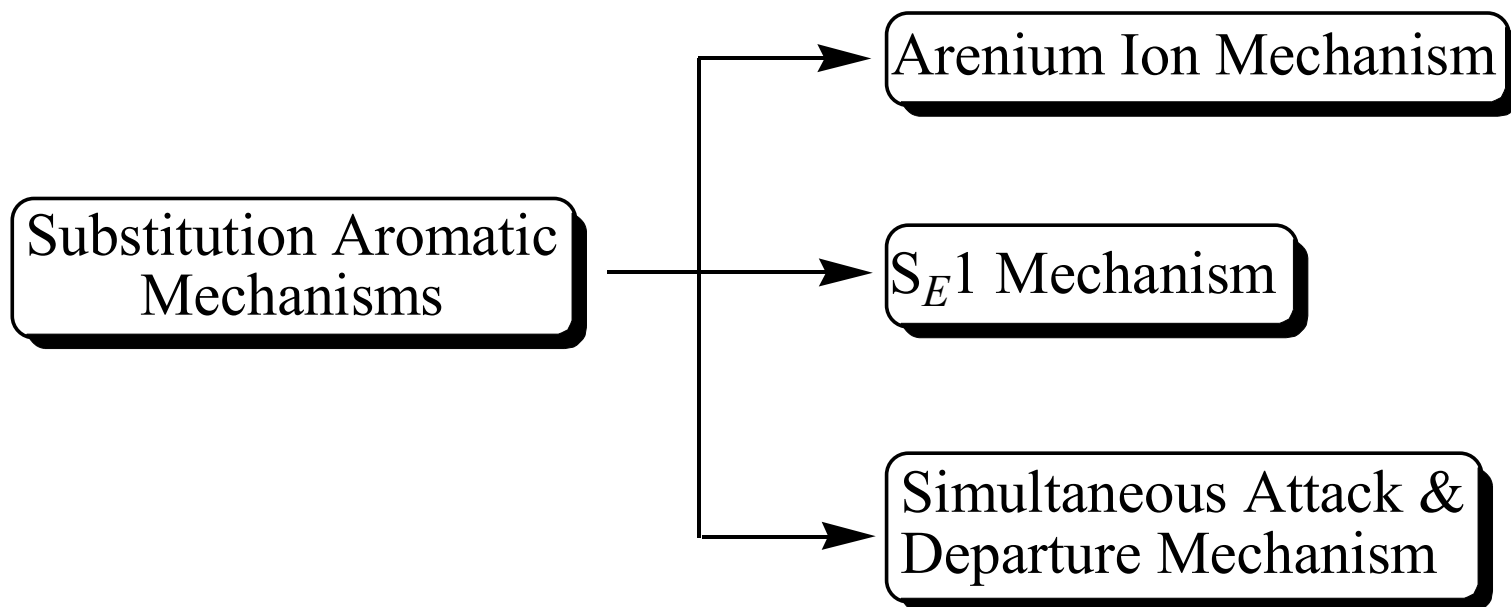
Online Lecture-13 (Week-5)

Dr Abdul Rauf Raza
(*Associate Professor*)
Department of Chemistry
University of Sargodha, Sargodha

Substitution Reactions



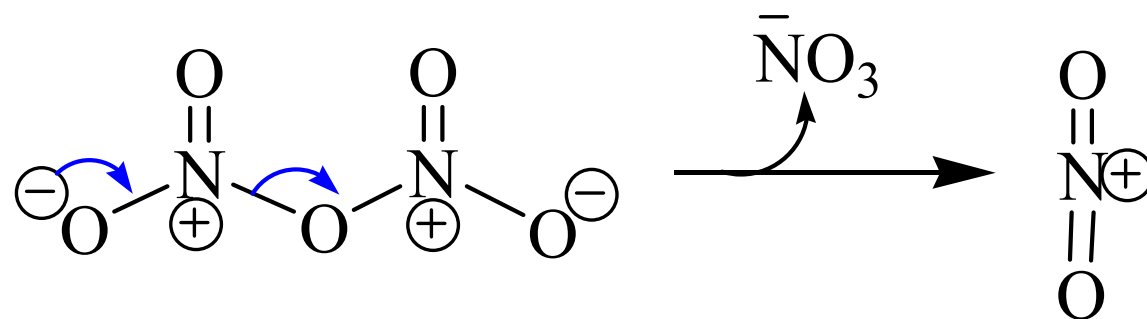
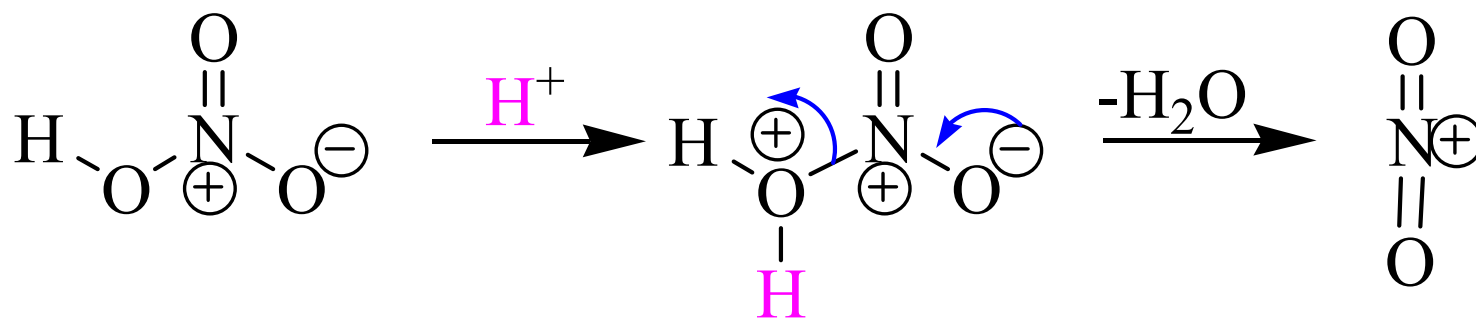
Arenium Ion Mechanism



$\text{E} = ^+\text{NO}_2, \text{HSO}_3^+, \text{X}^+, \text{R}^+, \text{RCO}^+$ etc.

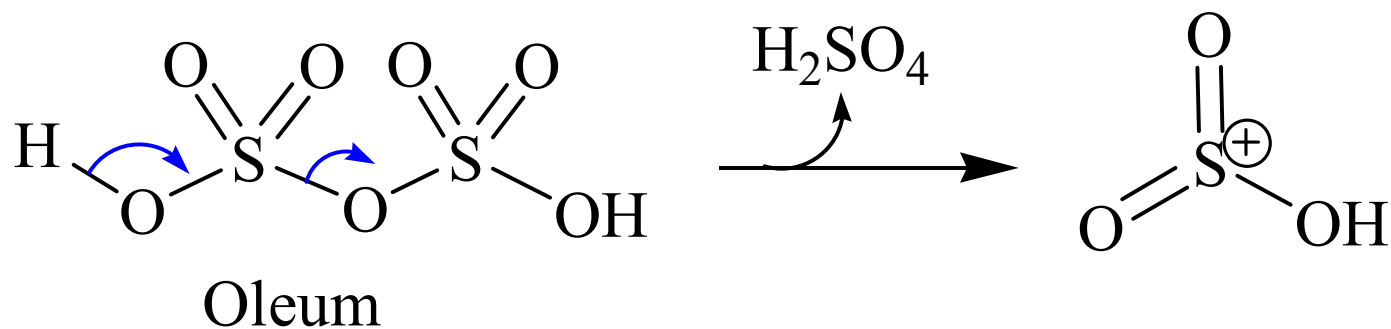
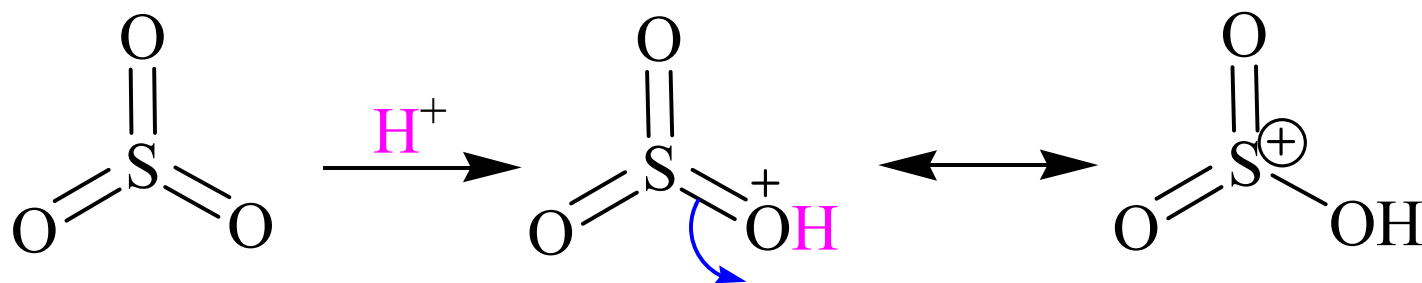
σ -Complex
Arenium Ion
Wheland Intermediate

Nitration

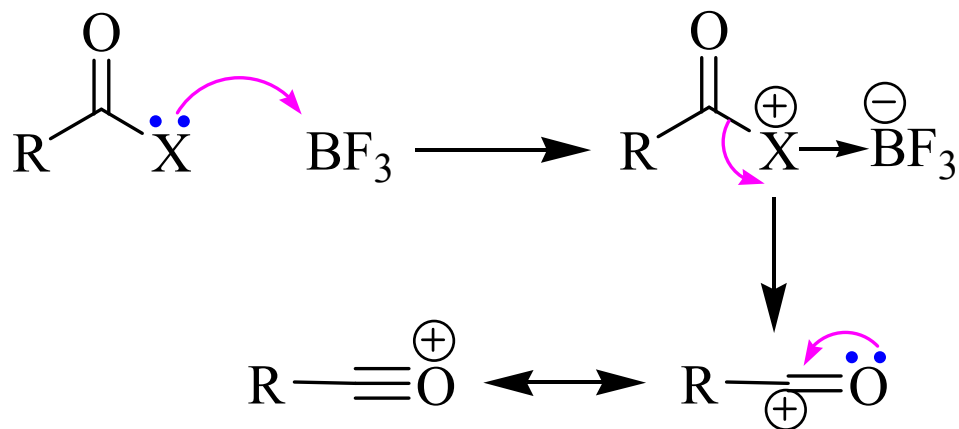
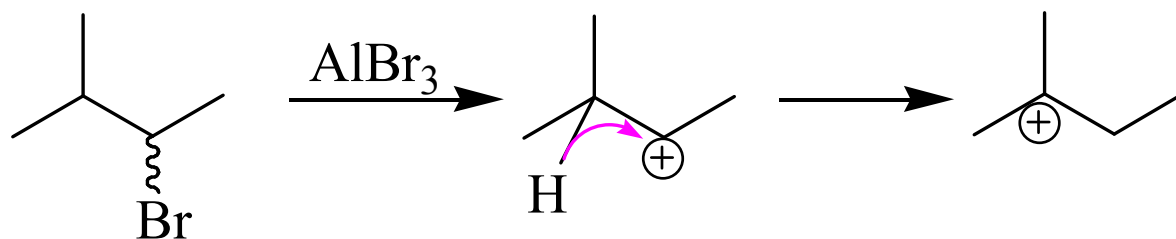
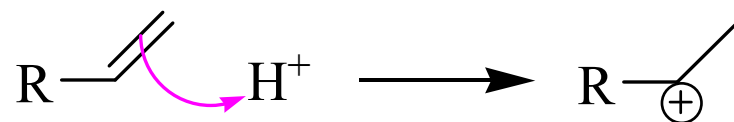
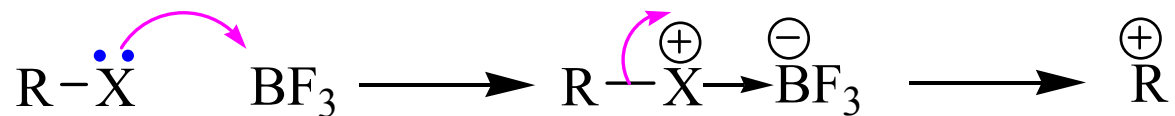


1. HNO_3
2. $\text{HNO}_3 + \text{H}_2\text{SO}_4$
3. $\text{HNO}_3 + \text{MeCOOH}$
4. N_2O_5
5. $[\text{NO}_2]^+ \text{SbF}_6^-$, $[\text{NO}_2]^+ \text{BF}_4^-$, $[\text{NO}_2]^+ \text{PF}_6^-$

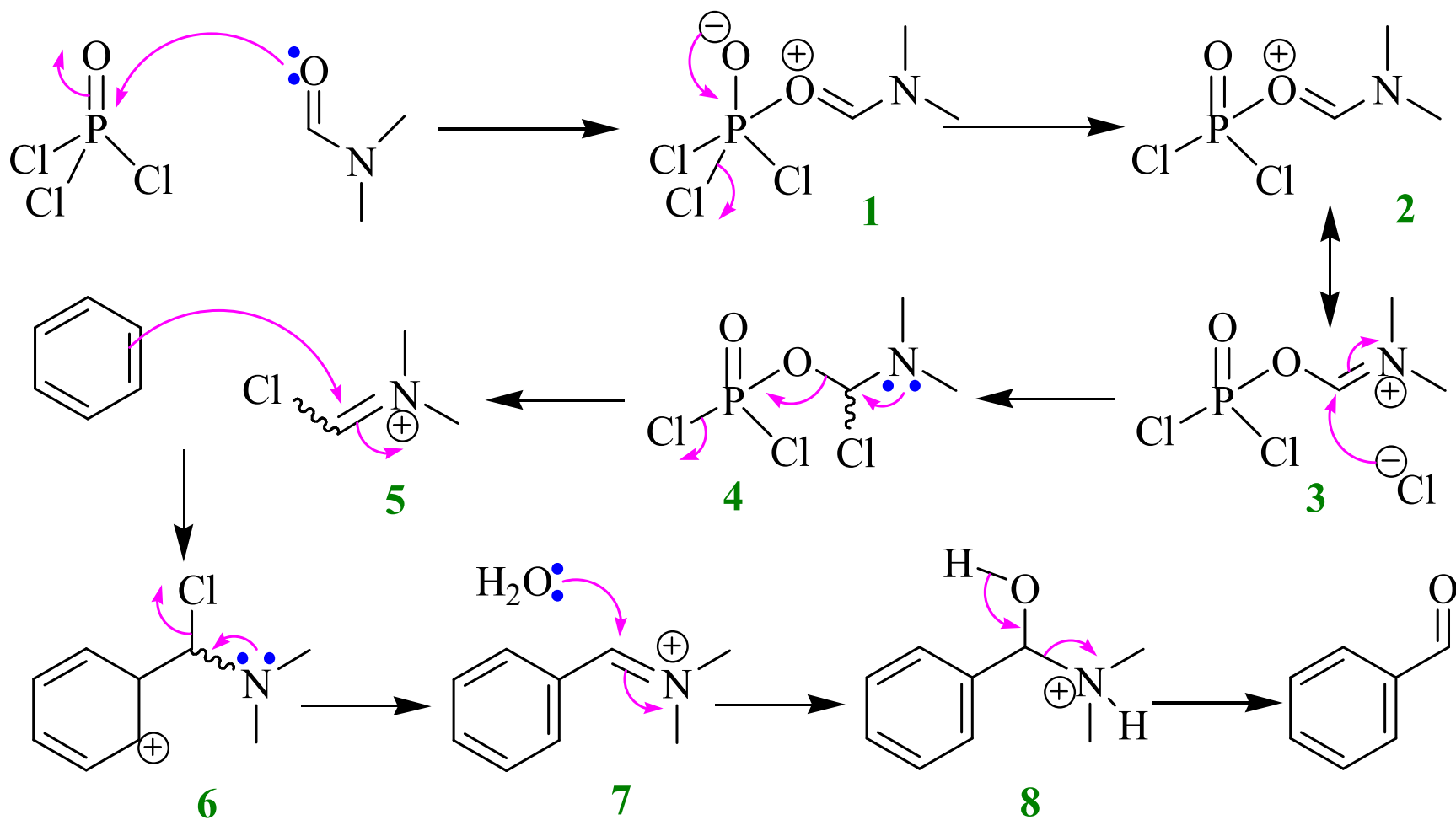
Sulphonation



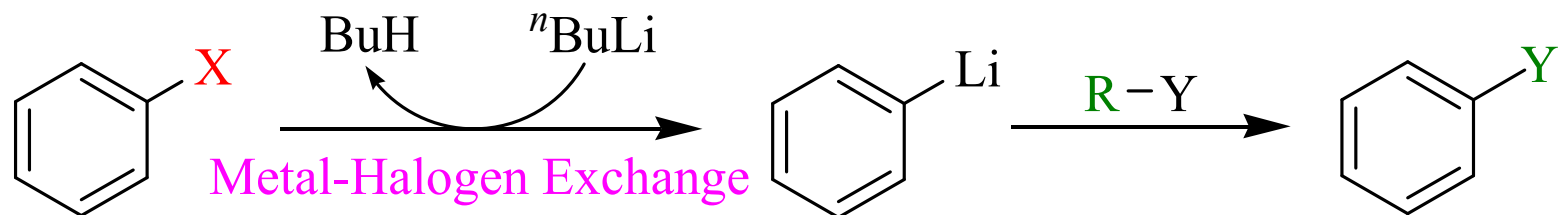
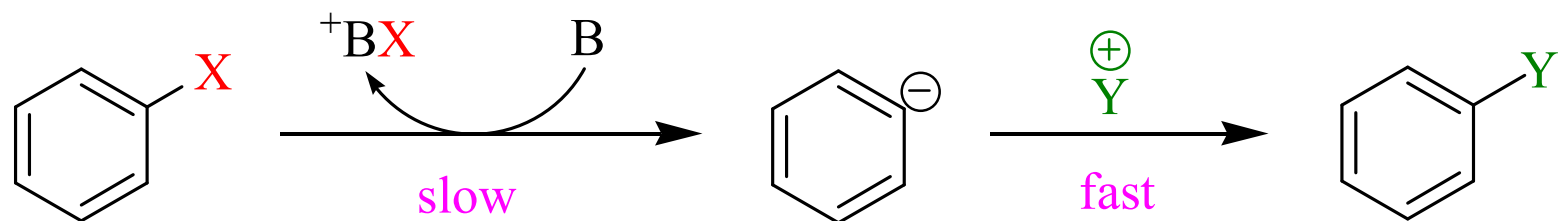
Friedle-Craft Alkylation / Acylation



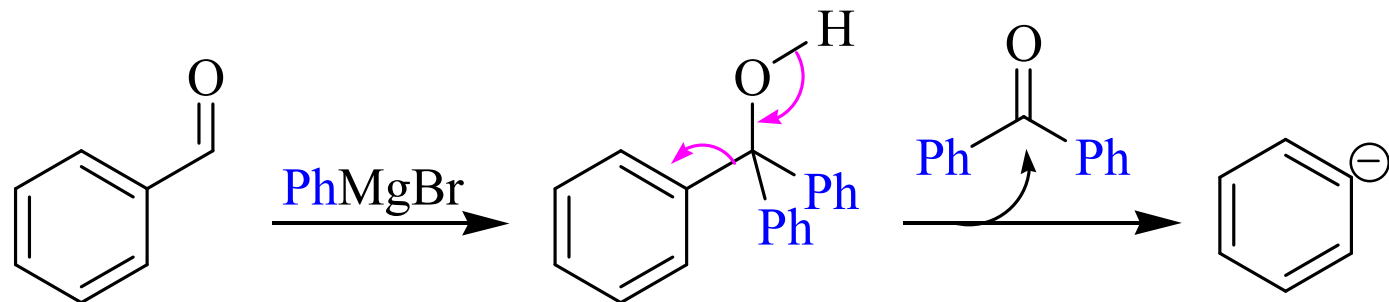
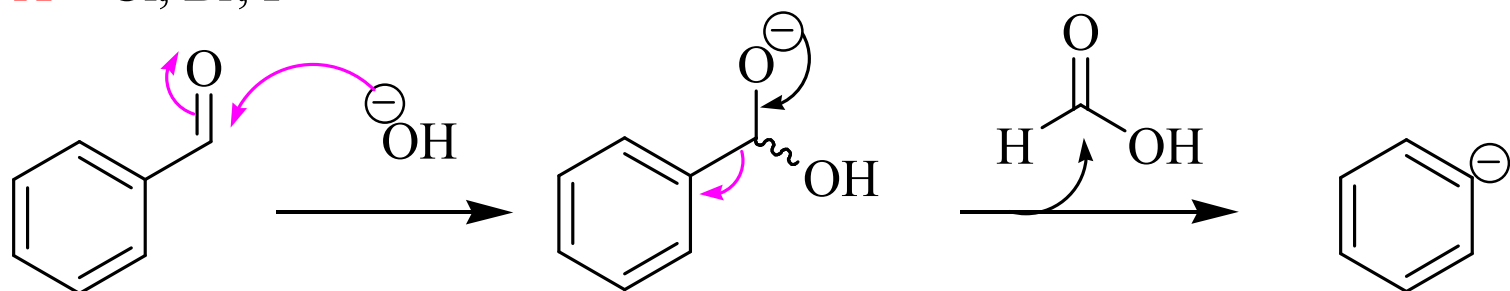
Formylation (Vilsmeier-Haak)



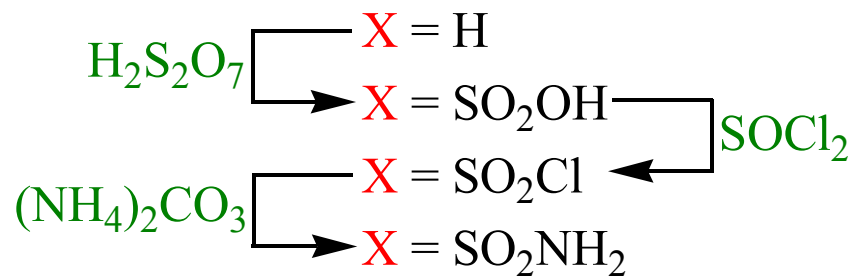
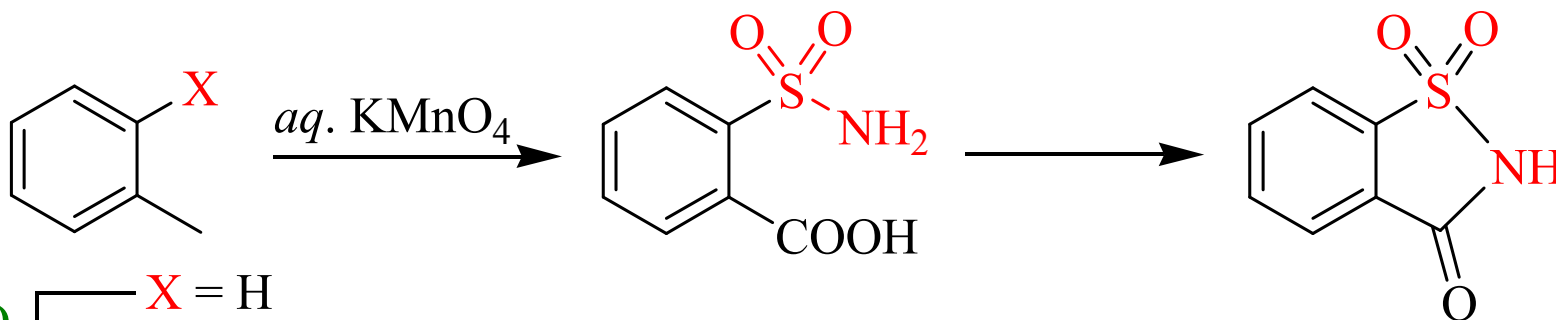
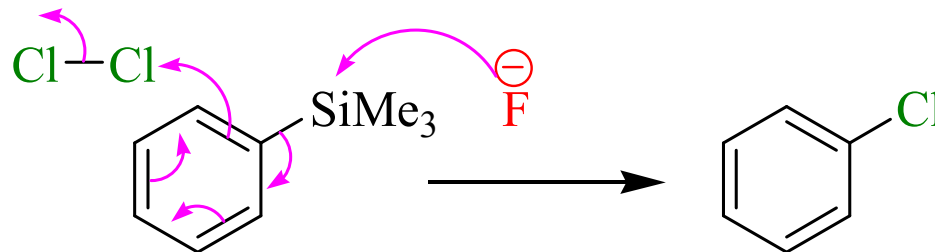
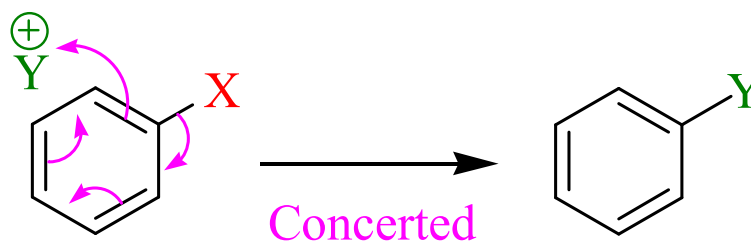
S_E1 Mechanism



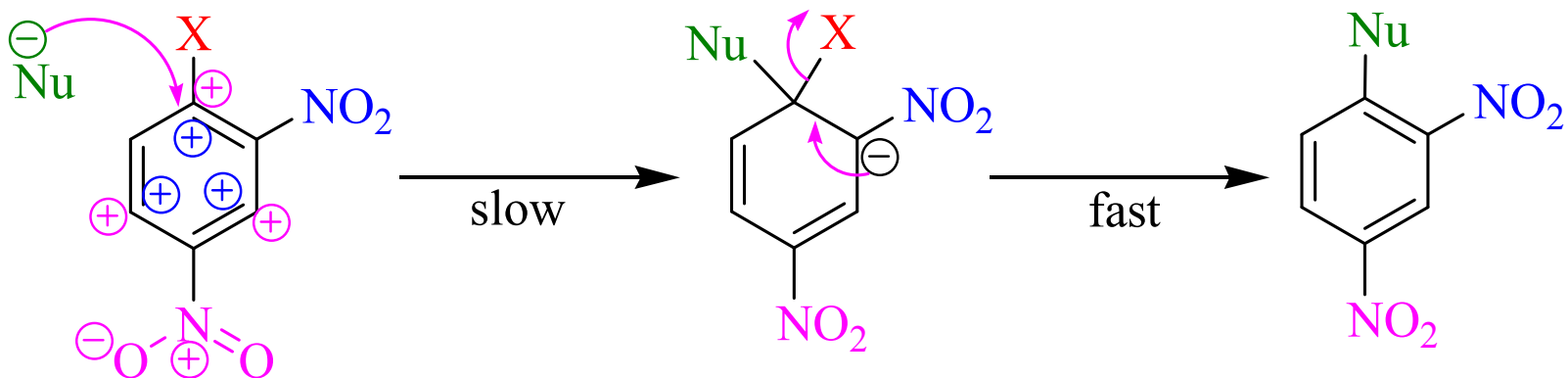
$X = \text{Cl, Br, I}$



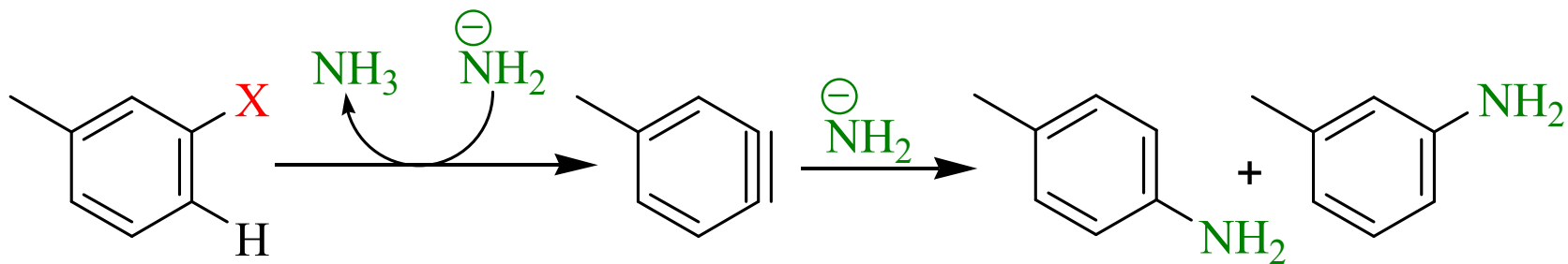
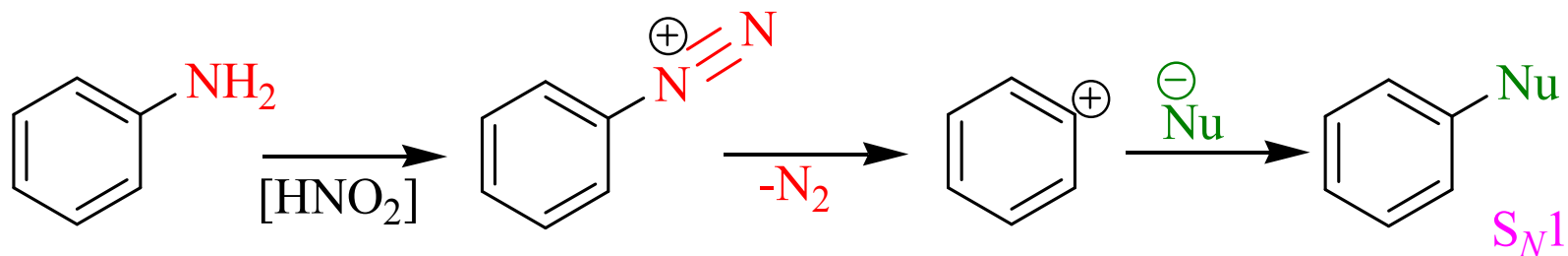
Simultaneous Attack & Departure



Substitution Aromatic Nucleophilic



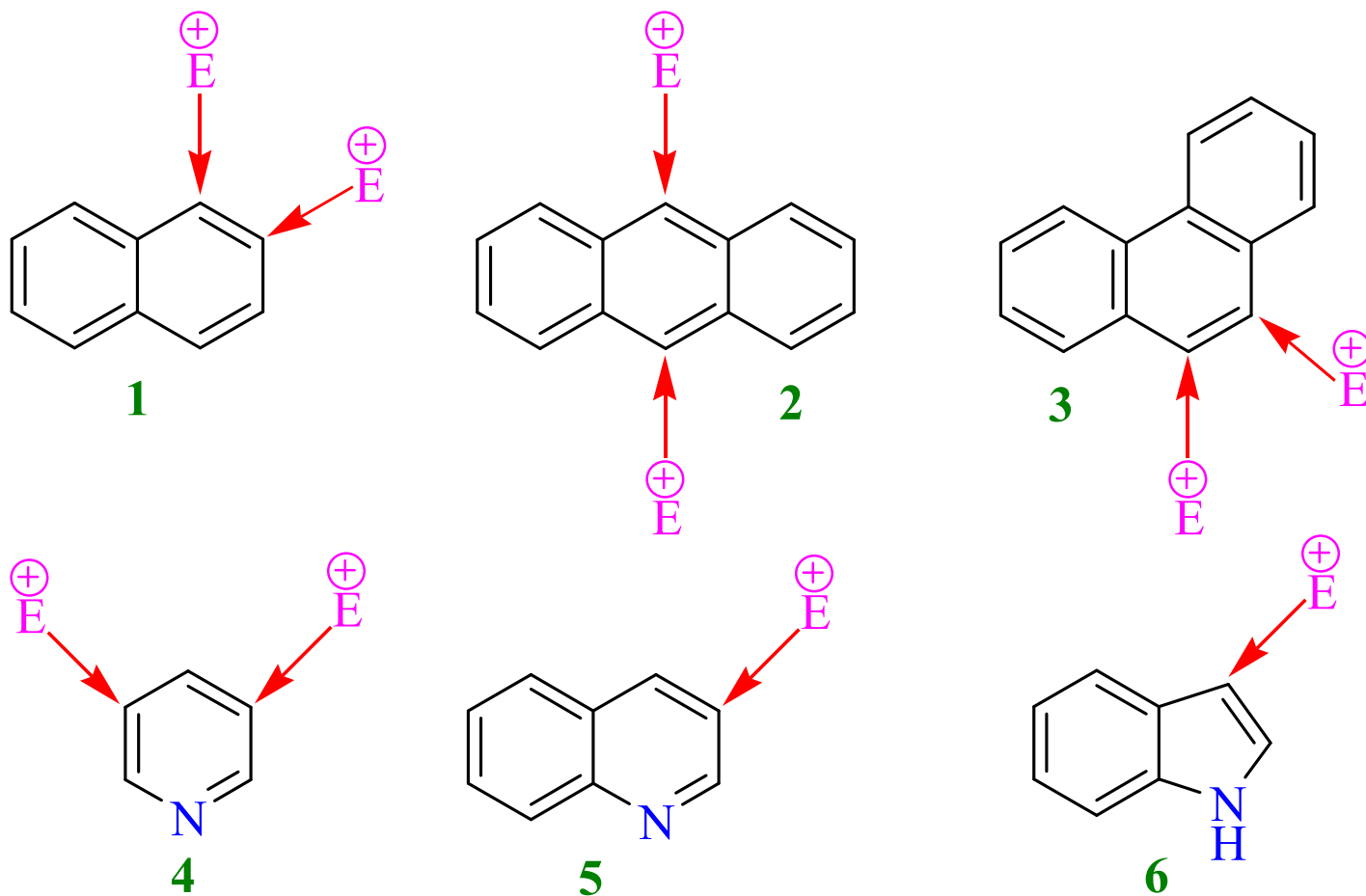
$X = Cl, Br, I, SOPh, SeOPh, SO_2Ph$ etc.



$X = Cl, Br, I$

Benzyne Mechanism

Aromatic Substrates



1 = Naphthalene

2 = Anthracene

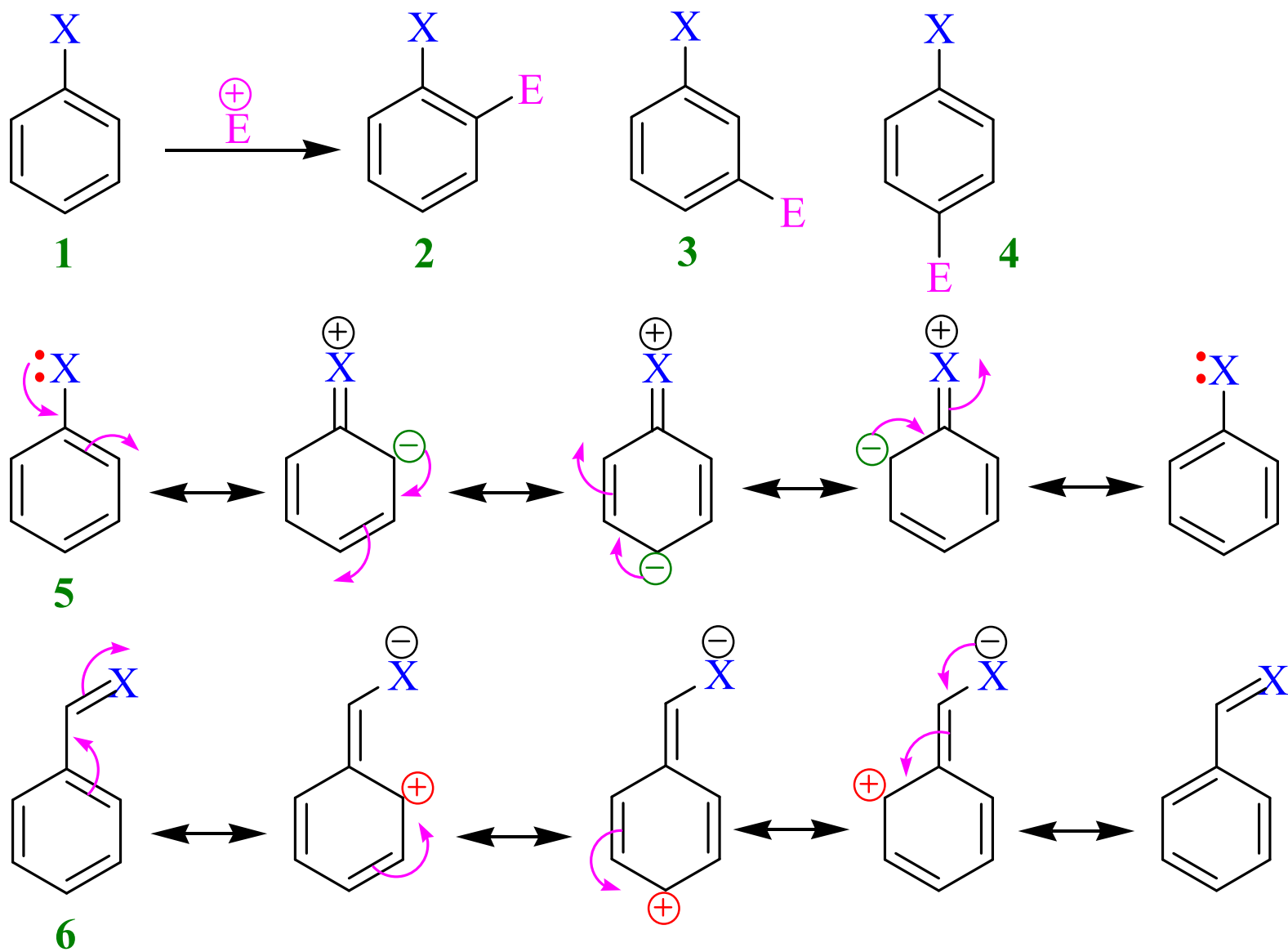
3 = Phenanthrene

4 = Pyridine (Azine)

5 = Quinolene (Benzo-1-azine)

6 = Indole (Benzo-1-azole)

Orientation of an Electrophile

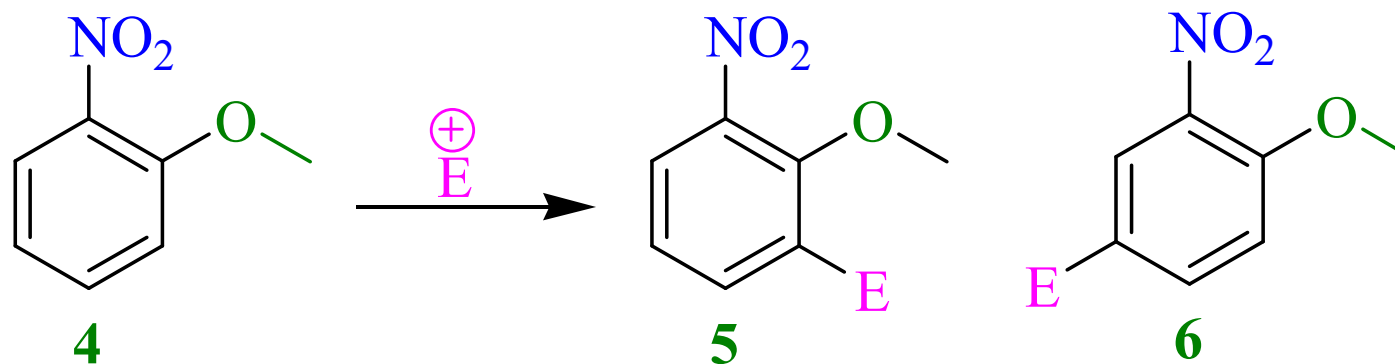
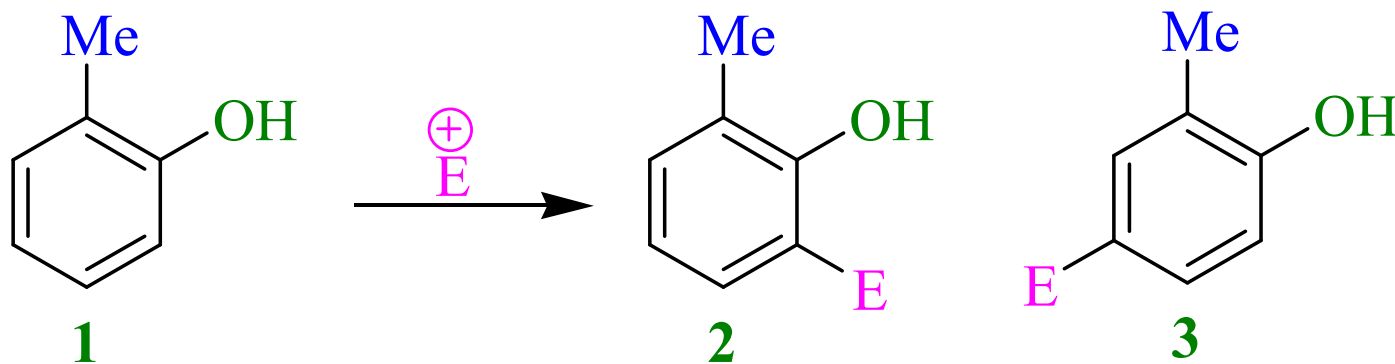


Orientation of an Electrophile

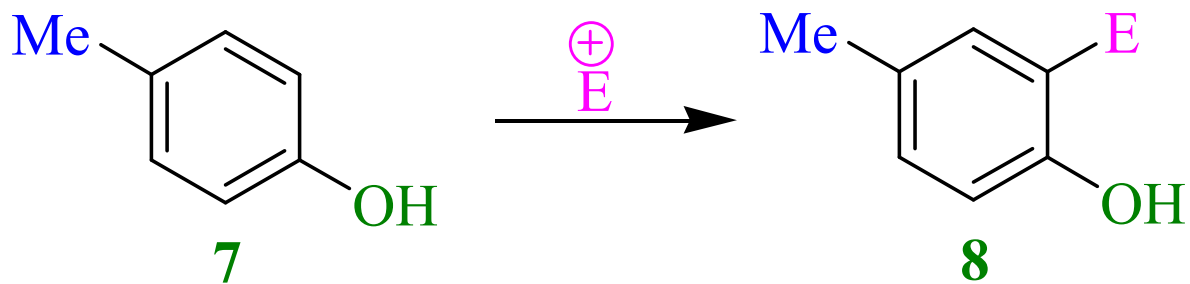
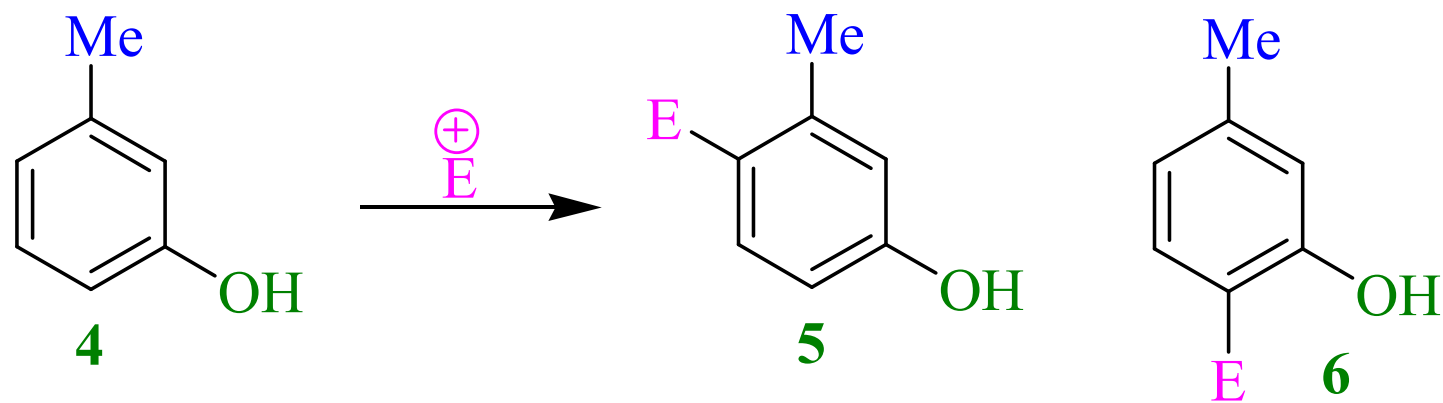
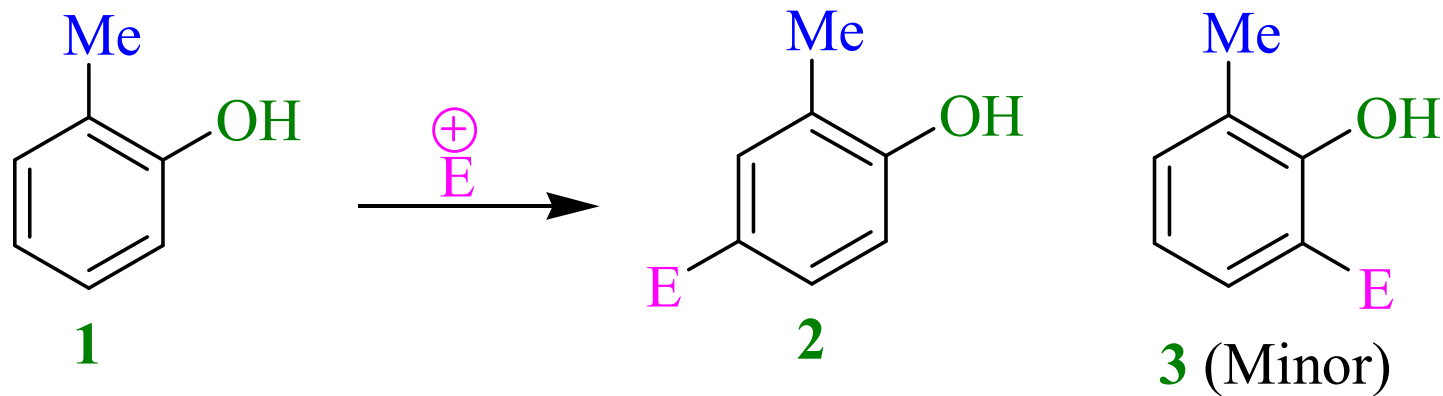
	X	I	R	Director	Ring	Examples
5	Alkyl	+I	-	<i>o / p</i>	Mild activator	Me, Et, ⁿ Pr, ⁱ Pr, ⁿ Bu, ⁱ Bu etc.
	Halogen	-I	+R	<i>o / p</i>	Mild deactivator	Cl, Br, I
	N, P, O, S	-I	+R	<i>o / p</i>	Strong activator	OH, OR, SH, SR, NH ₂ , N(H)R, NR ₂ etc.
6	O, S, N, P	-I	-R	<i>m</i>	Strong deactivator	al, one, oic acid, oate, oyl halide, amide, imine, nitro, carbazide etc.
	⁺ YR _n	-I	-	<i>m</i>	Strong deactivator	⁺ NR ₃ , ⁺ SR ₂

Rules of Orientation

If a strongly activating group competes with a weaker one / a deactivating one; the former controls the substitution

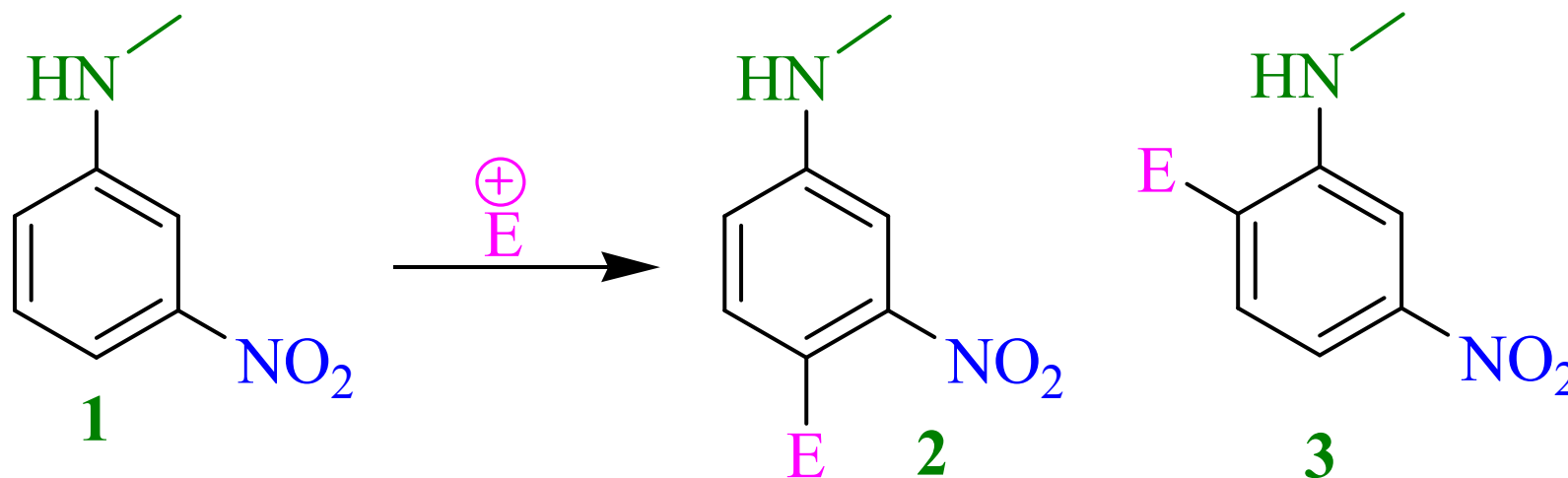


Practice



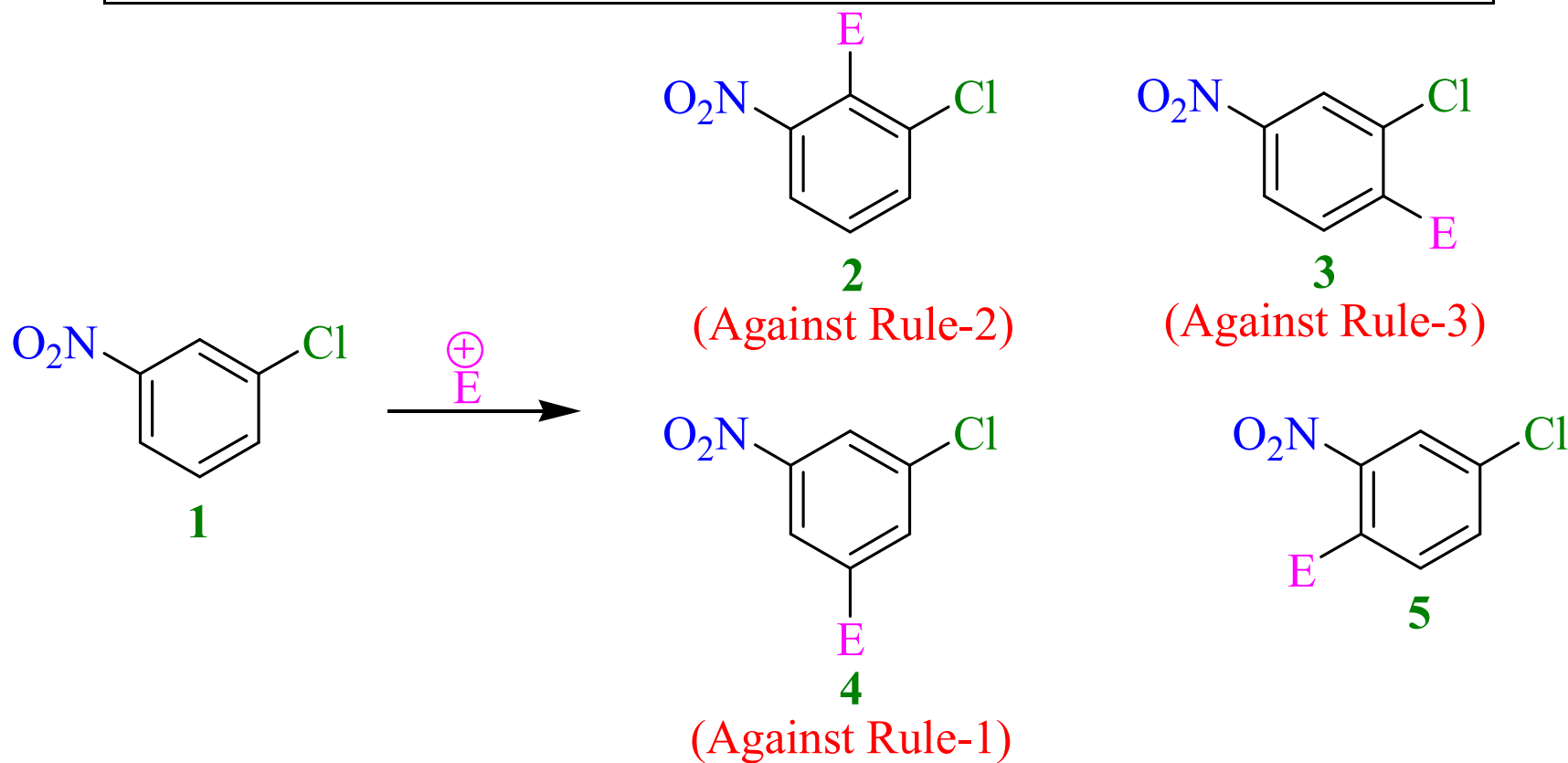
Rules of Orientation

The electrophile is least likely to approach between two groups (due to steric factor) positioned at *meta*

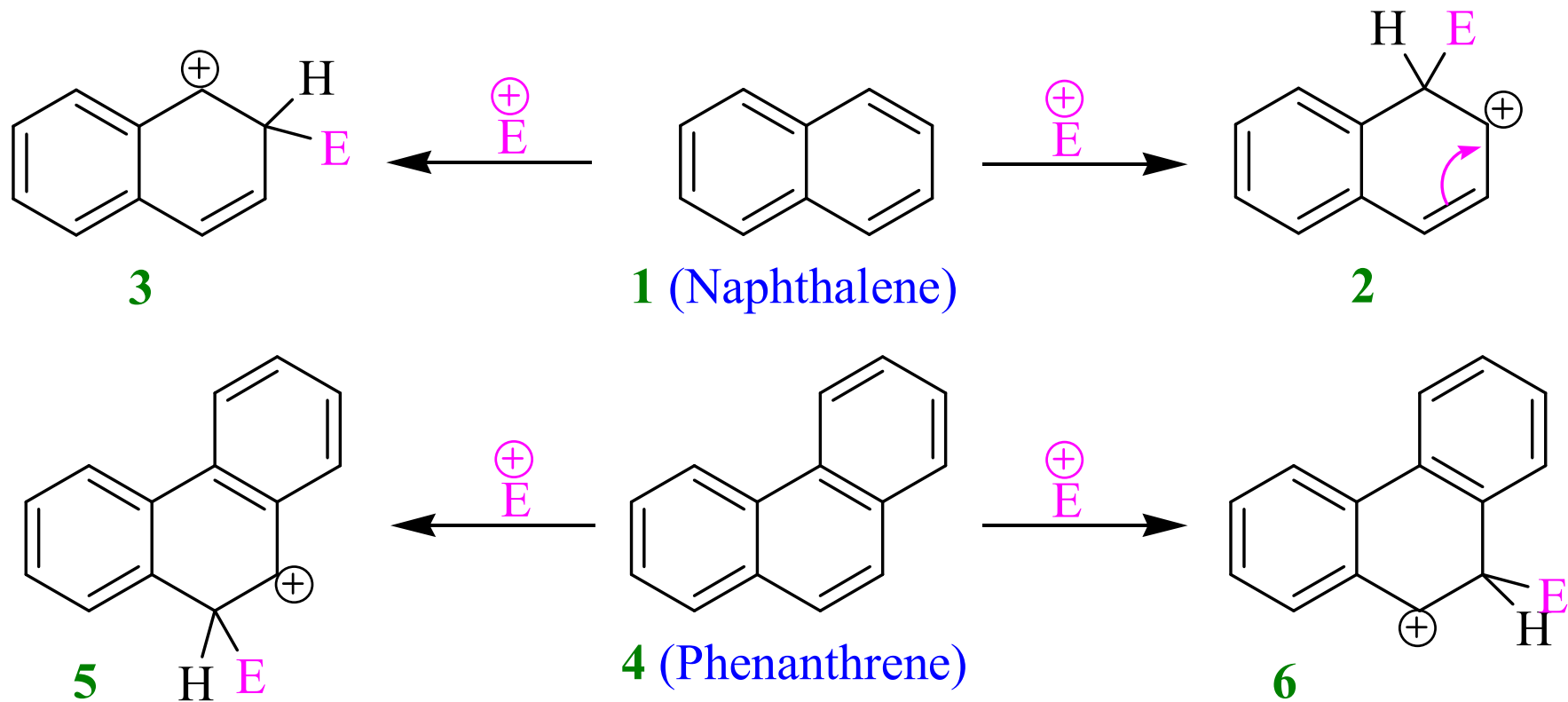


Rules of Orientation

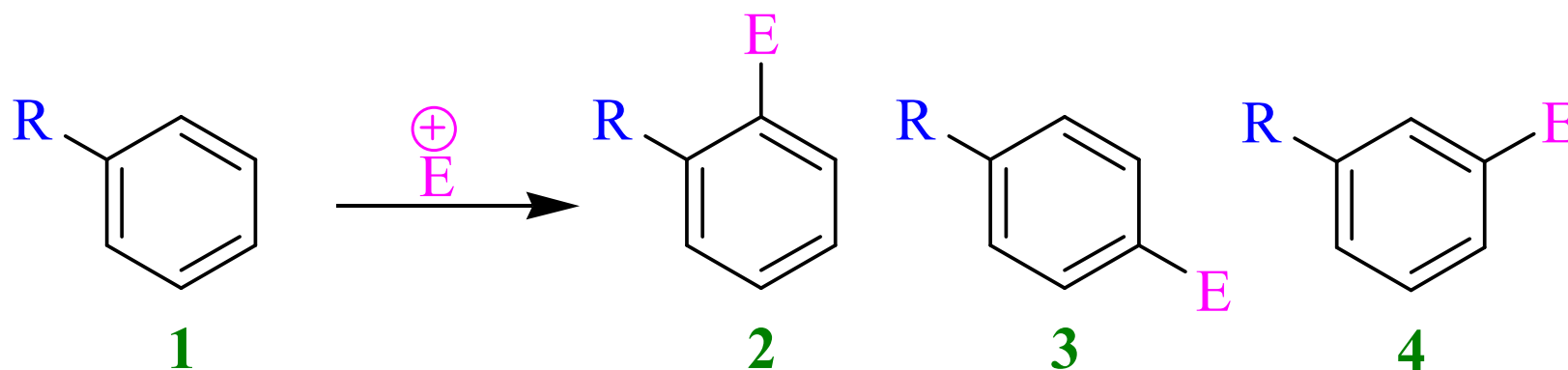
When a *m*-directing group is *m* to *o*, *p*-directing, the approaching electrophile is oriented at *ortho* to *m*-directing group



Orientation



Ortho / para Ratio

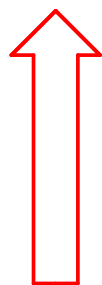


ortho : *para*

2 : 3

67 : 33 (theoretically)

R	<i>ortho</i>	<i>para</i>
F	12	88
Cl	30	70
Br	38	62
I	41	59



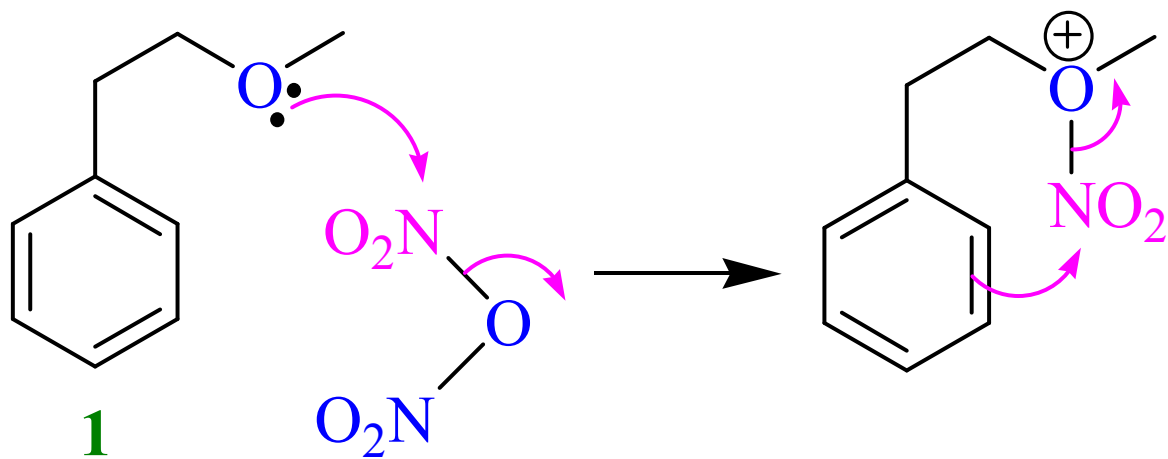
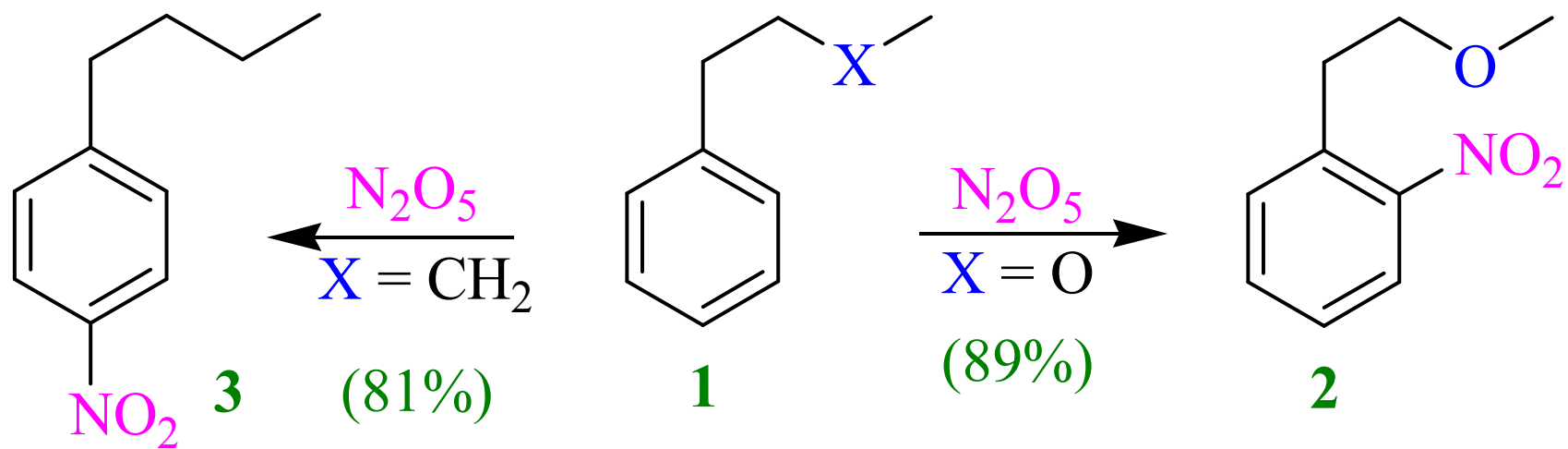
-I

*Steric
Crowding*



R	<i>ortho</i>	<i>para</i>
Me	61	39
Et	54	46
ⁿ Pr	38	72
ⁱ Pr	17	83

Ortho Effect



Suggested Reading

Chapter 21 (Page 473 to 497)

Chapter 22 (Page 513 to 526)

of “Organic Chemistry” by Clayden, J; Greeves,
N; Warren, S., 2nd Edition, Oxford
University Press, England (2008)