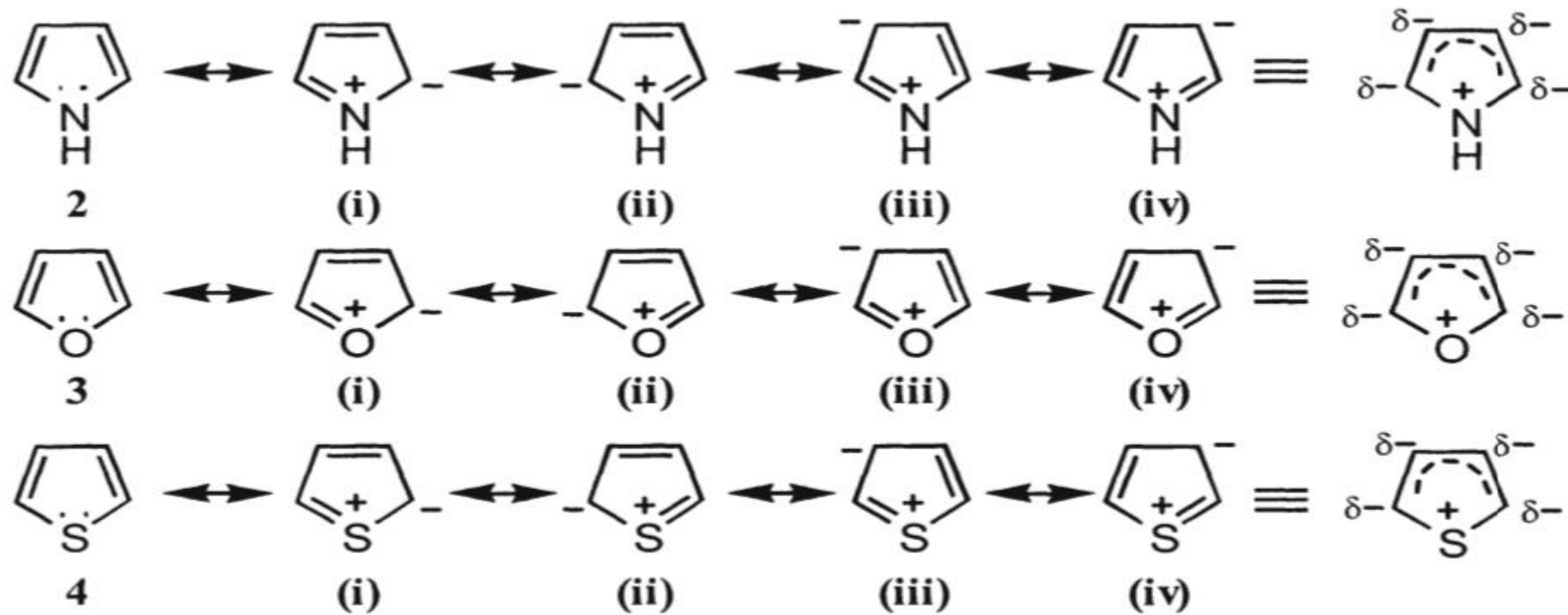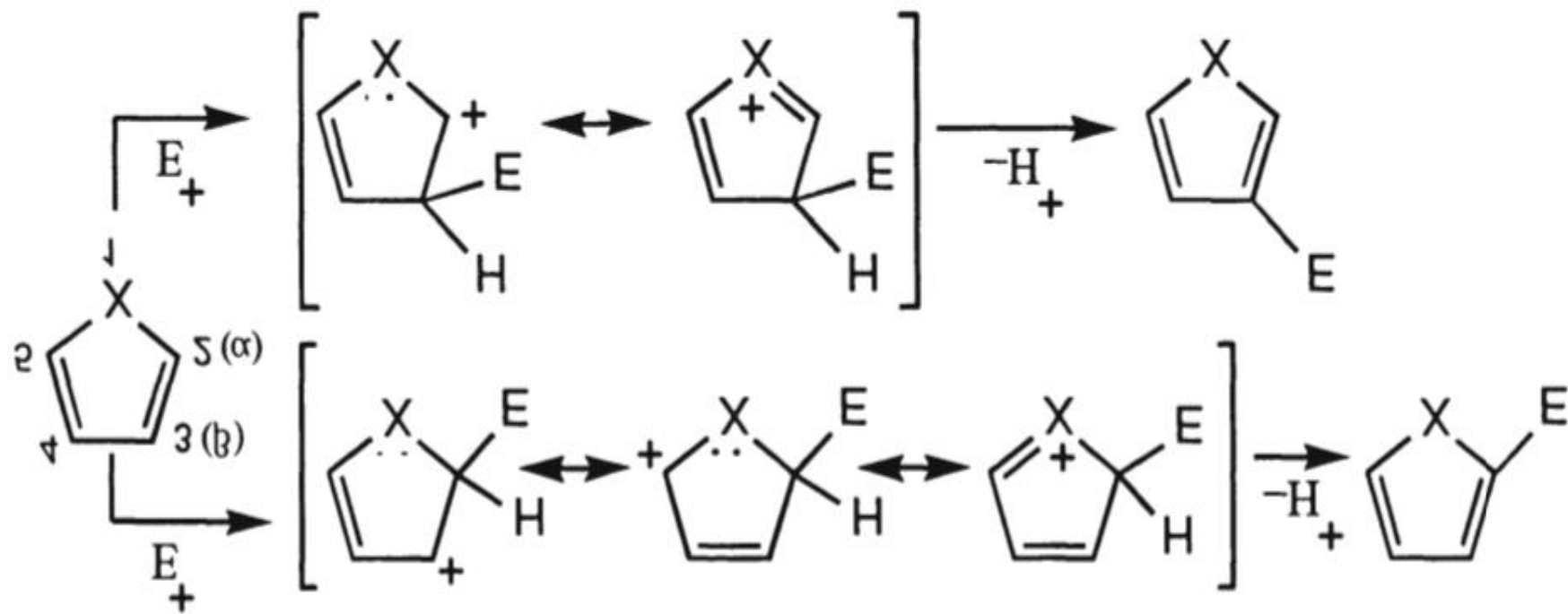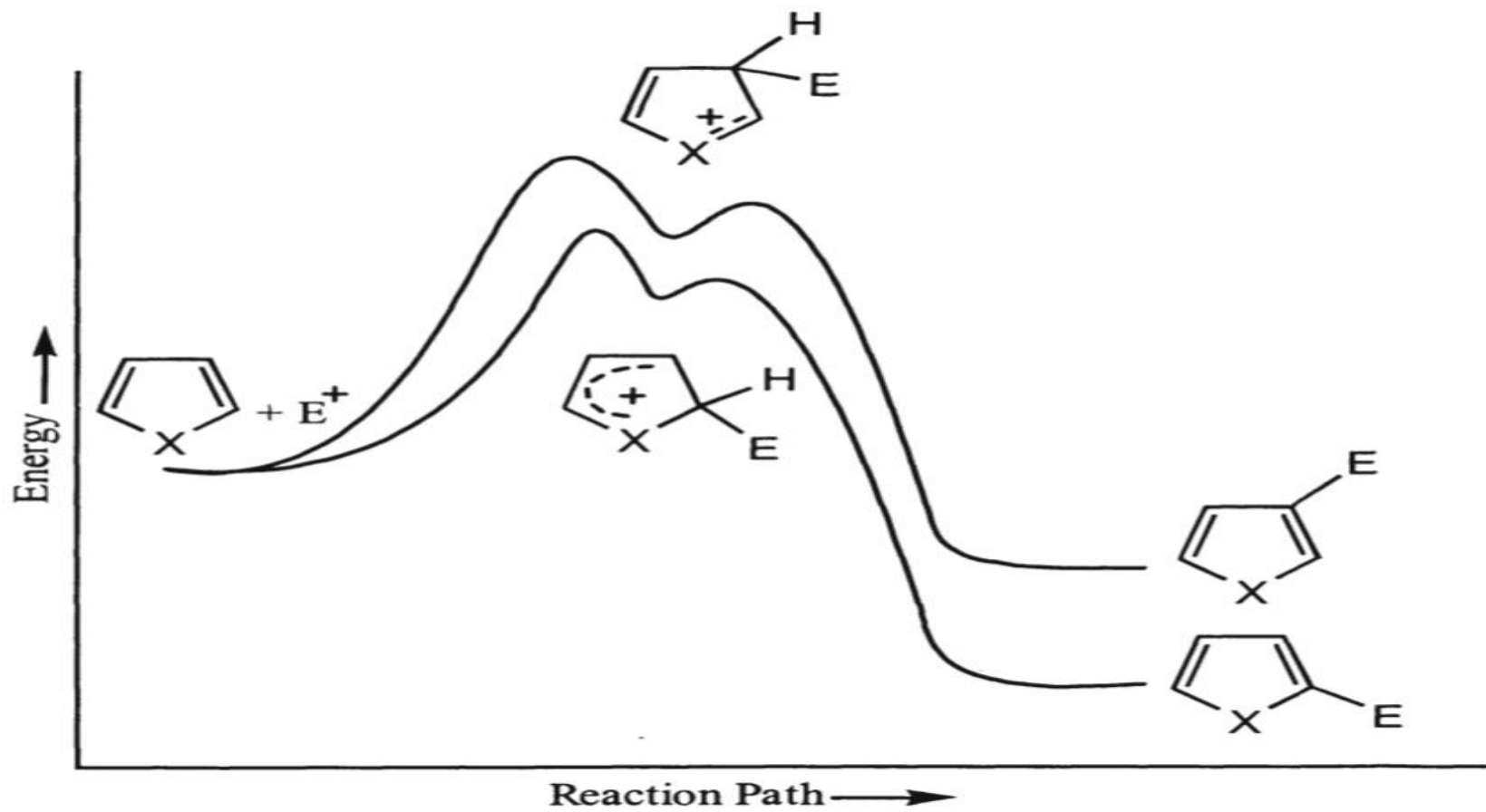# Electrophilic Substitution Reactions

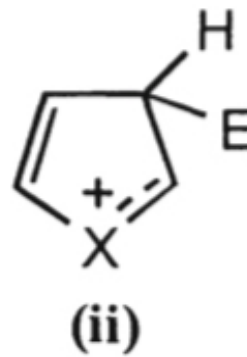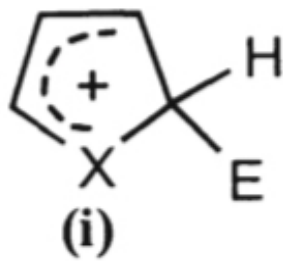Resonating structures of pyrrole, furan and thiophene

Electrophilic substitution in five-membered heterocycles
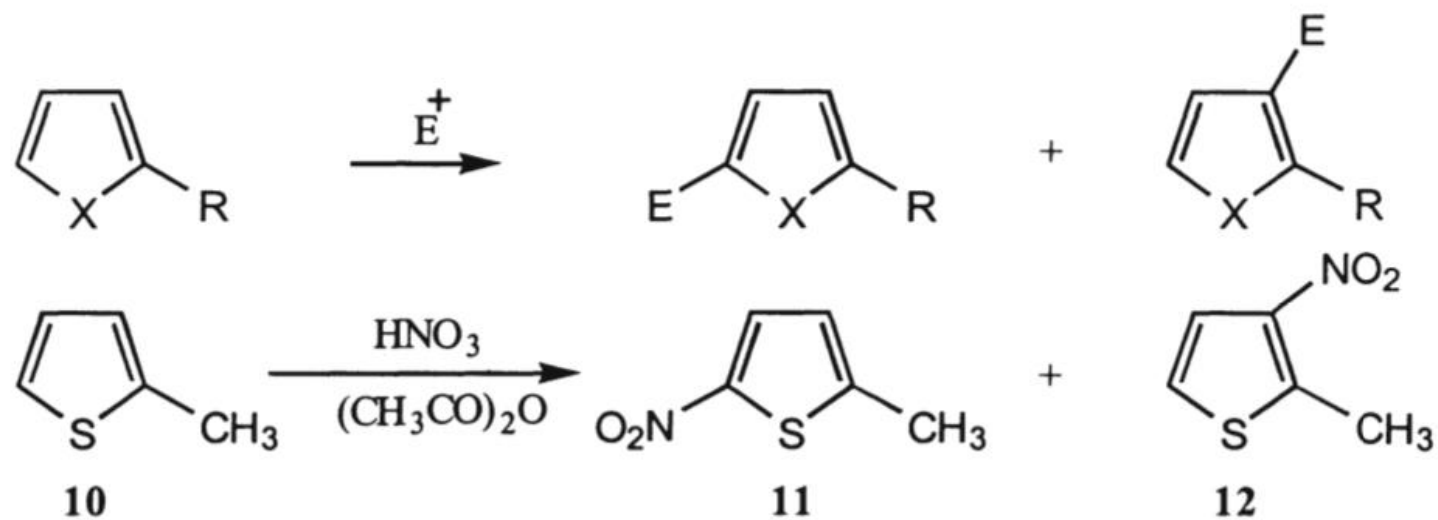
Energy profile diagram

Directing Effect of Ring Heteroatom

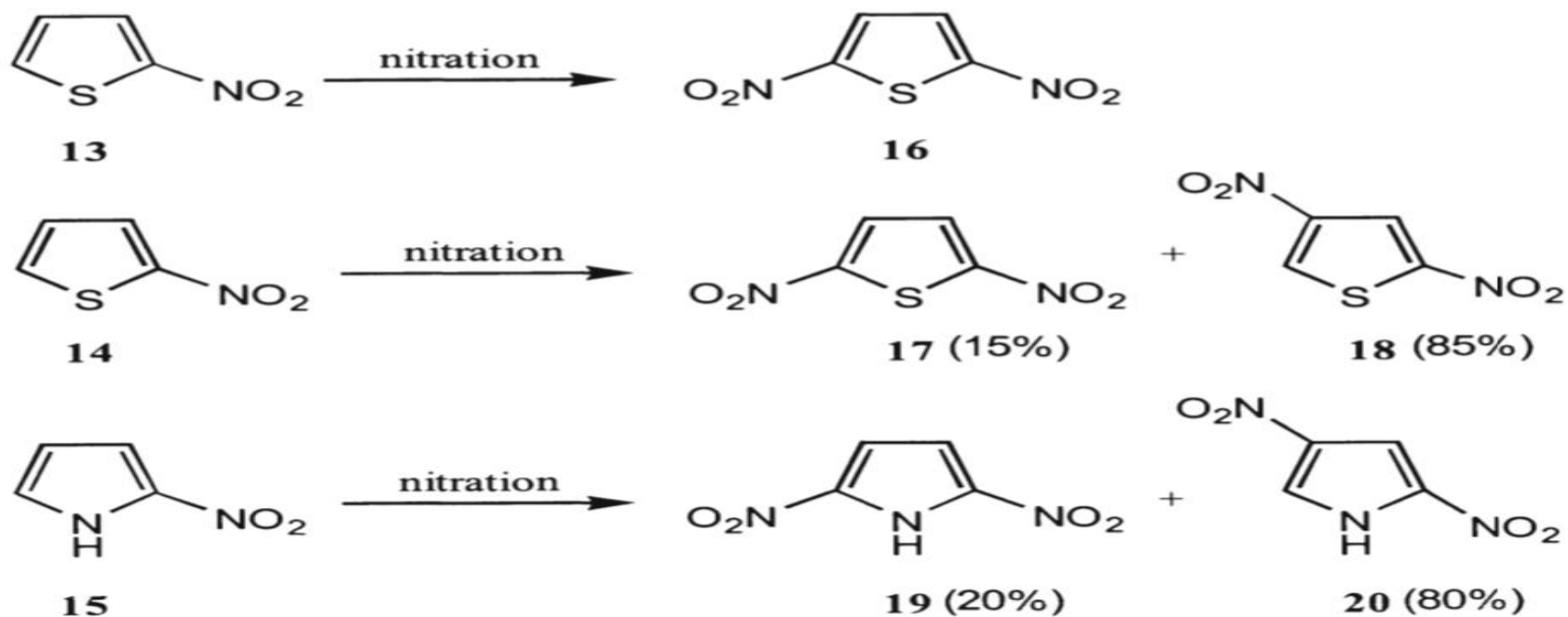# Directing Effects of Substituents in Monosubstituted Heterocycles

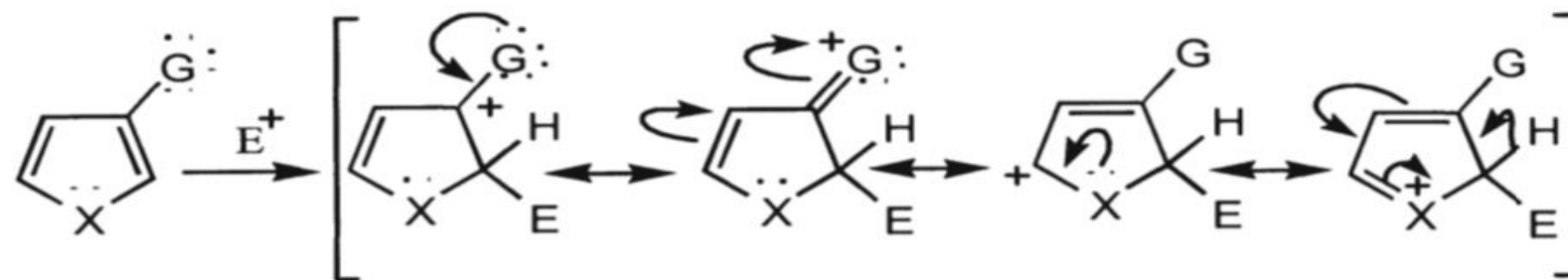(i) Effect of electron-releasing substituents at C-2

Scheme-6

(ii) Effect of electron-withdrawing substituents at C-2
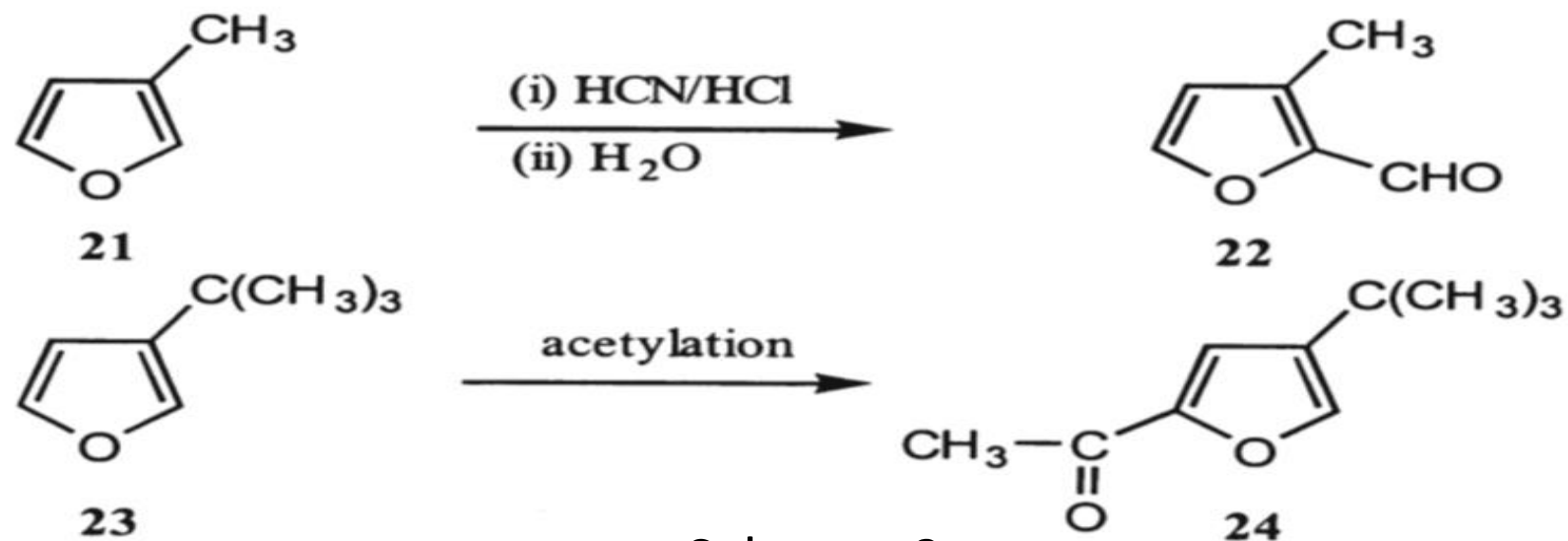
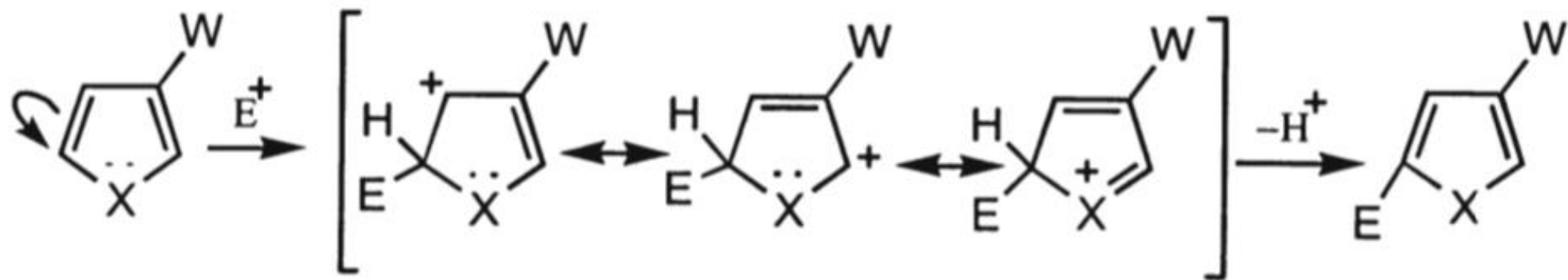(iii) Effect of electron-releasing substituents at C-3

Scheme-7

X = NH, O, S
G = electron-releasing group (halogen)

Scheme-8

Scheme-9

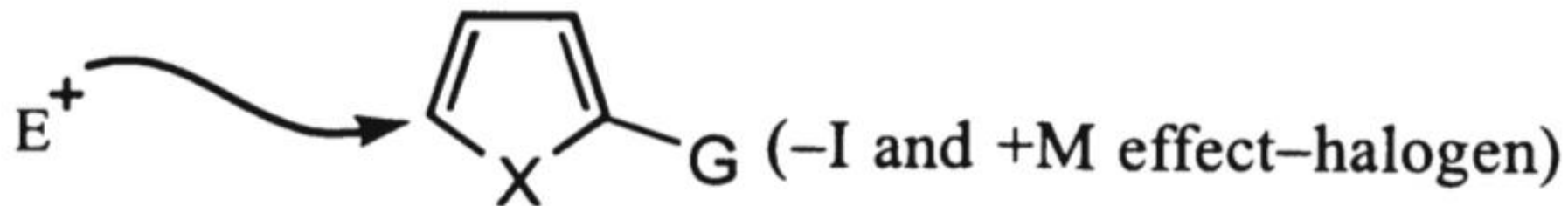## (iv) Effect ofelectron-withdrawing substituents at C-3
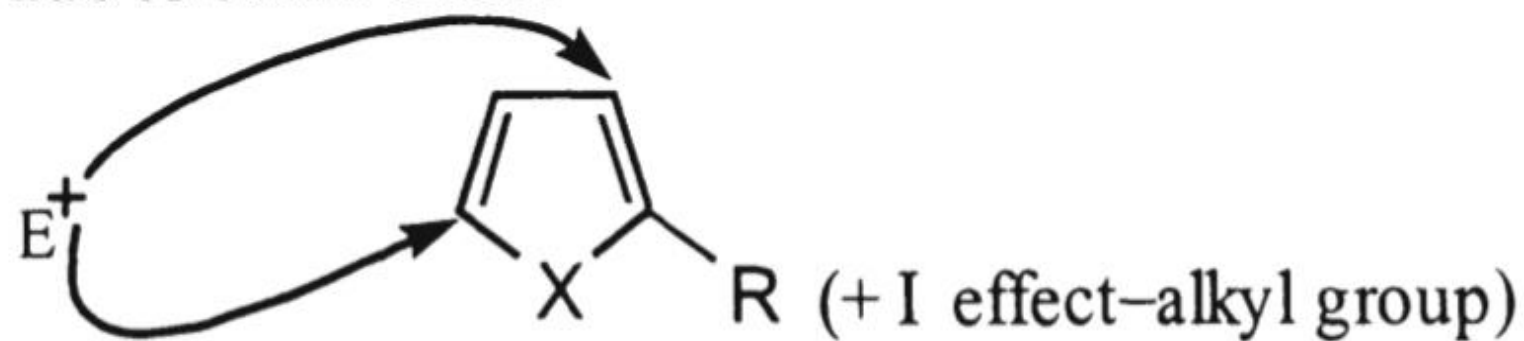

X = NH, O or S
W = electron-withdrawing group (–CHO)

Scheme-10

(i) Substituents with I and + M effects
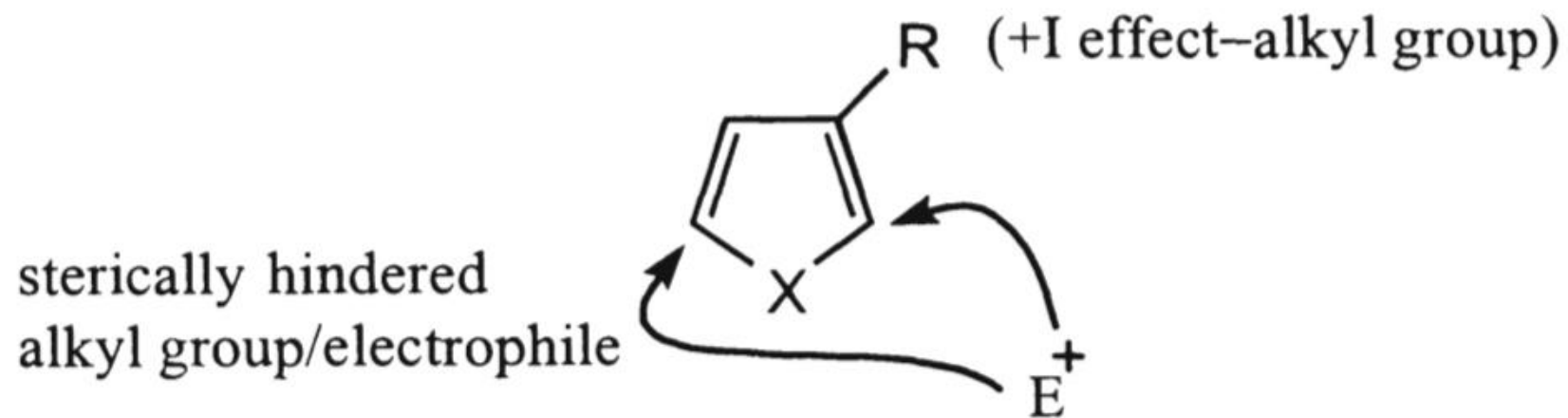
(a) substituents at C-2

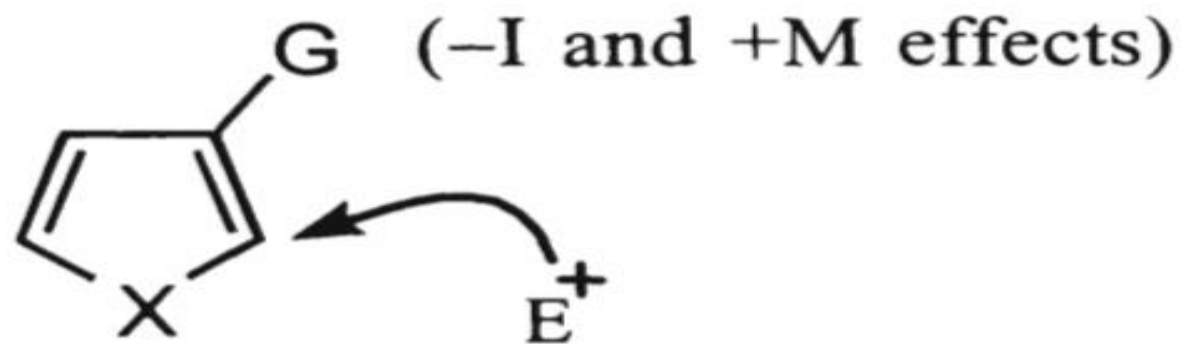E^+ 　　　　　　　　G (–I and +M effect–halogen)

due to ortho effect

E^+ 　　　　　　　　R (+I effect–alkyl group)

α-directing effect

(b) substituents at C-3

G   (–I and +M effects)

E⁺

R   (+I effect–alkyl group)

sterically hindered
alkyl group/electrophile

E⁺

(ii) Substituents with -1 and -M effects

(a) substituents at C-2

least deactivated position

E^+

most activated by
α-directing
effect of heteroatom

(−I and −M effects : −NO$_2$, −CN, −COR)

(C-4 is least deactivated
(C-5 is most activated by
α-directing effect of heteroatom)

(b) substituents at C-3

W (−I and −M effects)
(due to combined effect of
α-directing effect of heteroatom
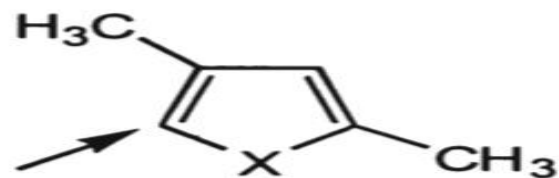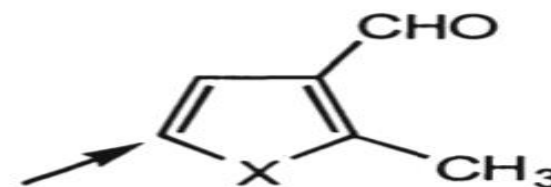and substituent effect)

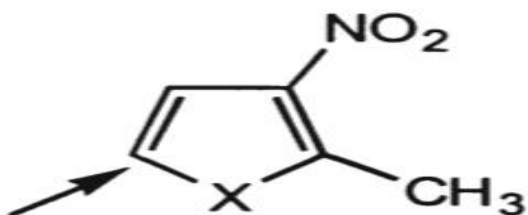# Directing Effects of Substituents in Disubstituted Heterocycles
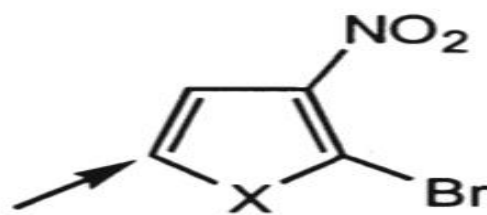

α-directing effect of heteroatom reinforced

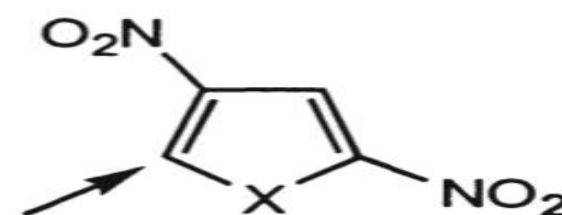α-directing effect of heteroatom + *ortho-* effect of electron-releasing substituent

α-directing effect of heteroatom + *meta-* directing effect of electron-withdrawing substituent (α-directing effect reinforced)

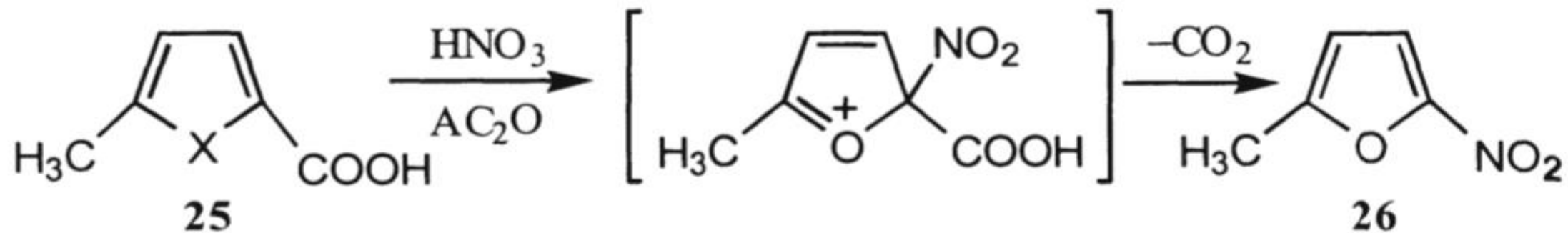α-directing effect of heteroatom + substituent effect (α-directing effect reinforced)

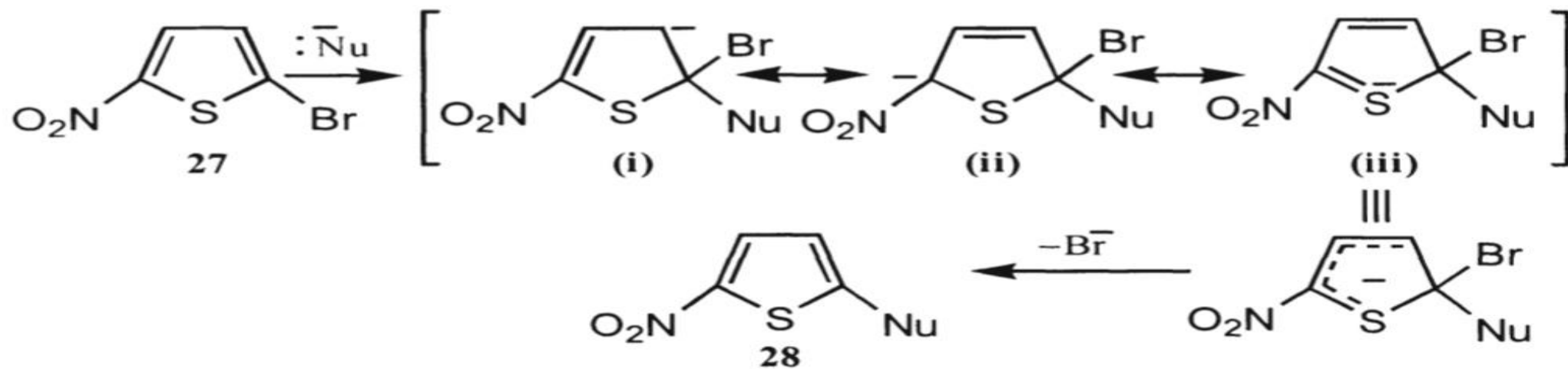α-directing effect of heteroatom + *meta-* directing effect of substituent

combined effect (α-directing effect of heteroatom + substituent effect)

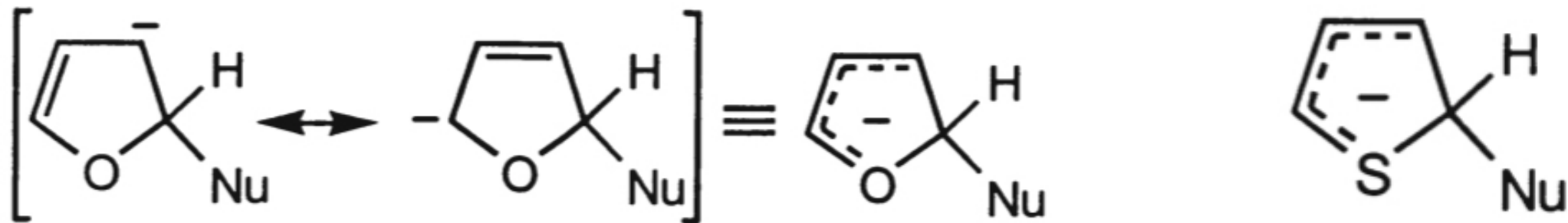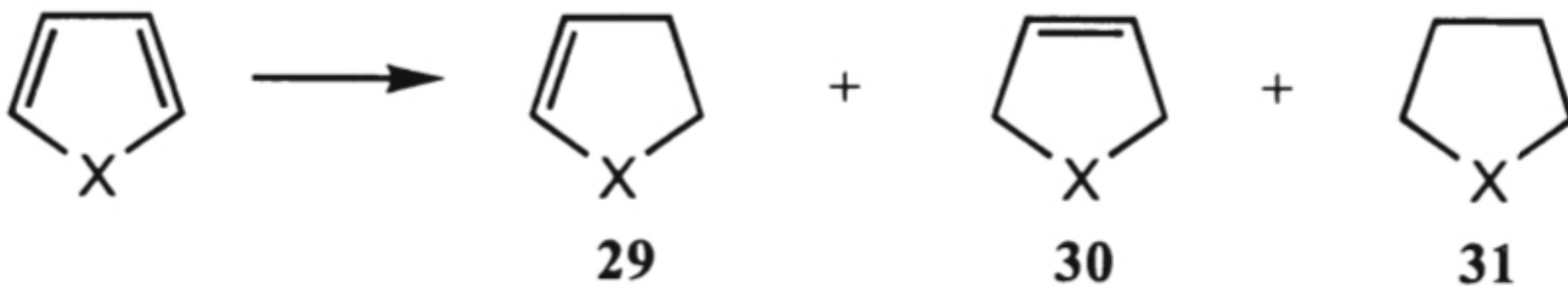Directing effects of substituents in disubstituted heterocycles
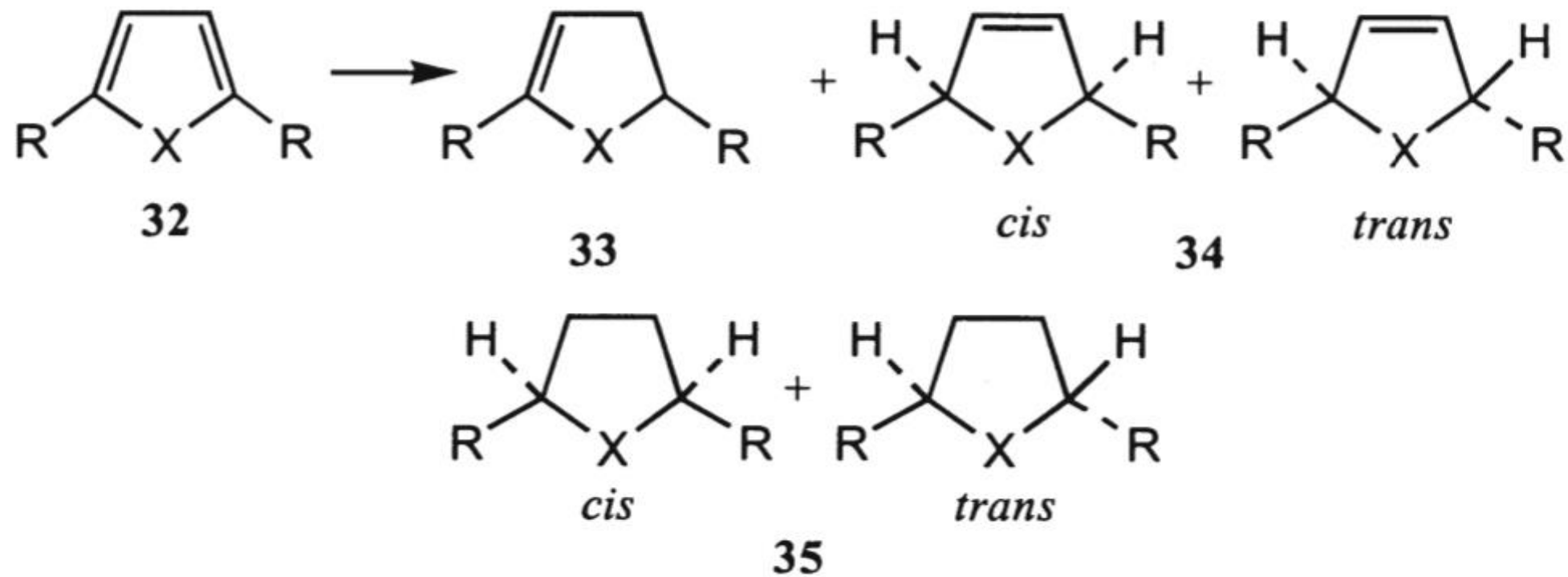
Scheme-11

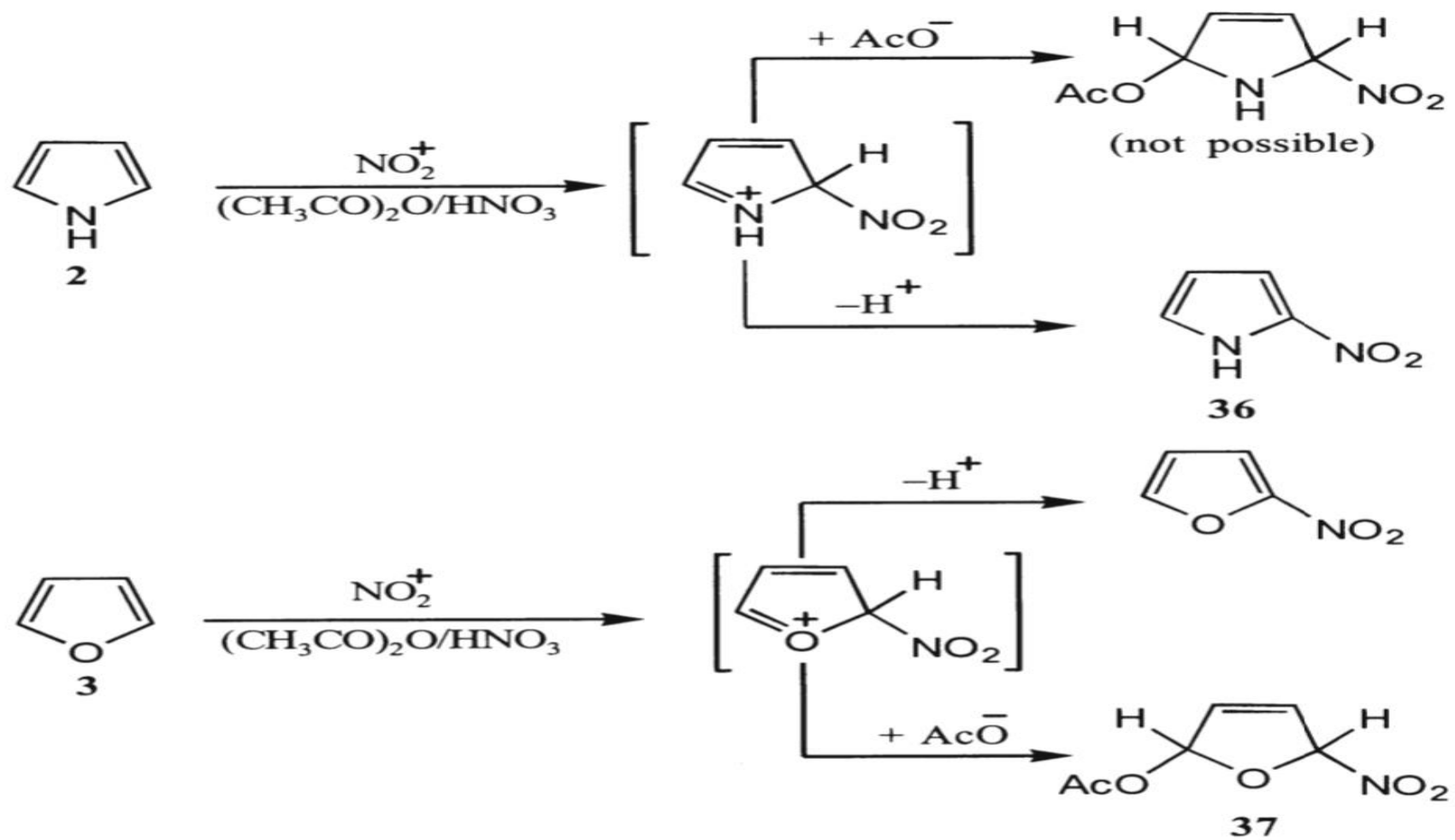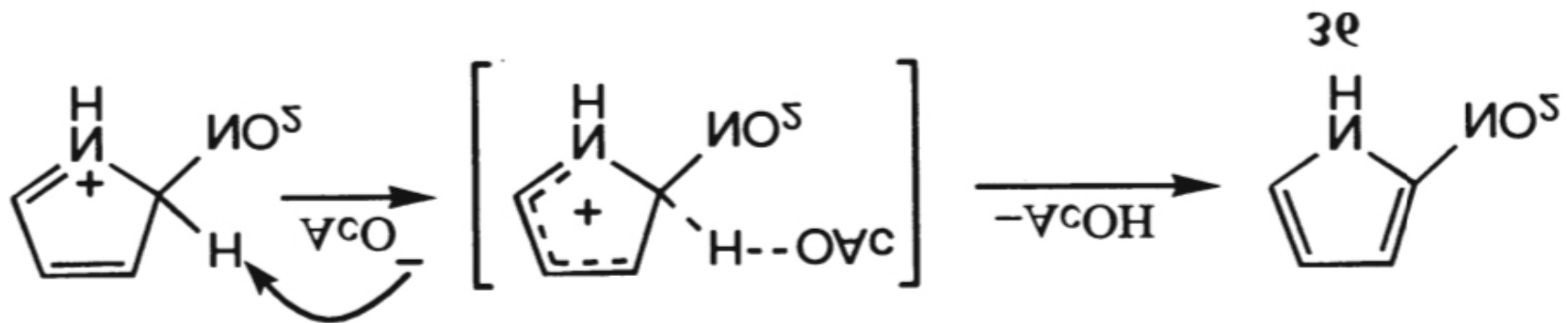# Nucleophilic Substitution Reactions
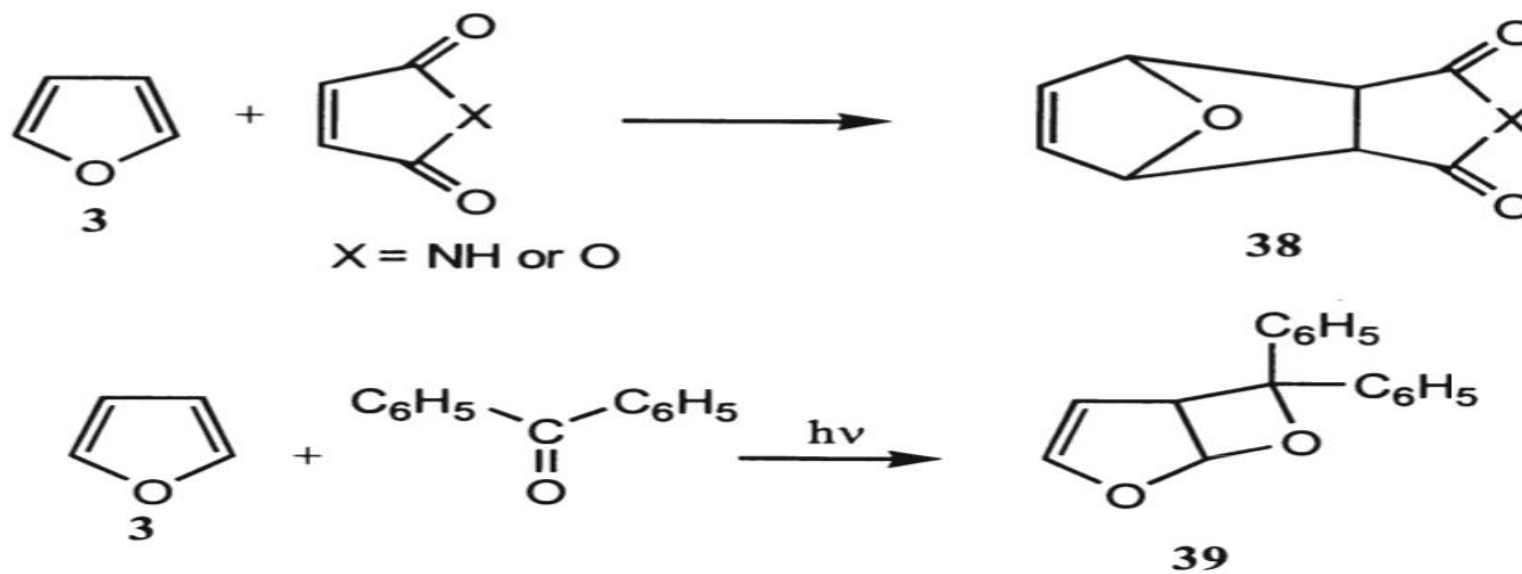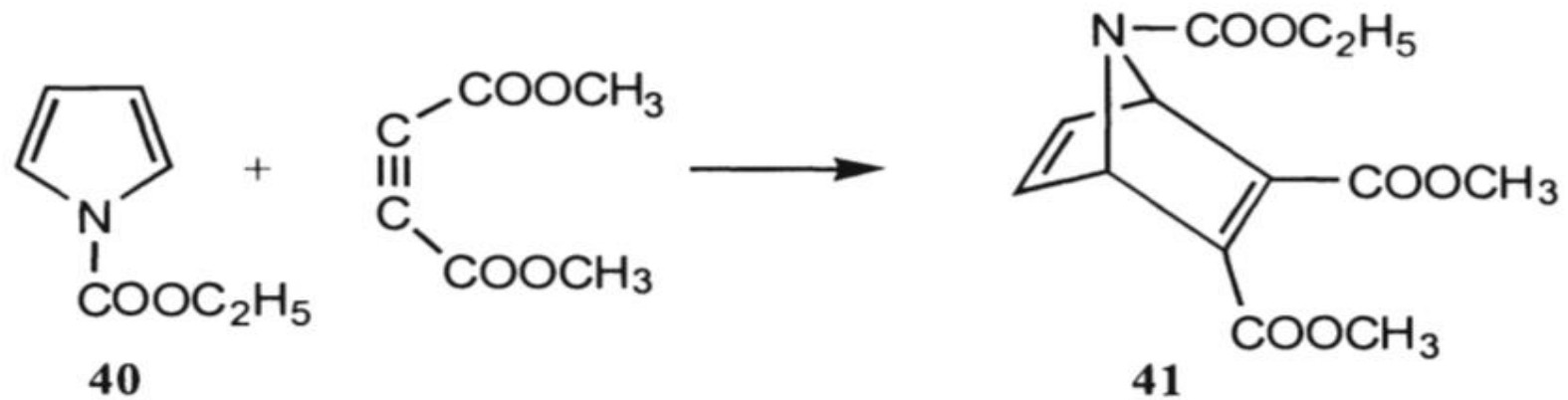

Scheme-12

Reduction

Scheme-13
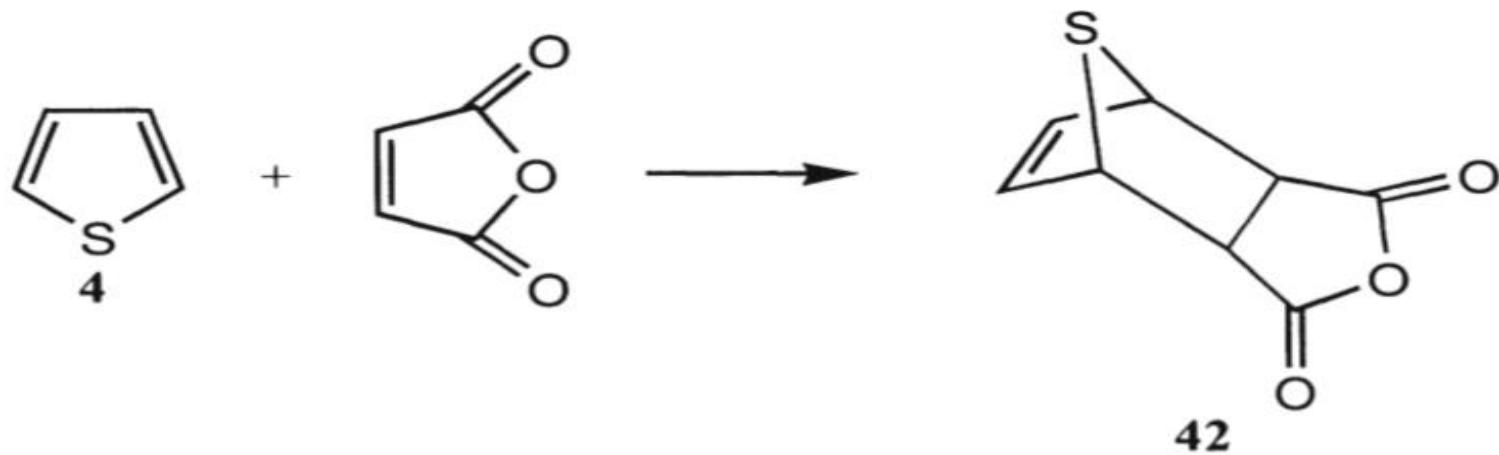
Scheme-14

AdditionReactions

Scheme-15

Scheme-16

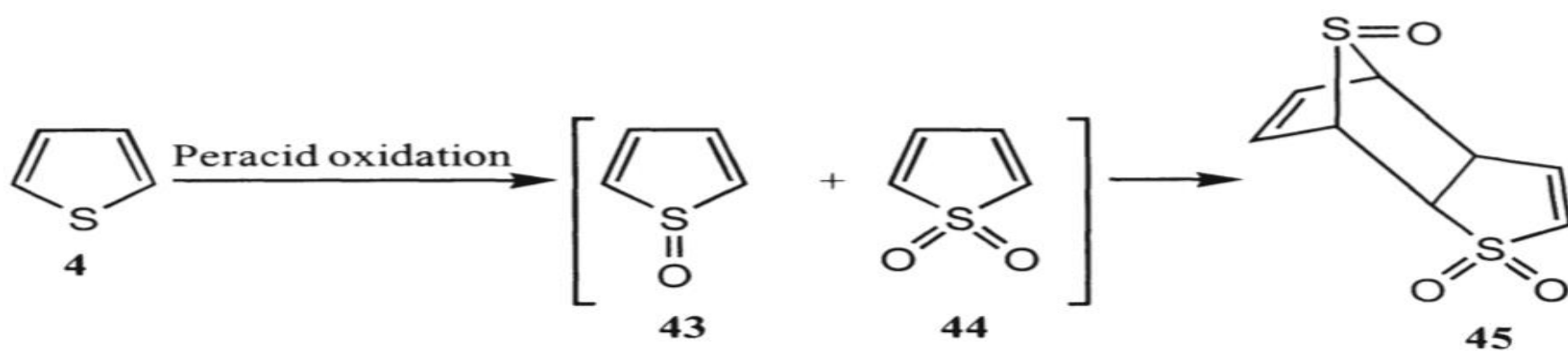# Cycloaddition Reactions

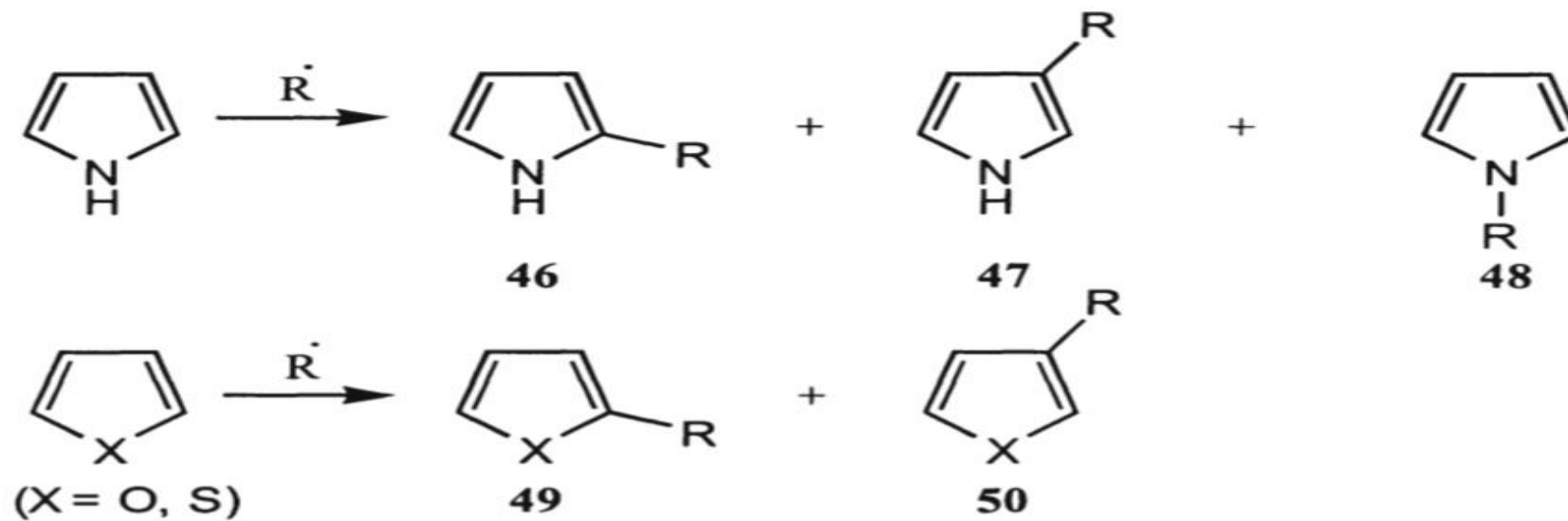X = NH or O
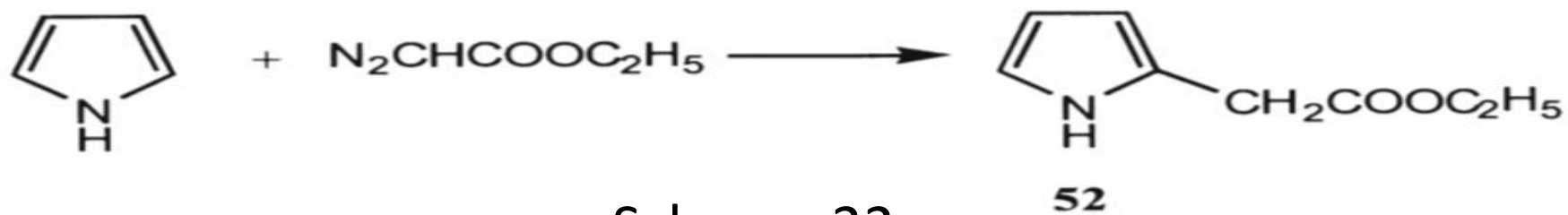
38

39

Scheme-17

Scheme-18

Scheme-19

Scheme-20

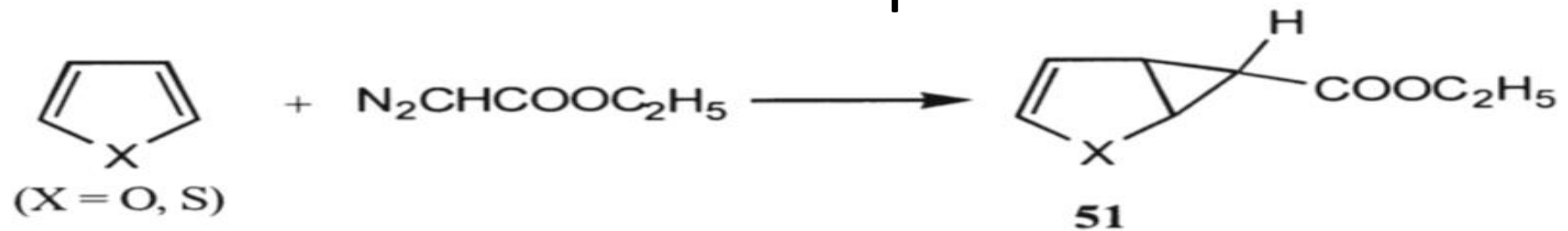# Reactions with Free Radicals

Scheme-21

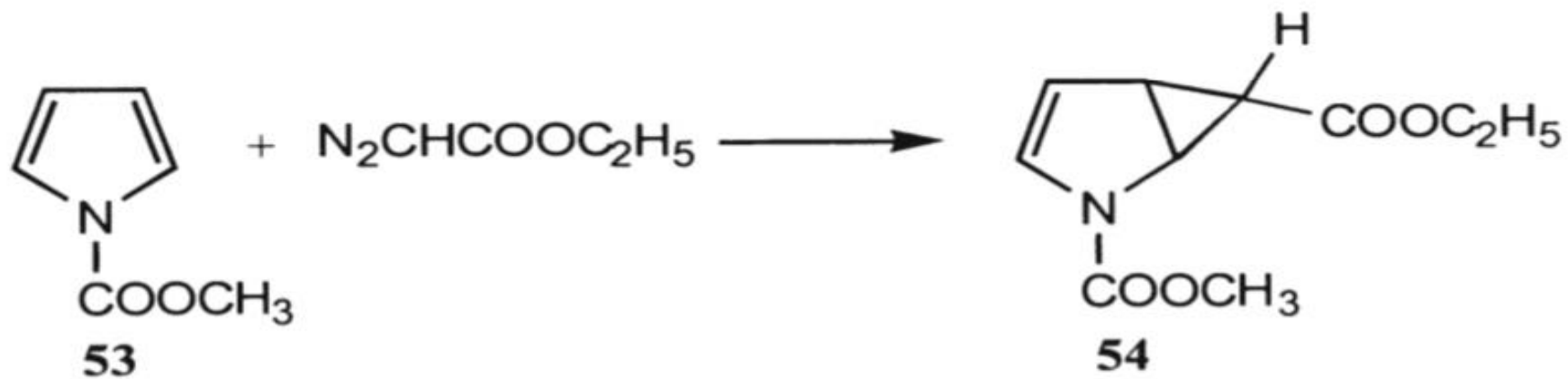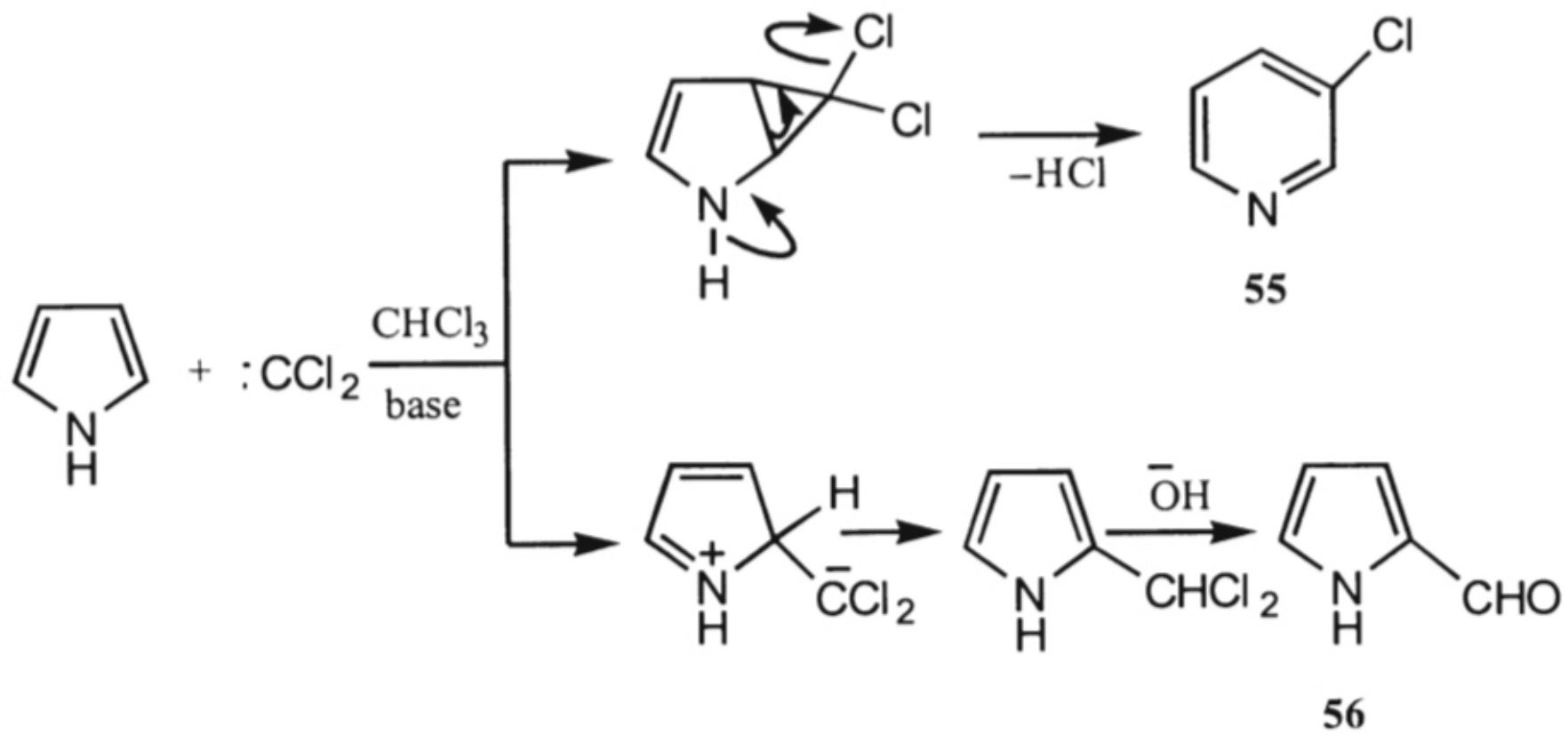# Reactions with Electron-Deficient Species

Scheme-22

Scheme-23

Scheme-24