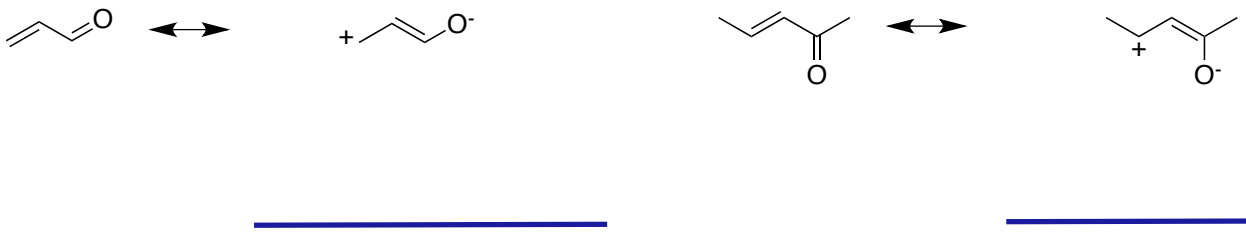
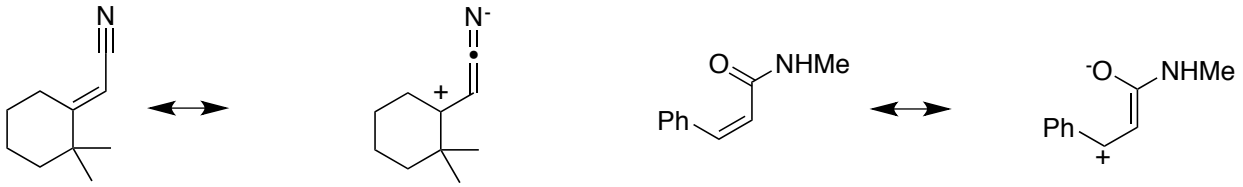
Conjugate Additions

from chapter(s) _____ in the recommended text

A. Introduction

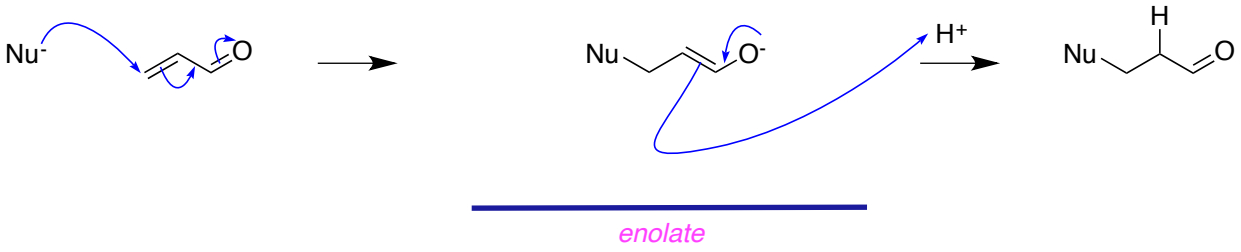
B. Polarization Of α,β-Unsaturated Carbonyl Compounds



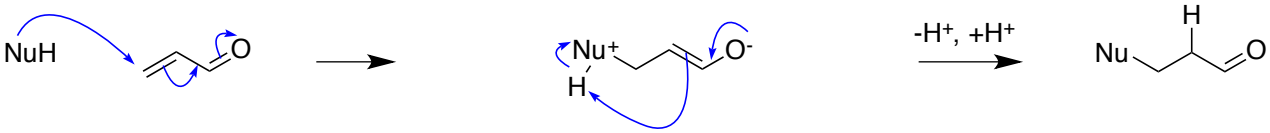


is
LUMO
more

C. Mechanisms Of Conjugated Addition



enolate



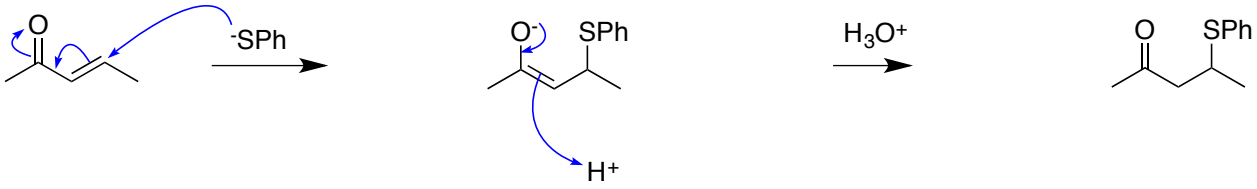
enolate

D. Examples Of Conjugate Additions

Amines And Thiols

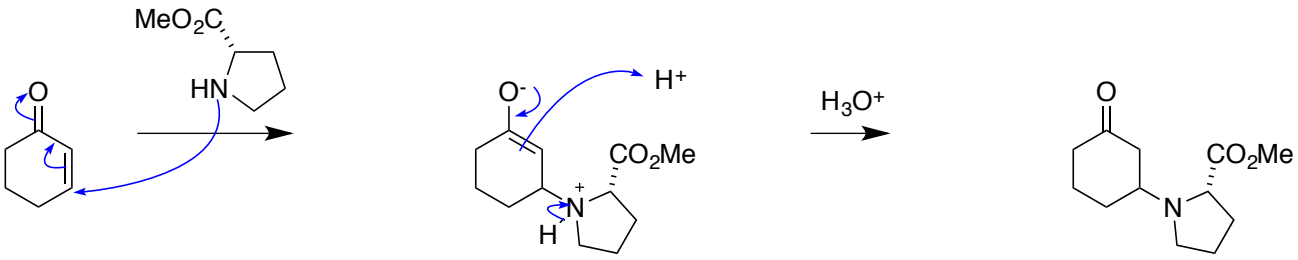
nucleophile

proton



enolate intermediate

1,4-addition product



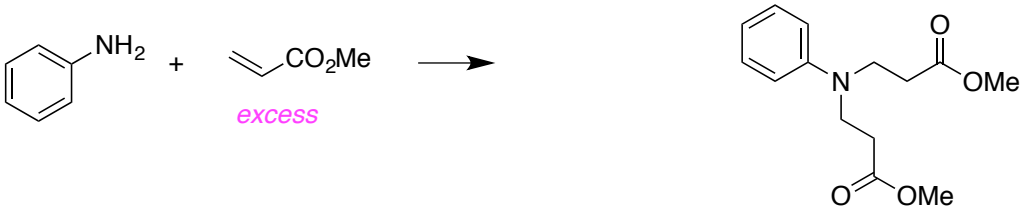
enolate intermediate

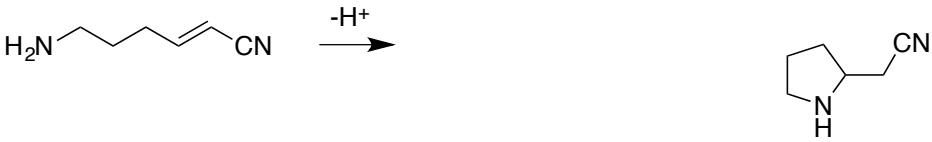
1,4-addition product


CO2Me
HSMe
SMe O
OMe

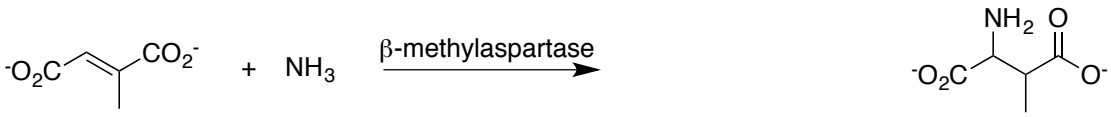

N
H
CONMe2
N
O
N

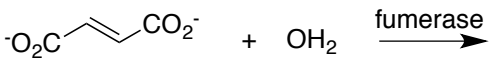

CO2Me
CO2Me
H2O
-H+
O
HO
OMe
CO2Me

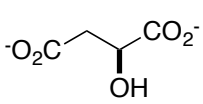




Enzyme-mediated Conjugated Additions

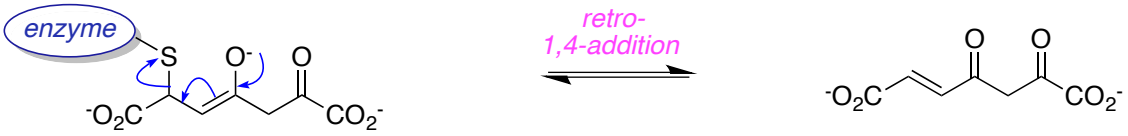






S-product

adduct

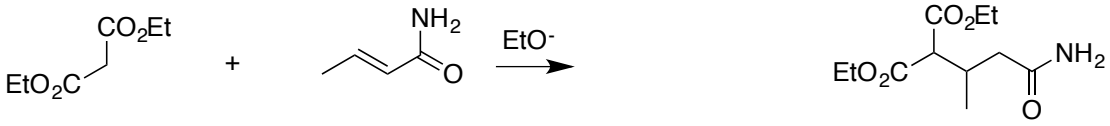


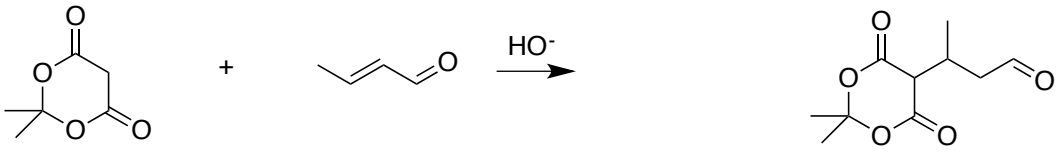
rotamer of initial adduct

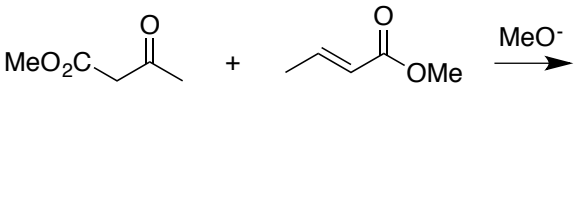
isomerized product

Stabilized *C*-Anion Nucleophiles

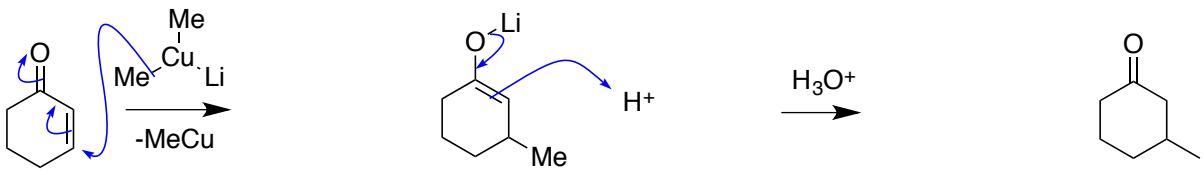
stoichiometric







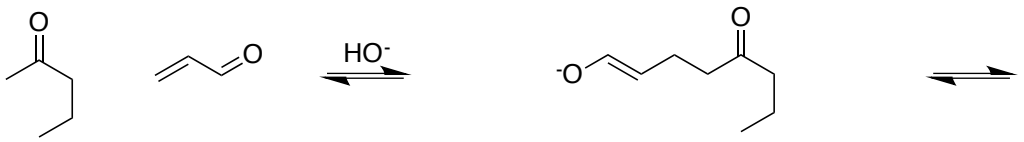
Organometallic Agents In Laboratory Chemistry



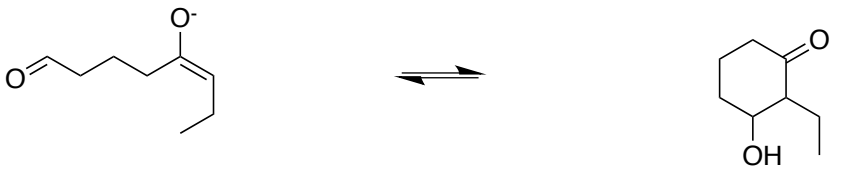
enolate intermediate

1,4-addition product

E. Conjugate Addition Then Aldol Condensation



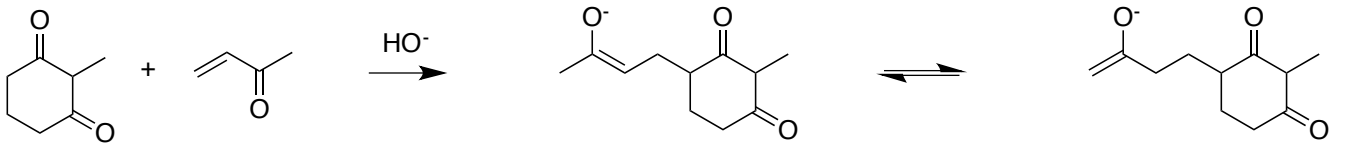
conjugate addition product



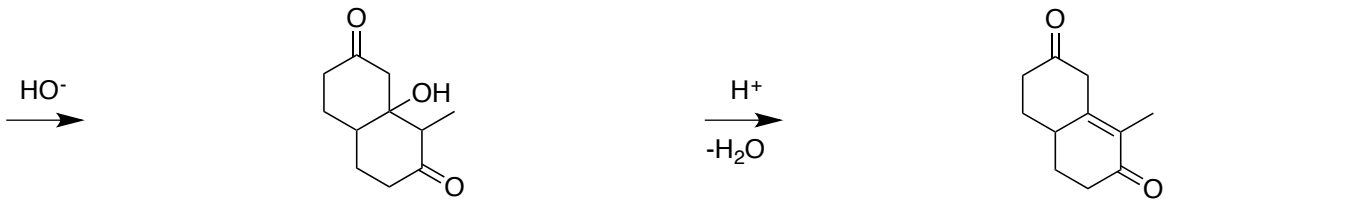
an enolate that can cyclize easily

cyclization product

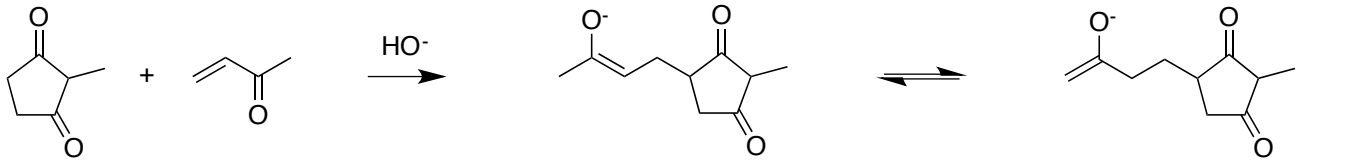
cyclic aldol/dehydration product



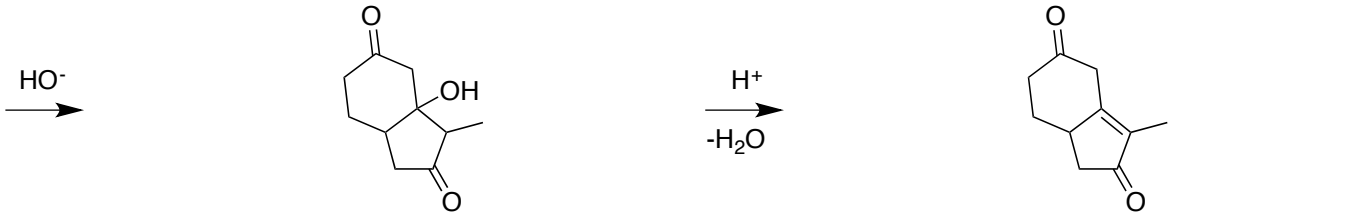
enolate from conjugate addition *terminal enolate*



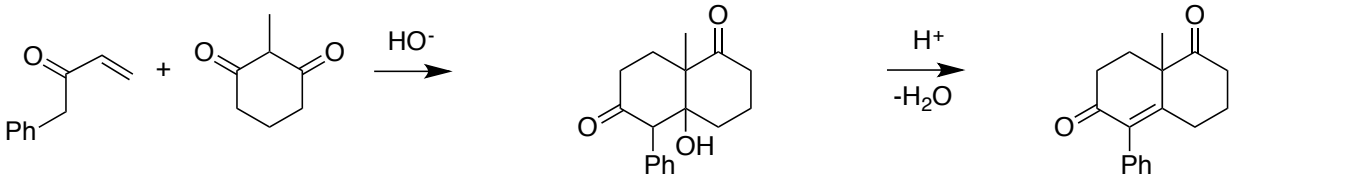
intramolecular cyclization product *enone*



enolate from conjugate addition *terminal enolate*

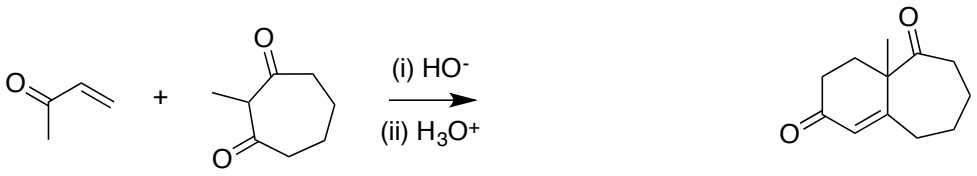


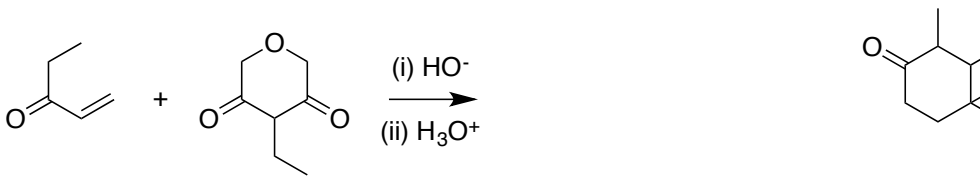
intramolecular cyclization product *enone*



intramolecular cyclization product

enone

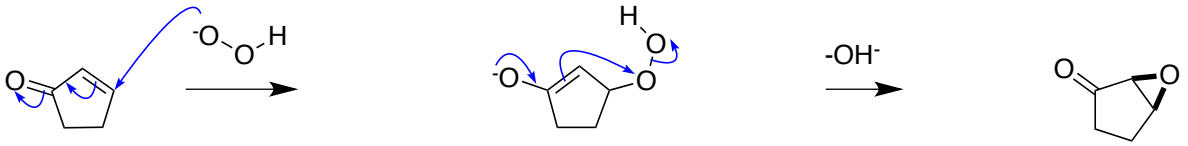




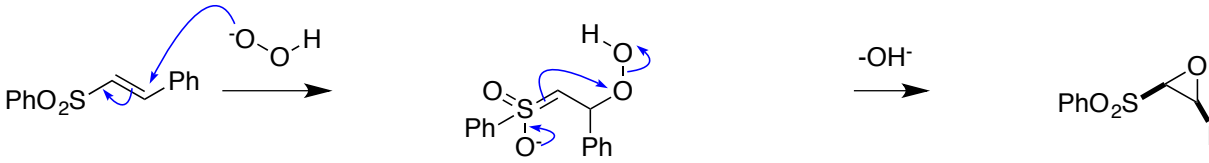
F. Nucleophilic Epoxidation

α-effect.

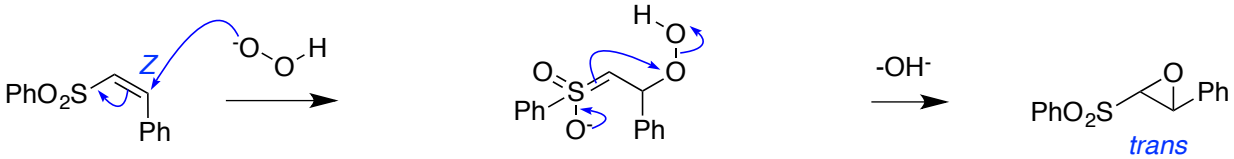
more



enolate intermediate *epoxide*



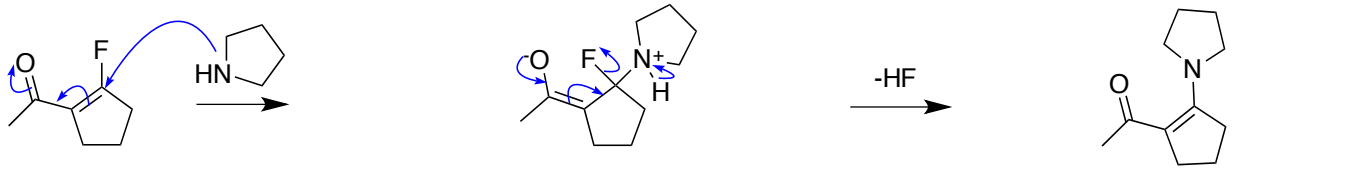
enolate *epoxide*



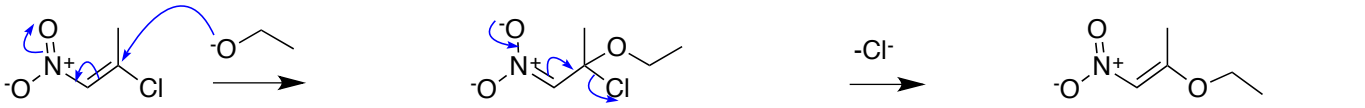
enolate intermediate

It *is not* possible

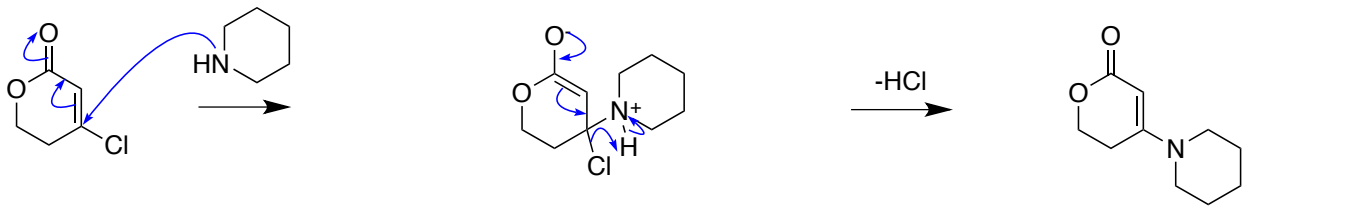
G. Addition Elimination Reactions



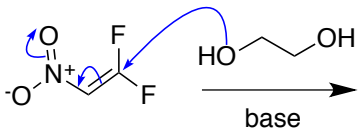
enolate *product*

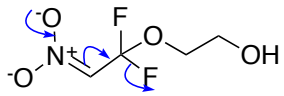


enolate *product*

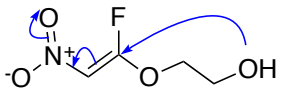


enolate *product*



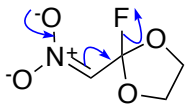


-F⁻

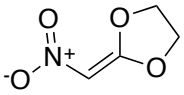


enolate *intermediate*

base

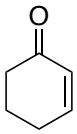


-F⁻

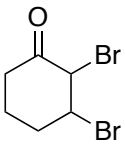


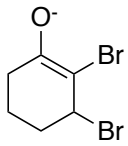
enolate *product*

Formation Of αBromo Enones



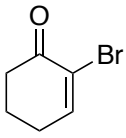
Br_2, base





dibromide intermediate *enolate*

-HBr



monobrominated product

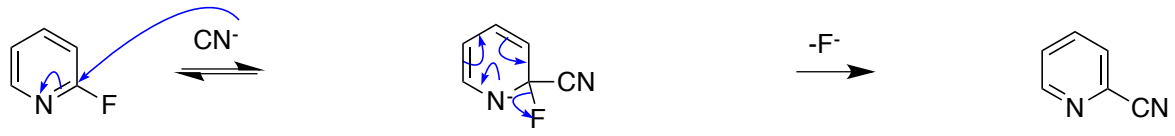
H. Nucleophilic Aromatic Substitution

S_NAr processes.

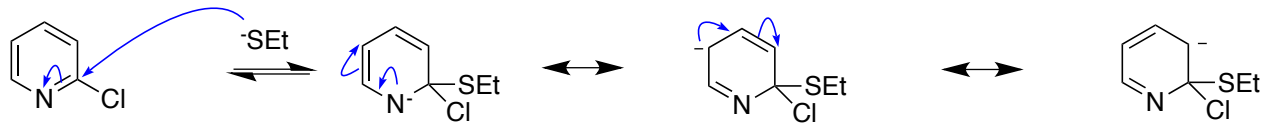
They involve *rate limiting*

anionic

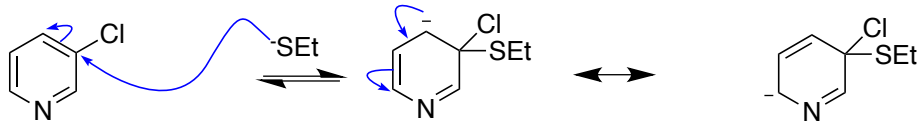
sp^3



2-chloropyridine



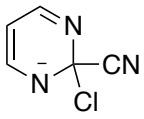
3-chloropyridine



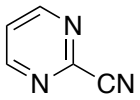
2-

2- and 4-

2-chloro-1,3-pyrimidine reacted with cyanide



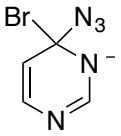
intermediate



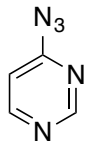
product

fast

4-bromo-1,3-pyrimidine reacted with azide



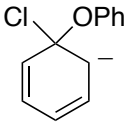
intermediate



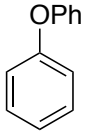
product

slow

chlorobenzene reacted with phenoxide



intermediate



product

slow