Organic chemistry

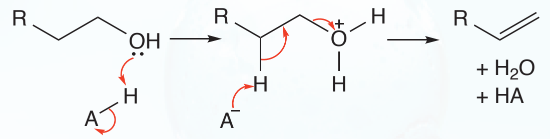
Reactions and mechanisms

William Stockburn gives an overview of reactions and mechanisms

Elimination (alcohol dehydration)

The first step is the protonation of the alcohol by the acid catalyst (H–A).

The second step is the leaving of the protonated alcohol group and the removal of a hydrogen atom, regenerating the acid catalyst:

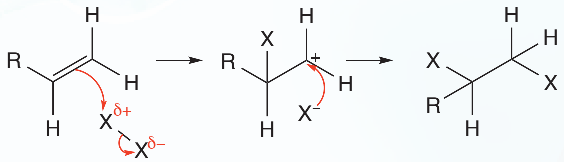


Electrophilic addition

Addition always takes place across the double bond.

X–X = F_2, Cl_2, Br_2 or I_2

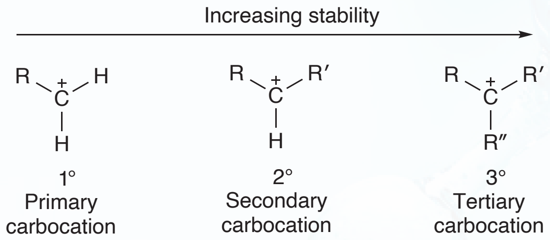
For this reaction X–X can also be H–F, H–Cl, H–Br or H–I:

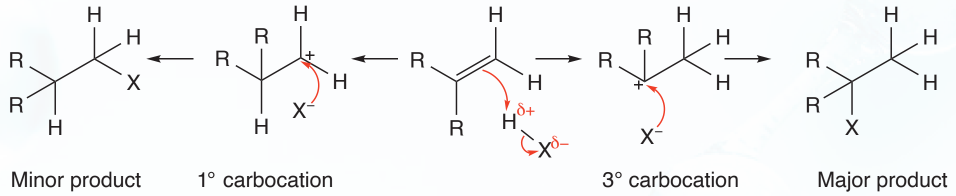


Major versus minor products

Unsymmetrical alkenes undergoing electrophilic addition produce two products – one major and one minor. The major/minor products are explained by the intermediate carbocation formed. The most stable carbocation intermediate leads to the major product.

The order of stability of carbocation intermediates is 3° > 2° > 1°:

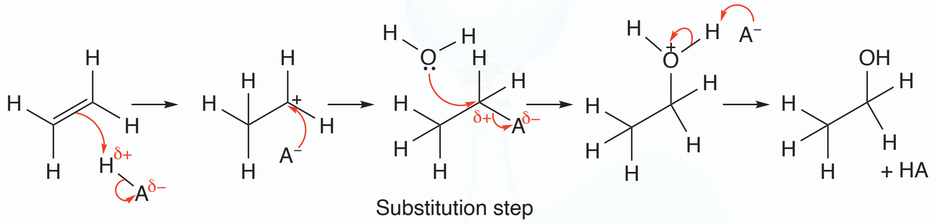




Hydration of ethene

This is an electrophilic addition mechanism with a substitution step in the middle.

H_2SO_4 is used as the acid catalyst (H–A):

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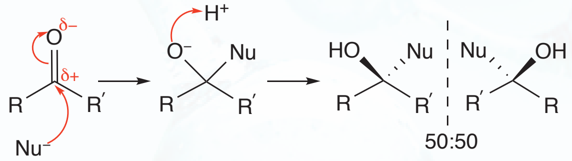
Nucleophilic reactions

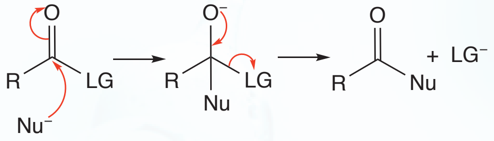
Nucleophilic addition



R = alkyl chain

Aldehyde R′ = H, ketone R′ = alkyl chain

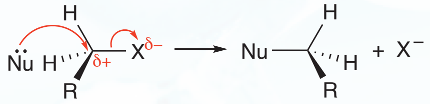
Nucleophilic addition–elimination



LG = leaving group (for example, Cl)

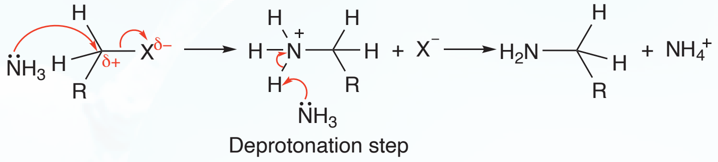
Nucleophilic substitution: general mechanism

A nucleophile attacks an electron-deficient carbon atom and the electron withdrawing group (X) leaves. The nucleophile must always have a spare pair of electrons it can donate to make the covalent bond:



Nucleophilic substitution: amine formation

When NH_3 or an amine (RNH_2 or R_2NH) is the nucleophile, there is an additional deprotonation step in the mechanism:



X = halogen

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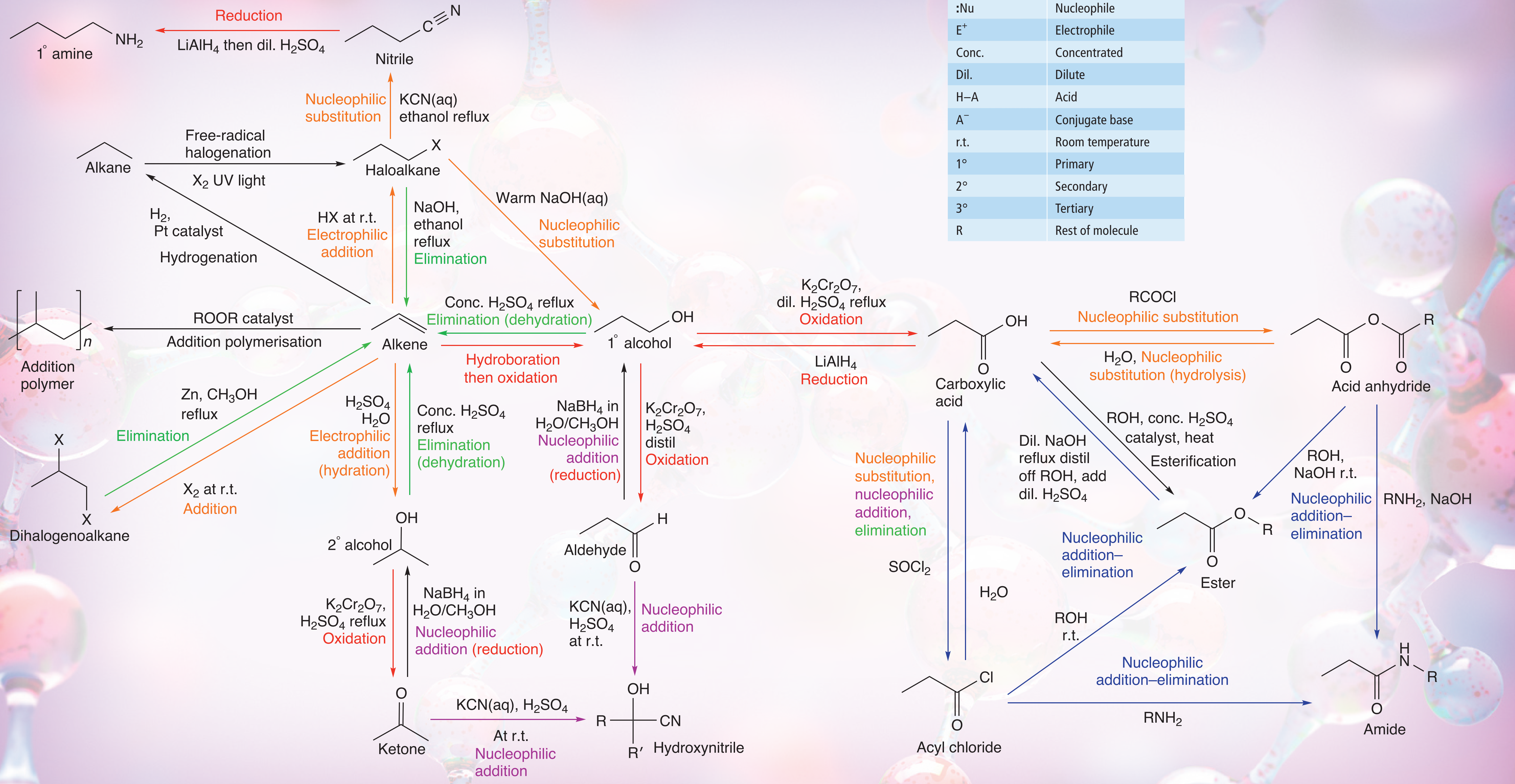
Chemistry review

Organic reactions overview

Key

Abbreviation	Meaning
:Nu	Nucleophile
E^+	Electrophile
Conc.	Concentrated
Dil.	Dilute
H–A	Acid
A^-	Conjugate base
r.t.	Room temperature
1°	Primary
2°	Secondary
3°	Tertiary
R	Rest of molecule



1° amine
NH_2
Reduction
$LiAlH_4$ then dil. H_2SO_4
Nitrile
C≡N
Nucleophilic substitution
KCN(aq) ethanol reflux

Alkane
Free-radical halogenation
X_2 UV light
Haloalkane
X

H_2, Pt catalyst
Hydrogenation

HX at r.t.
Electrophilic addition

NaOH, ethanol reflux
Elimination

Warm NaOH(aq)
Nucleophilic substitution

Addition polymer
n
ROOR catalyst
Addition polymerisation
Alkene

Conc. H_2SO_4 reflux
Elimination (dehydration)
1° alcohol
OH
Hydroboration then oxidation

$K_2Cr_2O_7$, dil. H_2SO_4 reflux
Oxidation
$LiAlH_4$
Reduction
Carboxylic acid
OH
O

RCOCl
Nucleophilic substitution
H_2O, Nucleophilic substitution (hydrolysis)
Acid anhydride
O
R
O
O

Dihalogenoalkane
X
X
Zn, CH_3OH reflux
Elimination
X_2 at r.t.
Addition

H_2SO_4 H_2O
Electrophilic addition (hydration)
Conc. H_2SO_4 reflux
Elimination (dehydration)

$NaBH_4$ in H_2O/CH_3OH
Nucleophilic addition (reduction)
$K_2Cr_2O_7$, H_2SO_4 distil
Oxidation

2° alcohol
OH
Aldehyde
H
O

$K_2Cr_2O_7$, H_2SO_4 reflux
Oxidation
$NaBH_4$ in H_2O/CH_3OH
Nucleophilic addition (reduction)

KCN(aq), H_2SO_4 at r.t.
Nucleophilic addition

Ketone
O
KCN(aq), H_2SO_4
At r.t.
Nucleophilic addition
Hydroxynitrile
OH
R
CN
R′

Nucleophilic substitution, nucleophilic addition, elimination
$SOCl_2$
H_2O

Dil. NaOH reflux distil off ROH, add dil. H_2SO_4
ROH, conc. H_2SO_4 catalyst, heat
Esterification
Nucleophilic addition–elimination
Ester
O
R
O

ROH, NaOH r.t.
Nucleophilic addition–elimination
RNH_2, NaOH

ROH r.t.
Acyl chloride
Cl
O
Nucleophilic addition–elimination
RNH_2
Amide
H
N
R
O

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