

1 Selected Nomenclature

A	Deprotonated acid
A-26	Amberlyst A-26 ion exchange resin
B:	Brønsted–Lowry base
BBN	9-borabicyclo[3.3.1]nonane
DCM	Dichloromethane
DMSO	Dimethyl sulfoxide, $(\text{CH}_3)_2\text{S}=\text{O}$
H — A	Brønsted–Lowry acid
mCPBA	<i>m</i> -chloroperoxybenzoic acid
NMO	<i>N</i> -methylmorpholine <i>N</i> -oxide
:Nu	Nucleophile
PCC	Pyridinium chlorochromate
R	Functional group
Tos	Tosyl, <i>p</i> -toluenesulfonyl, $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2^-$
X	Halogen
$\longleftrightarrow$	Resonance

2 Selected Reactions

Table 1: Preparation of Alcohols, Ethers, and Epoxides

Start	Type	Reagents	Mechanisms	Products
R — X	Substitution	H_2O	-X, +OH $\text{S}_{\text{N}}1$	Alcohol, X^-
		^-OH	-X, +OH $\text{S}_{\text{N}}2$	Alcohol, X^-
	Williamson	$^-\text{OR}'$	-X +OR' $\text{S}_{\text{N}}2$	Ether, X^-
HO — R — X	Intramolecular $\text{S}_{\text{N}}2$	B:	-X, -H $\text{S}_{\text{N}}2$	Epoxide, X^-

Table 2: Addition Reactions of Alkenes

Stereo	Type	Steps	Reagent	Mechanisms	Products
Syn	Hydroboration-oxidation	2	1. BH_3 or BBN 2. H_2O_2 , ^-OH	+OH, +H	Alcohol
Anti	Halogenation	2	X — X	+2X	Vicinal dihalide
	Halohydrin formation	3	X — X (Bridge)	+X, +OH	Halohydrin
Syn/Anti	Hydrohalogenation	2	H — X	+X, +H	Alkyl halide
	Hydration	3	1. H — OH 2. H_2SO_4	+OH, +H	Alcohol
		3	1. H — OR 2. H_2SO_4	+OR, +H	Ether

Table 3: Reactions Involving Acetylide Anions

Start	Reagents	Mechanisms	Products
Formation from term. alkyne	NaH or NaNH_2	-H	$\text{R} - \text{C} \equiv \text{C}^-$
Alkyl halide	$\text{R} - \text{C} \equiv \text{C}^-$	-X, +acetylide	$\text{R}' - \text{C} \equiv \text{C} - \text{R}$
Epoxide	1. $\text{R} - \text{C} \equiv \text{C}^-$ 2. H_2O	-H, +acetylide	Open ring, new C — C bond

Table 4: Reactions of Alcohols, Ethers, and Epoxides

Start	Type	Reagents	Mechanisms		Products
Alcohol	Dehydration	H ₂ SO ₄ or tosylic acid	-H, -OH, + π	E1 (2°, 3°), E2 (1°)	Trans alkene, H ₂ O
		1. POCl ₃ 2. pyridine	-H, -OH, + π	E2	Trans alkene, H ₂ O
	R — X	H — X or (1°): 1. ZnCl ₂ 2. HCl	-OH, +X	S _N 1 (2°, 3°), S _N 2 (1°)	Alkyl halide inv. (1°), rac. (3°)
		PBr ₃ or 1. SOCl ₂ 2. pyridine	-OH, +X	S _N 2	Alkyl halide (inv.)
	Alkyl tosylate	TosCl, pyridine	-H, +Tos	S _N 2 (:Nu ⁻), E2 (B ⁻)	R — O — Tos
Alkyl tosylate	Nucleophile	:Nu ⁻	-(O — Tos), +:Nu ⁻	S _N 2	R — Nu (inv.)
	Strong base	B ⁻	-H, -(O — Tos), + π	E2	Alkene
Ether	Cleavage	2 H — X	-H, +R, -H, +R'	S _N 1 or S _N 2	Alkyl halides, H ₂ O
Epoxide	Ring opening	1. :Nu ⁻ 2. H ₂ O	+H, +:Nu ⁻	S _N 2	Trans or anti products
		H — A	+H +A	S _N 1~S _N 2	

Table 5: Reduction and Oxidation Reactions

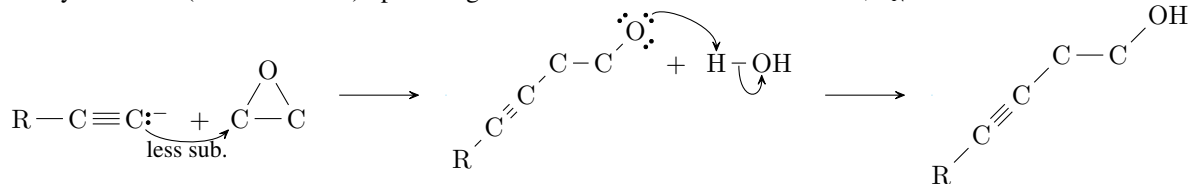
Start	Type	Reagents	Mechanisms	Products
Alkene	Reduction	H ₂ ; Pd, Pt, or Ni	- π , +2H	Syn alkane
	Ox. cleavage	1. O ₃ 2. Zn, H ₂ O or CH ₃ SCH ₃	- π , - σ , +2O	Ketone + aldehyde
		1. RCO ₃ H 2. H ₂ O	- π , +2OH	1,2-diol (anti)
	Dihydroxylation	KMnO ₄ , H ₂ O, HO ⁻ or 1. OsO ₄ , NMO 2. NaHSO ₃ , H ₂ O	- π , +2OH	1,2-diol (syn)
	Epoxidation	RCO ₃ H or mCPBA	- π , +2 σ , +O	Epoxide, carboxylic acid
Alkyne	Reduction	2H ₂ , Pd — C	-2 π , +4H	Syn alkane
		H ₂ , Lindlar	- π , +2H	Cis alkene
		Na, NH ₃	- π , +2H	Trans alkene
Internal alkyne	Ox. cleavage	1. O ₃ 2. H ₂ O	- π , - σ , +2OH	Carboxylic acids
Terminal alkyne		1. O ₃ 2. H ₂ O	- π , - σ , +2OH	Carboxylic acid, CO ₂
Alkyl halide	Reduction	1. LiAlH ₄ 2. H ₂ O	-X, +H	Alkane
Epoxide	Reduction	1. LiAlH ₄ 2. H ₂ O	+2H	Alcohol
1° Alcohol	Oxidation	PCC or HCrO ₄ ⁻	-2H, + π	Aldehyde
		CrO ₃ , H ₂ SO ₄ , H ₂ O	-2H, +O	Carboxylic acid
2° Alcohol	Oxidation	PCC or K ₂ Cr ₂ O ₇ , H ₂ SO ₄ , H ₂ O	-2H, + π	Ketone

3 Selected Mechanism Diagrams

3.1 Alkynes

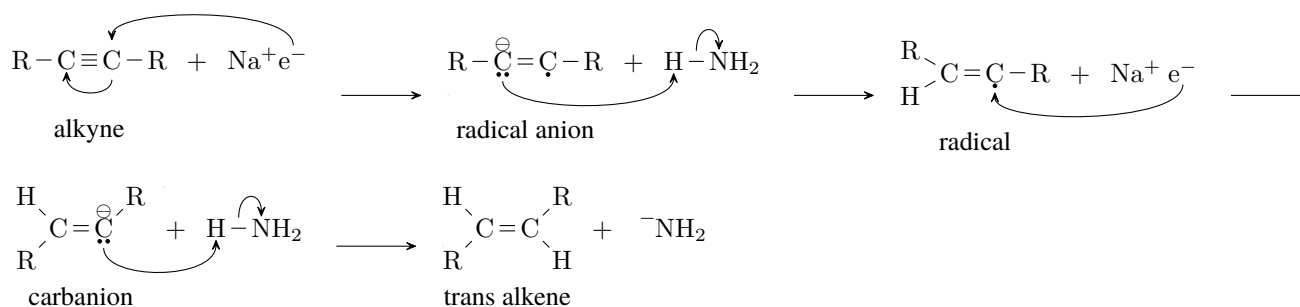
3.1.1 Opening Epoxide Ring with Acetylide Anion

Acetylide anion ($R-C\equiv C:^-$) opens ring and forms new carbon-carbon bond; S_N2 at less substituted end



3.1.2 Dissolving Metal Reduction of Alkyne to Trans Alkyne

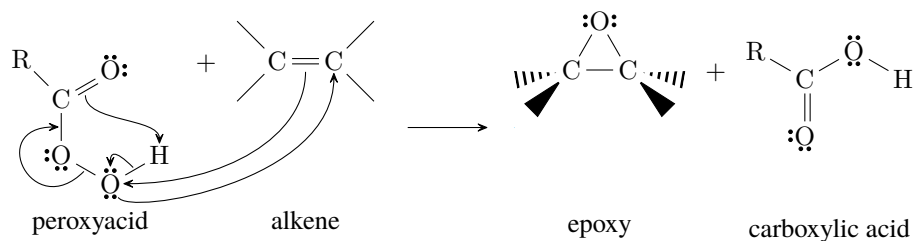
Na in NH_3 adds electron to triple bond followed by **anti addition** of H_2 to negative charge



3.2 Alkenes

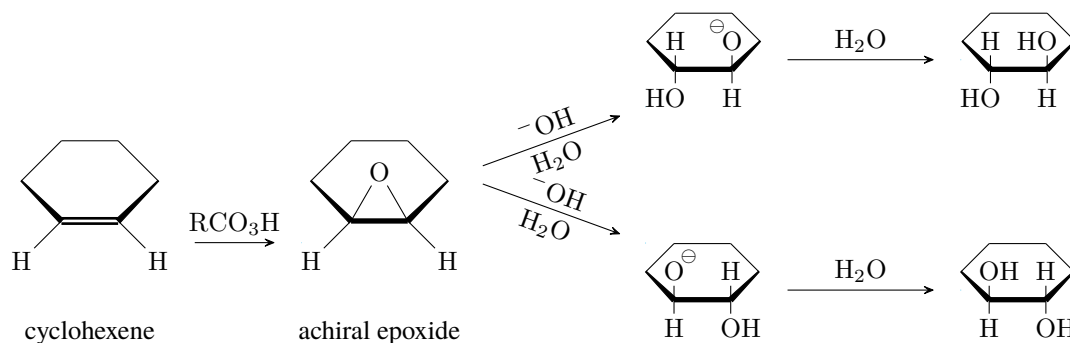
3.2.1 Epoxidation of an Alkene with a Peroxyacid

Syn addition of O to peroxyacid (RCO_3H); one step; stereospecific



3.2.2 Anti Dihydroxylation of Cyclohexene

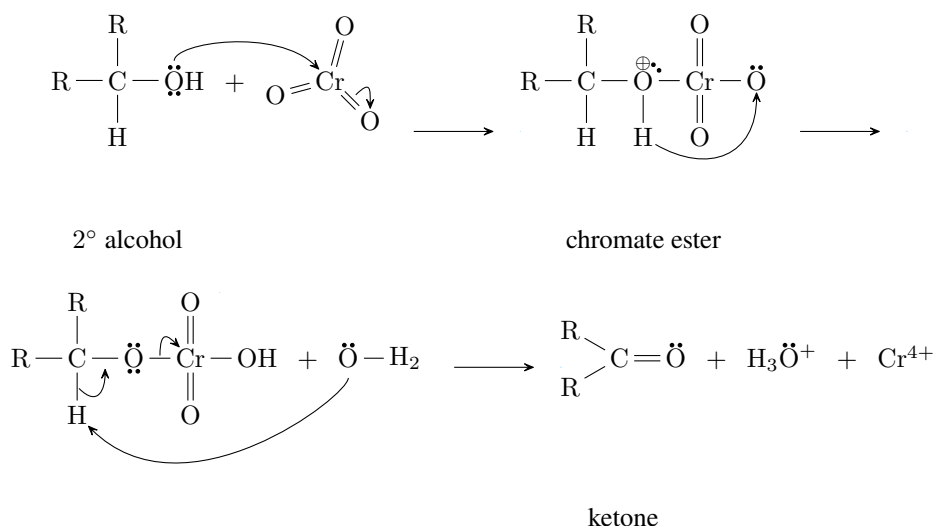
Epoxidation followed by opening of the ring forms *trans*-1,2-diols by **anti addition** of two OH groups



3.3 Alcohols

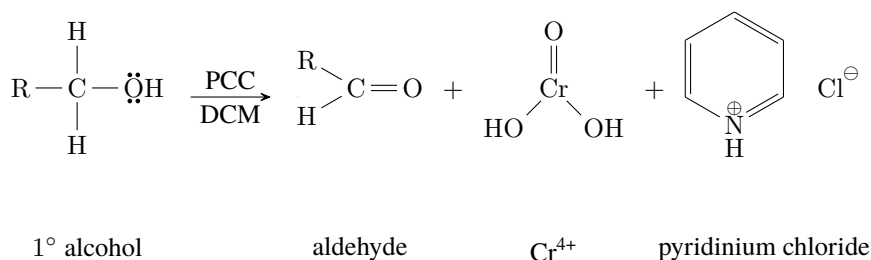
3.3.1 Oxidation of 2° Alcohol

Nucleophilic attack by CrO_3 (or PCC or A-26 resin) followed by proton transfer to form chromate ester, then removal of proton to oxidise carbon



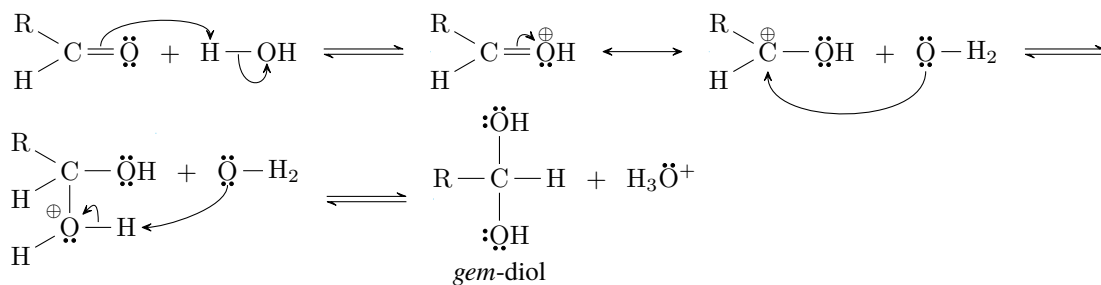
3.3.2 Oxidation of 1° Alcohol

Oxidation of a 1° alcohol by PCC in DCM or A-26 produces aldehyde



3.4 Hydration of Carbonyl Group

Carbonyl group is protonated by acid (such as H_2SO_4), followed by nucleophilic attack and then deprotonation to form a *gem*-diol (hydrate).



References

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