

SHORT NOTES ON ORGANIC CHEMISTRY



The organic chapters of Class 12 in NCERT order, then the Class 11 organic chapters — reactions, mechanisms, named reactions, tests and 214 solved examples

Haloalkanes and Haloarenes · Alcohols, Phenols and Ethers · Aldehydes, Ketones and Carboxylic Acids
· Amines · Biomolecules · Practical Organic Chemistry · Organic Chemistry: Some Basic Principles and
Techniques · Hydrocarbons

Short Notes on Organic Chemistry

for NEET (UG), JEE Main and JEE Advanced

MTA Team

First edition, 2026 · e-book

Price: ₹ 369

Published by **Master Testing Agency**, 401, Saket, Roorkee – 247667, Uttarakhand, India

www.mastertestingagency.com · support@mastertestingagency.com

This copy is for the personal study of the buyer. Do not share, resell or upload it anywhere.

© Master Testing Agency. All rights reserved. No part of this book may be copied, stored or sent in any form without written permission.

Numerical answers to the solved examples have been checked a second time by computer; the book is not printed if any of these checks fails. If you still find a mistake, please write to us.

CBSE, NCERT, JEE (Main) and JEE (Advanced) are conducted or published by the Central Board of Secondary Education, the National Council of Educational Research and Training, the National Testing Agency and the Indian Institutes of Technology. This book is an independent study aid and is not connected with any of them.

How to use these notes

These are revision notes: short, exact and complete. They are not a first textbook. Read a chapter of NCERT first; come here to fix every result in memory and to see how each one is used in a JEE question.

Order. Part I follows the organic chemistry chapters of the NCERT Class 12 textbook, in the same order. Part II then gives, in NCERT Class 11 order, the organic chapters of Class 11, which NEET, JEE Main and JEE Advanced also test.

In every chapter:

- boxed — key definitions and results, to be learnt by heart;
- red — shortcuts, traps and common mistakes;
- **Solved examples** — questions of the JEE type, each with a complete solution. Cover the solution, try the question, then check.

In the last week before the examination, reading only the boxes of every chapter is a complete revision of the syllabus.

MTA Team

Contents

How to use these notes	iii
I Class 12	1
1 Haloalkanes and Haloarenes	2
1.1 Classification, nomenclature and the C–X bond	2
1.2 Solvents and nucleophilicity	3
1.3 Preparation of haloalkanes	3
1.3.1 From alcohols	3
1.3.2 From hydrocarbons	5
1.3.3 Halogen exchange	5
1.4 Physical properties	5
1.5 Nucleophilic substitution: S_N2	6
1.6 Nucleophilic substitution: S_N1	7
1.7 Stereochemistry of substitution	8
1.8 Reactions of haloalkanes	9
1.9 Neighbouring group participation and allylic substitution	9
1.10 Elimination	11
1.11 Reactions with metals	11
1.12 Haloarenes: preparation	12
1.13 Haloarenes: chemical reactions	12
1.14 Polyhalogen compounds	14
2 Alcohols, Phenols and Ethers	15
2.1 Classification, nomenclature and structure	15
2.2 Preparation of alcohols	15
2.2.1 From alkenes	15
2.2.2 From alkyl halides	16
2.2.3 From carbonyl compounds, acids and esters: metal hydrides	16
2.2.4 From Grignard reagents	17
2.3 Preparation of phenols	19
2.4 Physical properties	19
2.5 Chemical reactions of alcohols	20
2.5.1 Acidic nature	20
2.5.2 Substitution of OH	20
2.5.3 Esterification	20
2.5.4 Dehydration	21
2.5.5 Oxidation	21
2.6 Chemical reactions of phenols	22

2.6.1	Acidity	22
2.6.2	Electrophilic substitution	23
2.6.3	Other reactions of phenol	24
2.7	Ethers	25
2.7.1	Preparation	25
2.7.2	Physical properties and electrophilic substitution	25
2.7.3	Cleavage of C–O bonds in ethers	25
3	Aldehydes, Ketones and Carboxylic Acids	27
3.1	Nomenclature and structure of the carbonyl group	27
3.2	Preparation of aldehydes and ketones	28
3.2.1	General methods	28
3.2.2	Aldehydes	28
3.2.3	Ketones	29
3.3	Physical properties	30
3.4	Nucleophilic addition reactions	30
3.4.1	Addition of HCN	31
3.4.2	Addition of sodium hydrogensulphite	31
3.4.3	Addition of alcohols: hemiacetals, acetals and ketals	31
3.4.4	Grignard reagents	32
3.4.5	Addition of ammonia and its derivatives	32
3.4.6	Addition of water	33
3.5	Reduction	33
3.6	Oxidation	34
3.6.1	Haloform reaction	35
3.7	Reactions due to α -hydrogen	35
3.7.1	Aldol condensation	36
3.8	Cannizzaro reaction and other named reactions	37
3.9	Carboxylic acids: preparation	38
3.10	Acidity of carboxylic acids	38
3.11	Reactions of carboxylic acids	39
3.12	Effect of heat on carboxylic acids	40
3.12.1	β -keto and β, γ -unsaturated acids	40
3.12.2	Dicarboxylic acids	41
3.12.3	Hydroxy acids	42
3.13	Tests and uses	43
4	Amines	44
4.1	Structure and classification	44
4.2	Nomenclature	44
4.3	Preparation of amines	45
4.3.1	1. Reduction of nitro compounds	45
4.3.2	2. Ammonolysis of alkyl halides (Hofmann's method)	45
4.3.3	3. Reduction of nitriles, isocyanides, amides and oximes	46
4.3.4	4. Gabriel phthalimide synthesis	46
4.3.5	5. Hofmann bromamide degradation and related rearrangements	47

4.4	Physical properties	49
4.5	Basic character	49
4.6	Chemical reactions	50
4.7	Diazonium salts	52
5	Biomolecules	56
5.1	Carbohydrates: classification	56
5.2	Configuration: D/L, the D-family, epimers	57
5.3	Glucose	58
5.4	Fructose	60
5.5	Disaccharides	61
5.6	Polysaccharides	62
5.7	Amino acids	63
5.8	Peptides and proteins	64
5.9	Enzymes	66
5.10	Vitamins	66
5.11	Nucleic acids	66
6	Practical Organic Chemistry	68
6.1	Tests for unsaturation and for alcohols	68
6.2	Tests for phenols	69
6.3	Tests for aldehydes, ketones and carboxylic acids	69
6.4	Tests for amines	70
6.5	Tests for biomolecules	71
6.6	Detection of elements	73
6.7	Quantitative analysis	74
6.8	Purification of organic compounds	76
II	Class 11 organic chapters	78
7	Organic Chemistry: Some Basic Principles and Techniques	79
7.1	Tetravalence of carbon and hybridisation	79
7.2	Structural representations	80
7.3	Classification of organic compounds	80
7.4	IUPAC nomenclature	81
7.5	Common names and their IUPAC names	82
7.5.1	Alkyl groups and alkanes	82
7.5.2	Alkenes, dienes and alkynes	83
7.5.3	Halogen compounds	83
7.5.4	Alcohols, phenols and ethers	83
7.5.5	Aldehydes and ketones	84
7.5.6	Carboxylic acids	84
7.5.7	Acid derivatives and nitrogen compounds	85
7.5.8	Aromatic compounds	85
7.5.9	Fused rings and other aromatic compounds	86
7.5.10	Heterocyclic compounds	87

7.5.11	Reagents, solvents and groups	87
7.6	Isomerism	88
7.7	Fundamental concepts of reaction mechanism	89
7.7.1	Reactive intermediates	90
7.8	Electronic displacements in a covalent bond	91
7.8.1	Inductive effect	91
7.8.2	Resonance (mesomeric) effect	91
7.8.3	Electromeric effect and hyperconjugation	91
7.8.4	Applications: acidity and basicity	92
7.9	Types of organic reactions	93
7.10	Methods of purification	94
7.11	Qualitative analysis	95
7.12	Quantitative analysis	96
8	Hydrocarbons	99
8.1	Classification	99
8.2	Reactive intermediates used in this chapter	99
8.3	Alkanes: preparation	100
8.4	Alkanes: properties	102
8.5	Conformations	105
8.6	Alkenes: structure and geometrical isomerism	107
8.7	Alkenes: preparation	110
8.8	Alkenes: reactions	111
8.9	Alkynes	113
8.10	Aromatic hydrocarbons: benzene and aromaticity	115
8.11	Electrophilic aromatic substitution	116
8.12	Carcinogenicity and toxicity	118

PART I

Class 12

Haloalkanes and Haloarenes

Replacing a hydrogen of an alkane or an arene by a halogen gives a haloalkane ($R-X$) or a haloarene ($Ar-X$). The polar $C-X$ bond makes haloalkanes the classic substrates for nucleophilic substitution (S_N1 , S_N2) and elimination ($E1$, $E2$); in haloarenes the same bond is strengthened by resonance, so they substitute only under forcing conditions or when activated by electron-withdrawing groups.

1.1 Classification, nomenclature and the $C-X$ bond

Classification

- By the number of halogen atoms: mono-, di-, tri-, ..., polyhalogen compounds.
- Halogen on an sp^3 carbon:** alkyl halides — primary (1°), secondary (2°), tertiary (3°) according to the carbon carrying X ; **allylic** halides (X on the carbon next to $C=C$, e.g. $CH_2=CH-CH_2Cl$); **benzylic** halides (X on the carbon next to an aromatic ring, e.g. $C_6H_5CH_2Cl$).
- Halogen on an sp^2 carbon:** **vinyl** halides (X on a $C=C$ carbon, $CH_2=CH-Cl$) and **aryl** halides (X on the ring, C_6H_5Cl).
- Dihalides: **geminal** (both X on one carbon, alkylidene halides, CH_3CHCl_2) and **vicinal** (X on adjacent carbons, alkylene dihalides, $ClCH_2CH_2Cl$).

Nomenclature

IUPAC names treat the halogen as a prefix (fluoro, chloro, bromo, iodo) on the longest chain, numbered so that the first substituent (alkyl or halogen alike) gets the lowest locant; prefixes are written in alphabetical order. Common names: alkyl group + halide.

Compound	Common name	IUPAC name
$CH_3CH_2CH(Cl)CH_3$	<i>sec</i> -butyl chloride	2-chlorobutane
$(CH_3)_3CCl$	<i>tert</i> -butyl chloride	2-chloro-2-methylpropane
$(CH_3)_2CHCH_2Cl$	isobutyl chloride	1-chloro-2-methylpropane
$CH_2=CHCH_2Br$	allyl bromide	3-bromoprop-1-ene
CH_2Cl_2 ; $CHCl_3$	methylene chloride; chloroform	dichloromethane; trichloromethane
$C_6H_5CH_2Cl$	benzyl chloride	(chloromethyl)benzene

For dihalobenzenes the common prefixes are *o*- (1,2), *m*- (1,3) and *p*- (1,4).

Nature of the $C-X$ bond

Halogen is more electronegative than carbon: $\overset{\delta+}{C}-\overset{\delta-}{X}$. Down the group the size of X grows, so the bond gets longer and weaker.

Bond	C-F	C-Cl	C-Br	C-I
Bond length in CH_3X (pm)	139	178	193	214
Bond enthalpy (kJ mol^{-1})	452	351	293	234
Dipole moment of CH_3X (D)	1.847	1.860	1.830	1.636

Dipole moment: $CH_3Cl > CH_3F > CH_3Br > CH_3I$ (in CH_3F the high charge separation is outweighed by the very short bond). The weaker the $C-X$ bond, the easier it breaks: reactivity $R-I > R-Br > R-Cl > R-F$.

Example 1.1 Give the IUPAC names of

(a) $(\text{CH}_3)_2\text{CHCH}(\text{Cl})\text{CH}_3$, (b) $\text{CH}_3\text{CH}=\text{C}(\text{Cl})\text{CH}_2\text{CH}(\text{CH}_3)_2$, (c) $(\text{CH}_3)_3\text{CCH}_2\text{CH}(\text{Br})\text{C}_6\text{H}_5$.

Solution. (a) The chain of four carbons carries Cl at C-2 and CH_3 at C-3. (b) Number from the end nearer the double bond: $\text{C}=\text{C}$ at C-2, Cl at C-3, CH_3 at C-5. (c) The chain runs from the CHBr carbon (C-1, bearing C_6H_5) to the *tert*-butyl end: Br at C-1, two methyls at C-3.

Answer: (a) 2-chloro-3-methylbutane; (b) 3-chloro-5-methylhex-2-ene; (c) 1-bromo-3,3-dimethyl-1-phenylbutane

1.2 Solvents and nucleophilicity

Kinds of solvent

- Polar protic solvents (PPS):** contain H bonded directly to an electronegative atom (O–H, N–H): H_2O , ROH, RCOOH , HCONH_2 (formamide). They solvate *both* cations and anions (anions by hydrogen bonding).
- Polar aprotic solvents (PAS):** polar, but with no H on an electronegative atom (the electronegative atom is bonded to C, S, P, ...): DMF $\text{HCON}(\text{CH}_3)_2$, DMSO $(\text{CH}_3)_2\text{S}=\text{O}$, acetone $(\text{CH}_3)_2\text{C}=\text{O}$, DMA $\text{CH}_3\text{CON}(\text{CH}_3)_2$, HMPA $[(\text{CH}_3)_2\text{N}]_3\text{P}=\text{O}$. They solvate cations well (through the negative O end) but leave anions almost bare (“naked”).
- Non-polar solvents:** alkanes, benzene, CCl_4 , etc.

Nucleophilicity

Nucleophilicity is the affinity of an attacking reagent for a positive centre (a carbon with low electron density); basicity is its affinity for H^+ .

- In PAS** the anion is free; the more concentrated its charge (smaller ion), the more reactive it is, so nucleophilicity follows basicity: $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ (stability of the anions: $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$).
- In PPS** small anions of high charge density are held by a shell of hydrogen-bonded solvent: solvation $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$, so high solvation means low nucleophilicity: $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$.

General trend	Basicity	Nucleophilicity
Along a period ($\text{CH}_3^- \rightarrow \text{NH}_2^- \rightarrow \text{OH}^- \rightarrow \text{F}^-$)	decreases	decreases
Down a group ($\text{F}^- \rightarrow \text{I}^-$, $\text{OH}^- \rightarrow \text{SH}^-$)	decreases	increases in PPS, decreases in PAS

Default solvent

If the solvent is not specified, assume a polar protic solvent. In PPS a larger, more polarisable nucleophile of the same group is better: $\text{SH}^- > \text{OH}^-$, $\text{I}^- > \text{Cl}^-$, $\text{RS}^- > \text{RO}^-$.

Example 1.2 Which is the better nucleophile in a polar protic solvent, OH^- or SH^- ? Which is the stronger base?

Solution. OH^- is small, with a high charge density, so it is strongly hydrogen bonded (solvated) by the protic solvent; SH^- is larger, less solvated and more polarisable. Basicity falls down the group (H_2S is the stronger acid), so OH^- is the stronger base.

Answer: SH^- is the better nucleophile; OH^- is the stronger base

1.3 Preparation of haloalkanes

From alcohols

Alcohol + HX



Mechanism for $2^\circ/3^\circ$ alcohols ($\text{S}_{\text{N}}1$): $\text{R-OH} \xrightarrow{\text{H}^+} \text{R-OH}_2^+ \xrightarrow{-\text{H}_2\text{O}} \text{R}^+ \xrightarrow{\text{X}^-} \text{R-X}$. A carbocation is formed, so

rearrangement is possible; electron-donating groups (which stabilise R^+) increase the rate. 1° alcohols react by S_N2 on $R-OH_2^+$.

- **HI**: no special condition needed. Made *in situ* from NaI/H_3PO_4 ; NaI/H_2SO_4 is *not* used, because conc. H_2SO_4 oxidises HI to I_2 .
- **HBr**: slight heating; $NaBr/H_3PO_4$ or $NaBr/H_2SO_4$ can be used.
- **HCl**: heating is needed; or dry HCl with a Lewis acid, i.e. conc. HCl /anhydrous $ZnCl_2$ (**Groove's process**).

Example 1.3 Name the reagent used in Groove's process and give the product from 2-methylpropan-2-ol and from ethanol.

Solution. Groove's process: conc. HCl with anhydrous $ZnCl_2$ (the Lewis acid helps $C-O$ cleavage). The 3° alcohol reacts at room temperature by S_N1 ; ethanol needs heating (S_N2 on the protonated alcohol).

Answer: $(CH_3)_3COH \longrightarrow (CH_3)_3CCl$; $CH_3CH_2OH \xrightarrow{\Delta} CH_3CH_2Cl$

Lucas test (conc. HCl + anhydrous $ZnCl_2$, Lucas reagent)

The alkyl chloride formed is insoluble and makes the solution turbid.

Alcohol	Mechanism	Observation at room temperature
3° (and benzylic, allylic)	S_N1	turbidity immediately
2°	S_N1	turbidity in about 5–7 minutes
1°	S_N2	no turbidity at room temperature (only on heating)

Example 1.4 Which of the following give immediate turbidity with Lucas reagent? (1) 2-methylpropan-2-ol; (2) propan-1-ol; (3) butan-2-ol; (4) 1-phenylethanol; (5) phenol; (6) 2-methylbutan-2-ol; (7) 1-cyclopropylethanol; (8) bicyclo[2.2.1]heptan-1-ol (OH at the bridgehead).

Solution. Immediate turbidity needs a stable carbocation. (1) and (6) give 3° cations; (4) gives a benzylic cation stabilised by resonance; (7) gives a cyclopropylmethyl cation, strongly stabilised by the bent $C-C$ σ bonds of the ring (" σ -resonance"). (2) is 1° (no turbidity), (3) is 2° (turbidity only after 5–7 min), (5) phenol does not react ($C-O$ has partial double-bond character and an aryl cation is very unstable), and (8) would need a bridgehead cation, which cannot become planar.

Answer: Four: (1), (4), (6) and (7)

Phosphorus halides and thionyl chloride

- **Red P/Br_2** (or red P/I_2) makes PBr_3 (PI_3) *in situ*: $3R-OH + PBr_3 \longrightarrow 3R-Br + H_3PO_3$ (three moles of alcohol per mole of PX_3).

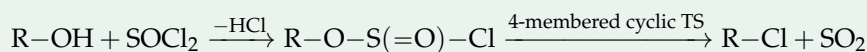
- $R-OH + PCl_3 \longrightarrow RCl + H_3PO_3$ (3:1); $R-OH + PCl_5 \longrightarrow R-Cl + HCl + POCl_3$.

With PX_3 and PX_5 the mechanism is S_N2 (the halide attacks the carbon of $R-O-PX_2$); formation of the strong $P=O$ bond is the driving force; a chiral alcohol gives the **inverted** halide.

Darzens process: $SOCl_2$



The alcohol attacks S to give an alkyl chlorosulfite $R-O-S(=O)Cl$ (and HCl). This loses SO_2 through a four-membered cyclic transition state in which the Cl is delivered from the *same side* as the departing O : S_Ni (internal nucleophilic substitution), with **retention** of configuration.

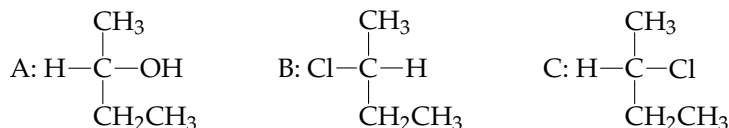


In the cyclic transition state the $C-O$ bond breaks while $C-Cl$ forms on the same face, so Cl takes the place of the old OH . Best method for alkyl chlorides: both by-products are gases, so the chloride is obtained pure and in high yield.

SOCl₂ with pyridine

If a base such as pyridine or R₃N is added, it takes up HCl; free Cl⁻ then attacks the chlorosulfite from the back: S_N2, **inversion**. SOCl₂ alone: retention; SOCl₂/pyridine: inversion.

Example 1.5 (R)-Butan-2-ol (Fischer projection A below) is treated with (i) PCl₃, (ii) PCl₅, (iii) SOCl₂, (iv) SOCl₂/pyridine. Give the product in each case.



Solution. (i) and (ii) are S_N2: inversion, so Cl takes the position opposite to the old OH: B, (S)-2-chlorobutane. (iii) S_Ni: retention: C, (R)-2-chlorobutane. (iv) S_N2: inversion: B.

Answer: (i), (ii), (iv): B, (S)-2-chlorobutane (inversion); (iii): C, (R)-2-chlorobutane (retention)

From hydrocarbons

Halogenation of alkanes and addition to alkenes

- **Free-radical halogenation:** CH₄ + Cl₂ $\xrightarrow{h\nu}$ CH₃Cl + HCl, continuing to CH₂Cl₂, CHCl₃, CCl₄. Gives mixtures of isomers; ease of H abstraction 3° > 2° > 1°. Not a good laboratory method.
- **HX to alkenes:** Markovnikov addition through the more stable carbocation: CH₃CH=CH₂ + HBr → CH₃CHBrCH₃. In the presence of a peroxide, HBr (only HBr) adds anti-Markovnikov (Kharasch effect): CH₃CH=CH₂ $\xrightarrow{\text{HBr}/(\text{PhCO})_2\text{O}_2}$ CH₃CH₂CH₂Br.
- **X₂ to alkenes:** CH₂=CH₂ + Br₂ $\xrightarrow{\text{CCl}_4}$ BrCH₂CH₂Br (vicinal dibromide; anti addition). Decolourisation of red-brown bromine solution is a test for C=C.

Example 1.6 How many structurally different monochloro products are formed by the free-radical chlorination of 2-methylbutane? How many of them are chiral?

Solution. 2-Methylbutane (CH₃)₂CHCH₂CH₃ has four kinds of H: the two equivalent CH₃ groups on C-2, the CH (C-2), the CH₂ (C-3) and the CH₃ at C-4. Products: 1-chloro-2-methylbutane (chiral C-2), 2-chloro-2-methylbutane, 2-chloro-3-methylbutane (chiral C-2) and 1-chloro-3-methylbutane.

Answer: 4 constitutional isomers, of which 2 are chiral (so 6 products counting each enantiomer)

Halogen exchange

Finkelstein and Swarts reactions

- **Finkelstein:** R-X + NaI $\xrightarrow{\text{dry acetone}}$ R-I + NaX↓ (X = Cl, Br; S_N2). NaI is soluble in dry acetone (it is fairly covalent), while NaCl and NaBr are ionic and insoluble; their precipitation drives the equilibrium forward (Le Chatelier). Without dry acetone the reaction does not proceed.
- **Swarts:** R-X + AgF → R-F + AgX↓ (also with Hg₂F₂, CoF₂, SbF₃). Best method for alkyl fluorides.

1.4 Physical properties

Boiling point, density, solubility

- Boiling point ∝ molecular mass and ∝ $\frac{1}{\text{branching}}$; for the same alkyl group: R-I > R-Br > R-Cl > R-F (larger, more polarisable halogen, stronger van der Waals forces). Haloalkanes boil higher than alkanes of

similar mass (dipole–dipole forces).

- Density increases with the number of halogens and their atomic mass: CH_2Cl_2 (1.336) < CHCl_3 (1.489) < CCl_4 (1.595 g mL⁻¹); bromo and iodo compounds, and polychloro compounds, are denser than water.
- Only slightly soluble in water (the energy to break water's hydrogen bonds is not recovered), soluble in organic solvents.

Melting point and symmetry

The more symmetrical isomer packs better in the crystal lattice, so its melting point is higher (typically the isomer in which the bond dipoles cancel): *p*-dichlorobenzene (m.p. 326 K) > *o*- (256 K) and *m*-dichlorobenzene (249 K); *trans*-but-2-ene > *cis*-but-2-ene; 1,2,4,5-tetrachlorobenzene > 1,2,3,4-tetrachlorobenzene.

Example 1.7 Arrange in increasing order of boiling point: (a) 1-chloropropane, (b) 2-chloropropane, (c) 1-chlorobutane.

Solution. (c) has the largest molecular mass; of the two isomers of mass 78.5, the branched (b) has the smaller surface area and weaker van der Waals forces.

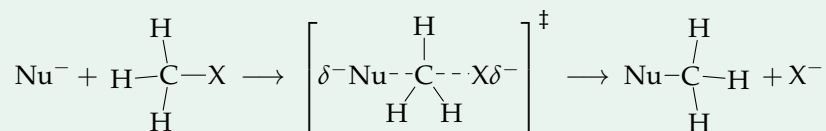
Answer: (b) < (a) < (c), i.e. b.p. order c > a > b

1.5 Nucleophilic substitution: S_N2

Types of nucleophilic substitution met in JEE

S_N1, S_N2, S_Ni (internal, SOCl₂), S_N1' and S_N2' (allylic, with shift of the double bond), S_Ni', S_NNGP (neighbouring group participation), S_NAE (addition–elimination), S_N2Ar (aromatic, through the Meisenheimer complex) and S_N1Ar (aromatic, through an aryl cation, e.g. diazonium salts).

S_N2: bimolecular nucleophilic substitution



- One step; no intermediate. The nucleophile attacks from the side *opposite* to the leaving group (back-side attack).
- Rate = $k[\text{RX}][\text{Nu}^-]$ (second order); e.g. rate = $k[\text{CH}_3\text{Br}][\text{OH}^-]$.
- In the transition state the carbon is sp²-like with five groups around it (about 10 electrons): partial bonds to Nu and X lie along a line, the other three groups are in a plane — a crowded, very unstable TS.
- **Walden inversion:** the configuration is inverted, like an umbrella turned inside out. R/S labels may or may not change (they depend on priorities, not on geometry).

Factors favouring S_N2

1. High concentration of nucleophile (rate depends on [Nu⁻]).
2. Strong nucleophile; polar aprotic solvent (anion not solvated).
3. Little steric hindrance: $\text{CH}_3\text{X} > 1^\circ > 2^\circ > 3^\circ$ (3° practically does not react by S_N2); branching at the β-carbon also slows it (neopentyl halides are very slow).
4. Good leaving group: $\text{R-I} > \text{R-Br} > \text{R-Cl} > \text{R-F}$.
5. An adjacent π system or electron-withdrawing C=O group (benzylic, allylic, α-halo ketones RCOCH_2X) speeds up S_N2 by delocalising the electron density of the crowded transition state.

Example 1.8 Arrange in decreasing order of S_N2 reactivity: (a) C₆H₅COCH₂Cl, (b) CH₃Cl, (c) CH₃CH₂Cl, (d) (CH₃)₃CCl.

Solution. (a) is a primary halide next to C=O: the electron-withdrawing carbonyl group (conjugated with the transition state) makes α-halo ketones extremely reactive. Then the least hindered CH₃Cl, then the 1° ethyl chloride, which is bulkier; the 3° halide is the slowest.

Answer: $a > b > c > d$

Example 1.9 Arrange in decreasing order of S_N2 reactivity: (a) $C_6H_5CH_2Cl$, (b) CH_3CH_2Cl , (c) $CH_2=CHCH_2Cl$.

Solution. In the benzylic and allylic transition states the π system overlaps with the p orbital of the reacting carbon, dispersing electron density and stabilising the TS; the phenyl ring does this more effectively than a vinyl group. Ethyl chloride has no such help.

Answer: $a > c > b$

Example 1.10 Arrange in decreasing order of rate of S_N2 reaction of CH_3CH_2Br in aqueous ethanol with (a) 1 M NaOH, (b) 2 M NaOH, (c) 2 M NaSH.

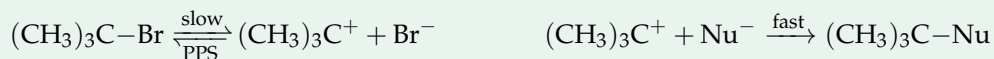
Solution. Rate = $k[RBr][Nu^-]$: doubling $[OH^-]$ doubles the rate, so $b > a$. At the same concentration SH^- is the better nucleophile in a protic solvent (less solvated), so $c > b$.

Answer: $c > b > a$

1.6 Nucleophilic substitution: S_N1

S_N1 : unimolecular nucleophilic substitution

Occurs in polar protic solvents of high dielectric constant (H_2O , EtOH, ROH, RCOOH), which ionise the C–X bond and solvate the ions.



- Two steps; the rate-determining step is ionisation to a planar (sp^2) carbocation. Rate = $k[RX]$, independent of $[Nu^-]$.
- Nucleophile attacks the planar carbocation from either face: a chiral substrate gives **racemisation** (in practice with some excess of inversion). Rearrangement of the carbocation (hydride or methyl shift) is possible.
- Rate $\propto$ ease of C–X dissociation: $R-I > R-Br > R-Cl > R-F$.
- Rate $\propto$ stability of the carbocation: benzylic, allylic, $3^\circ > 2^\circ > 1^\circ > CH_3$.

Two finer points for S_N1 orders

- For halides of the *same degree*, more branching near the C–X carbon means more crowding (more repulsion felt by the leaving group); ionisation relieves this strain, so the C–X bond breaks more easily: rate of S_N1 increases with branching.
- Judge the rate by the carbocation formed *just after* C–X breaks, not by the rearranged one (rearrangement happens after the rate-determining step).

Example 1.11 Arrange in decreasing order of S_N1 reactivity: (1) 2-chloro-2-methylpropane, (2) 2-chlorobutane, (3) 1-chlorobutane, (4) 1-chloro-2-methylpropane.

Solution. $3^\circ > 2^\circ > 1^\circ$. Among the two primary halides, (4) is more branched next to the C–Cl carbon; by the rule above it ionises more easily than (3). (The primary cation formed first is what counts, even though it would rearrange to the 3° cation.)

Answer: $1 > 2 > 4 > 3$

Example 1.12 Arrange in decreasing order of S_N1 reactivity: (1) $C_6H_5CH(Cl)CH_3$, (2) $(CH_3)_3CCl$, (3) $(CH_3)_2CHCl$.

Solution. (1) gives a 2° benzylic cation, stabilised by resonance with the ring: here this 2° cation is more stable than the 3° *tert*-butyl cation (hyperconjugation only). (3) gives a simple 2° cation.

Answer: $1 > 2 > 3$

Halides that undergo neither S_N1 nor S_N2

Aryl halides (X directly on a benzene ring), vinyl halides (X directly on a C=C carbon) and bridgehead halides (e.g. 1-chlorobicyclo[2.2.1]heptane). Reasons: partial double-bond character of C–X and sp^2 carbon (aryl, vinyl); the cation would be very unstable (aryl, vinyl) or could not become planar (bridgehead); back-side attack is blocked by the ring (aryl, bridgehead).

S_N1 or S_N2 ?

	S_N1	S_N2
Order	first: rate = $k[RX]$	second: rate = $k[RX][Nu^-]$
Substrate	$3^\circ > 2^\circ > 1^\circ$	$CH_3 > 1^\circ > 2^\circ > 3^\circ$
Solvent	polar protic	polar aprotic
Nucleophile	weak (H_2O , ROH) is enough	strong, concentrated
Stereochemistry	racemisation	inversion
Rearrangement	possible	never
Benzylic and allylic halides react fast by <i>both</i> mechanisms.		

1.7 Stereochemistry of substitution

Optical activity and chirality

- Plane-polarised light** vibrates in one plane (produced by a Nicol prism). Optically active compounds rotate this plane, as measured in a polarimeter: **dextrorotatory** (*d*, +, clockwise) or **laevorotatory** (*l*, –, anticlockwise).
- Optical activity comes from molecular **asymmetry**. An object not superimposable on its mirror image is **chiral**; a carbon with four different groups is a **stereocentre** (asymmetric carbon), e.g. C-2 of butan-2-ol and of 2-chlorobutane.
- Enantiomers**: non-superimposable mirror images. Same physical properties except the sign of rotation (equal and opposite).
- Racemic mixture** (*dl* or $\pm$): equal amounts of the two enantiomers; zero net rotation (external compensation). Conversion of an enantiomer into a racemic mixture is **racemisation**.
- Retention**: the spatial arrangement of bonds at the stereocentre is the same in product and reactant; **inversion**: the product has the opposite (mirror) arrangement. A molecule with *n* stereocentres has at most 2^n stereoisomers (fewer when a meso form exists).

Example 1.13 How many stereoisomers does 2,3-dichlorobutane have? Which of them are optically active?

Solution. Two stereocentres: at most $2^2 = 4$. But the (2*R*,3*S*) form has a plane of symmetry (the two halves are alike), so (2*R*,3*S*) $\equiv$ (2*S*,3*R*) is one meso compound. Total = $4 - 1$.

Answer: 3: the optically active pair (2*R*,3*R*) and (2*S*,3*S*), and the inactive meso form

Example 1.14 R–Br is converted into *trans*-1-chloro-3-methylcyclohexane by the sequence (i) NaOH, (ii) PCl_5 , (iii) NaI/acetone, (iv) NaOH, (v) $SOCl_2$ /pyridine, each step being an S_N2 substitution. Identify R–Br.

Solution. Every step is S_N2 at the same carbon, so each inverts it: five inversions give a net inversion. Working backwards from the product (Cl *trans* to CH_3): $SOCl_2$ /py (inversion) came from the *cis* alcohol; NaOH from the *trans* iodide; NaI from the *cis* chloride; PCl_5 from the *trans* alcohol; NaOH from the *cis* bromide.

Answer: *cis*-1-bromo-3-methylcyclohexane (Br on the same side as CH_3)

1.8 Reactions of haloalkanes

Precipitation and affinities

- Ag^+ has a high affinity for halide: AgCl white, AgBr pale yellow, AgI yellow precipitates; it pulls X off ($\text{S}_{\text{N}}1$ -like character).
- Zn and P have a high affinity for oxygen ($\text{P}=\text{O}$ in the PX_3/PX_5 reactions).

Substitution products of R-X

Reagent	Product	Remark
NaOH/KOH (aq)	$\text{R}-\text{OH}$	$\text{S}_{\text{N}}2$ (1° , 2°)
H_2O	$\text{R}-\text{OH} + \text{HX}$	$\text{S}_{\text{N}}1$ (2° , 3°)
moist Ag_2O (AgOH)	$\text{R}-\text{OH} + \text{AgX} \downarrow$	
dry Ag_2O	$\text{R}-\text{O}-\text{R}$	$2\text{RX} + \text{Ag}_2\text{O} \longrightarrow \text{R}_2\text{O} + 2\text{AgX}$
$\text{R}'\text{ONa}$	$\text{R}-\text{O}-\text{R}'$	Williamson synthesis
NH_3	$\text{R}-\text{NH}_2$ (and R_2NH , R_3N , $\text{R}_4\text{N}^+\text{X}^-$)	
KCN (ionic)	$\text{R}-\text{CN}$ alkyl cyanide	attack through C
AgCN (covalent)	$\text{R}-\text{NC}$ isocyanide	attack through N
KNO_2 (ionic)	$\text{R}-\text{O}-\text{N}=\text{O}$ alkyl nitrite	attack through O
AgNO_2 (covalent)	$\text{R}-\text{NO}_2$ nitroalkane	attack through N
$\text{R}'\text{COOAg}$	$\text{R}'\text{COOR}$ ester	
LiAlH_4	$\text{R}-\text{H}$	reduction (H^- as Nu)
$\text{R}'-\text{M}$ (e.g. $\text{R}'_2\text{CuLi}$)	$\text{R}-\text{R}' + \text{MX}$	R'^- as Nu
$\text{NaI}/\text{acetone}$; AgF	$\text{R}-\text{I}$; $\text{R}-\text{F}$	Finkelstein; Swarts

Ambident nucleophiles

CN^- and NO_2^- can attack through two different atoms. Free cyanide (ionic KCN) attacks through C, forming the stronger C-C bond; in covalent AgCN the carbon is bonded to Ag, so only the lone pair on N is free: isocyanide. Likewise ionic KNO_2 gives alkyl nitrites (attack through O) and covalent AgNO_2 gives nitroalkanes (attack through N).

Example 1.15 Give the products of bromoethane with (a) KCN , (b) AgCN , (c) KNO_2 , (d) AgNO_2 , (e) dry Ag_2O .

Solution. Apply the table: ionic reagents attack through C (cyanide) or O (nitrite); silver salts through N; dry silver oxide gives an ether.

Answer: (a) $\text{CH}_3\text{CH}_2\text{CN}$; (b) $\text{CH}_3\text{CH}_2\text{NC}$; (c) $\text{CH}_3\text{CH}_2\text{ONO}$; (d) $\text{CH}_3\text{CH}_2\text{NO}_2$; (e) $(\text{CH}_3\text{CH}_2)_2\text{O}$

1.9 Neighbouring group participation and allylic substitution

$\text{S}_{\text{N}}\text{NGP}$

A group inside the molecule with a lone pair or π electrons acts as an internal nucleophile: it displaces the leaving group (first inversion), giving a cyclic intermediate, which the external nucleophile opens (second inversion). Net result: **retention**, and a much faster reaction (anchimeric assistance).

- Requirements: an internal nucleophile, placed *anti* (antiperiplanar) to the leaving group.
- Groups that can participate: $-\text{O}-$, $-\text{NH}-$, $-\text{COO}-$, $-\text{NH}_2$, $-\text{NHR}$, $-\text{NR}_2$, $-\text{SR}$, $-\text{SH}$, $-\text{OCOR}$, $-\text{CONH}_2$, $-\text{I}$, $-\text{Br}$, $-\text{Cl}$, $-\text{CH}=\text{CH}_2$, phenyl.
- If the internal nucleophile and the leaving group are in one chain at a suitable distance, the cyclic product may itself be isolated (intramolecular substitution: epoxides, THF, dioxane, ...).

Example 1.16 Give the stereochemistry of the product: (a) a chiral CH_3CHDCl with aqueous NaOH ; (b) a chiral 2-chloro-2-deuterioethanoic acid $\text{HOOC}-\text{CHDCl}$ with (i) aqueous NaOH , (ii) slight acidification.

Solution. (a) Simple $\text{S}_{\text{N}}2$: 100% inversion. (b) NaOH gives the carboxylate $-\text{COO}^-$, which is anti to Cl and attacks the α -carbon from the back (inversion), giving a three-membered α -lactone; OH^- then opens it at the same carbon from the back (second inversion). Two inversions: overall retention. Acidification gives the free acid $\text{HOOC}-\text{CHD}-\text{OH}$.

Answer: (a) CH_3CHDOH with 100% inversion ($\text{S}_{\text{N}}2$); (b) $\text{HOOC}-\text{CHDOH}$ with 100% retention ($\text{S}_{\text{N}}\text{NGP}$)

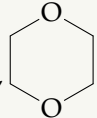
Example 1.17 2-(Methylthio)cyclohexyl chloride is heated with aqueous NaOH . Predict the stereochemistry of the product (a) for the *cis* isomer, (b) for the *trans* isomer.

Solution. (a) In the *cis* isomer the SMe group cannot reach the back side of $\text{C}-\text{Cl}$, so ordinary $\text{S}_{\text{N}}2$ occurs with inversion: OH ends up *trans* to SMe . (b) In the *trans* isomer SMe can be anti to Cl ; it displaces Cl^- to give a cyclic episulfonium ion, opened by OH^- from the back: double inversion, retention; OH stays *trans* to SMe , and the reaction is much faster.

Answer: (a) *trans*-2-(methylthio)cyclohexanol by inversion ($\text{S}_{\text{N}}2$); (b) *trans*-2-(methylthio)cyclohexanol by retention (NGP), formed much faster

Example 1.18 Give the product of $\text{ClCH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2\text{Cl}$ with aqueous NaOH .

Solution. One Cl is replaced by OH : $\text{ClCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$. In base the alkoxide formed attacks the other CH_2Cl intramolecularly, closing a six-membered ring with two O atoms.

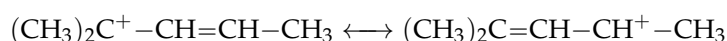
Answer: 1,4-dioxane,  (by intramolecular substitution)

$\text{S}_{\text{N}}1'$ and $\text{S}_{\text{N}}2'$ (allylic systems)

- $\text{S}_{\text{N}}1'$: the allylic carbocation is a resonance hybrid; the product obtained from the *other* resonance structure (Nu on the carbon at the far end, double bond shifted) is the $\text{S}_{\text{N}}1'$ product.
- $\text{S}_{\text{N}}2'$: the nucleophile attacks the far end of the $\text{C}=\text{C}$ of an allylic halide in one step; the double bond shifts and X leaves: $\text{Nu}^- + \text{C}=\text{C}-\text{C}-\text{X} \longrightarrow \text{Nu}-\text{C}-\text{C}=\text{C} + \text{X}^-$.

Example 1.19 Give the products of 2-methylpent-3-en-2-ol, $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}=\text{CHCH}_3$, with HBr .

Solution. Protonation and loss of water give a 3° allylic cation:



Br^- attacks either end.

Answer: $(\text{CH}_3)_2\text{CBr}-\text{CH}=\text{CHCH}_3$ ($\text{S}_{\text{N}}1$) and $(\text{CH}_3)_2\text{C}=\text{CH}-\text{CHBrCH}_3$ ($\text{S}_{\text{N}}1'$)

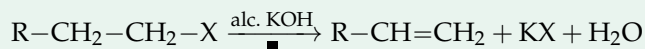
Example 1.20 Allyl chloride labelled with ^{14}C at the terminal $=\text{CH}_2$ carbon, $^{14}\text{CH}_2=\text{CH}-\text{CH}_2\text{Cl}$, is treated with aqueous NaOH . Give the products.

Solution. Direct $\text{S}_{\text{N}}2$ at CH_2Cl keeps the label on the alkene carbon; $\text{S}_{\text{N}}2'$ attack at the labelled carbon moves the double bond.

Answer: $^{14}\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$ ($\text{S}_{\text{N}}2$) and $\text{HO}-^{14}\text{CH}_2-\text{CH}=\text{CH}_2$ ($\text{S}_{\text{N}}2'$)

1.10 Elimination

β -Elimination (dehydrohalogenation)



- **E2:** one step, strong base, anti-periplanar H and X; rate = $k[\text{RX}][\text{B}^-]$.
- **E1:** through a carbocation (rearrangement possible), PPS and heat; rate = $k[\text{RX}]$.
- **E1cB:** through a carbanion, when an electron-withdrawing group makes the β -H acidic.
- **Saytzeff (Zaitsev) rule:** the more substituted (more stable) alkene is the major product: 2-bromobutane gives but-2-ene (80%) > but-1-ene (20%). A bulky base ($(\text{CH}_3)_3\text{CO}-\text{K}^+$) or a poor leaving group (F, NR_3^+) gives the less substituted **Hofmann** alkene.

Substitution versus elimination

$\text{S}_{\text{N}}1$ and E1 go through a carbocation (rearrangement possible); $\text{S}_{\text{N}}2$ and E2 are one step and need a strong nucleophile/base.

PPS	PPS, Δ	RO^- (alc. KOH)	RO^- , Δ	good Nu (aq. KOH, RS^-)
$\text{S}_{\text{N}}1$	E1	E2 (2° , 3°); $\text{S}_{\text{N}}2$ (1° un- branched)	E2 ; E1cB with EWG	$\text{S}_{\text{N}}2$ (1° , 2°); E2 (3°); $\text{S}_{\text{N}}1$ (3° , PPS)

Example 1.21 Give the main product of 2-chlorobutane with (a) H_2O ; (b) H_2O , Δ ; (c) EtONa ; (d) $t\text{-BuONa}$; (e) EtSNa ; (f) EtONa , Δ .

Solution. (a) PPS, weak nucleophile: $\text{S}_{\text{N}}1$. (b) PPS with heat: E1 , Saytzeff. (c) Strong base: E2 , Saytzeff. (d) Bulky strong base: E2 , Hofmann. (e) EtS^- is a strong nucleophile but a weak base: $\text{S}_{\text{N}}2$. (f) Base and heat: E2 .

Answer: (a) butan-2-ol; (b) but-2-ene; (c) but-2-ene; (d) but-1-ene; (e) $\text{CH}_3\text{CH}(\text{SEt})\text{CH}_2\text{CH}_3$, 2-(ethylthio)butane; (f) but-2-ene

Example 1.22 Give the main product of 2-chloro-3-methylbutane, $(\text{CH}_3)_2\text{CH}-\text{CHCl}-\text{CH}_3$, with (a) $t\text{-BuOK}$, Δ ; (b) alc. KOH, Δ ; (c) CH_3OH ; (d) (i) AgF , (ii) EtONa , Δ .

Solution. (a) Bulky base, E2 : the less substituted (Hofmann) alkene. (b) E2 with a small base: Saytzeff. (c) Methanol is a PPS: $\text{S}_{\text{N}}1$; the 2° cation undergoes a 1,2-hydride shift to the 3° cation $(\text{CH}_3)_2\text{C}^+\text{CH}_2\text{CH}_3$, which is captured by CH_3OH . (d) Swarts gives the fluoride; with F as a poor leaving group E2 has carbanion-like character and the less substituted alkene is the major product.

Answer: (a) 3-methylbut-1-ene; (b) 2-methylbut-2-ene; (c) 2-methoxy-2-methylbutane $(\text{CH}_3)_2\text{C}(\text{OCH}_3)\text{CH}_2\text{CH}_3$; (d) 3-methylbut-1-ene

1.11 Reactions with metals

Grignard and Wurtz

- **Grignard reagent:** $\text{R}-\text{X} + \text{Mg} \xrightarrow{\text{dry ether}} \text{R}-\text{MgX}$. The C-Mg bond is polar covalent ($\text{R}^{\delta-}-\text{Mg}^{\delta+}$); R acts as a carbanion. It reacts with any compound having acidic H (water, alcohols, amines, terminal alkynes) to give the hydrocarbon: $\text{RMgX} + \text{H}_2\text{O} \longrightarrow \text{RH} + \text{Mg}(\text{OH})\text{X}$; so it must be made and kept dry.
- **Wurtz reaction:** $2\text{RX} + 2\text{Na} \xrightarrow{\text{dry ether}} \text{R}-\text{R} + 2\text{NaX}$ (alkanes with twice the number of carbons). With two different halides a mixture of three alkanes forms.

Example 1.23 A mixture of bromomethane and bromoethane is treated with sodium in dry ether. How many alkanes are formed, and which?

Solution. Each radical/anion couples with either partner: CH_3-CH_3 , $\text{CH}_3-\text{CH}_2\text{CH}_3$, $\text{CH}_3\text{CH}_2-\text{CH}_2\text{CH}_3$.

Answer: 3: ethane, propane and butane

1.12 Haloarenes: preparation

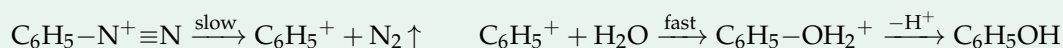
From arenes and from diazonium salts

- Electrophilic substitution:** $\text{C}_6\text{H}_6 + \text{Cl}_2 \xrightarrow[\text{dark}]{\text{Fe or FeCl}_3} \text{C}_6\text{H}_5\text{Cl} + \text{HCl}$ (Lewis acid makes Cl^+). Iodination is reversible and needs an oxidant (HNO_3 , HIO_4) to remove HI; fluorine is too reactive. Toluene gives *o*- and *p*-chlorotoluene.

- From benzene diazonium chloride (BDC):** $\text{C}_6\text{H}_5\text{NH}_2 \xrightarrow[0-5^\circ\text{C}]{\text{NaNO}_2/\text{HCl}} \text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$, then

Reagent on $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$	Product	Name
$\text{Cu}_2\text{Cl}_2/\text{HCl}$; $\text{Cu}_2\text{Br}_2/\text{HBr}$	$\text{C}_6\text{H}_5\text{Cl}$; $\text{C}_6\text{H}_5\text{Br}$	Sandmeyer reaction (Cu(I) salts)
Cu/HCl ; Cu/HBr	$\text{C}_6\text{H}_5\text{Cl}$; $\text{C}_6\text{H}_5\text{Br}$	Gattermann reaction (Cu powder)
KI (warm)	$\text{C}_6\text{H}_5\text{I}$	no catalyst needed
(i) HBF_4 , (ii) Δ	$\text{C}_6\text{H}_5\text{F}$ (+ $\text{BF}_3 + \text{N}_2$)	Balz-Schiemann reaction
H_2O , warm	$\text{C}_6\text{H}_5\text{OH}$	$\text{S}_{\text{N}}1\text{Ar}$

$\text{S}_{\text{N}}1\text{Ar}$ of diazonium salts



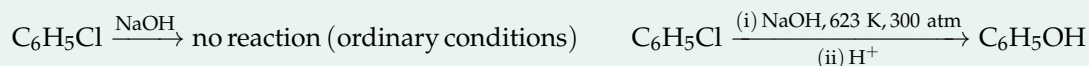
An aryl cation is the intermediate; its formation is the rate-determining step (N_2 is an excellent leaving group). The rate is independent of the nucleophile.

1.13 Haloarenes: chemical reactions

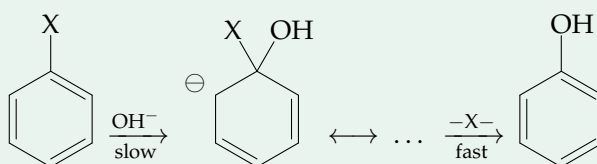
Why aryl halides resist nucleophilic substitution

- Resonance:** a lone pair of X is delocalised into the ring; C–X acquires partial double-bond character (C–Cl 169 pm in chlorobenzene against 177 pm in CH_3Cl).
- The carbon is sp^2 : more s character, more electronegative, so it holds the bonding pair more tightly.
- The phenyl cation is not resonance stabilised ($\text{S}_{\text{N}}1$ impossible).
- The electron-rich ring repels the incoming nucleophile, and back-side attack is impossible ($\text{S}_{\text{N}}2$ impossible).

Dow's process and the $\text{S}_{\text{N}}2\text{Ar}$ (addition–elimination) mechanism



Mechanism: OH^- adds to the carbon carrying X (slow, rate-determining), giving a resonance-stabilised carbanion, the **Meisenheimer (σ^-) complex**, with the negative charge on the carbons *ortho* and *para* to the attacked carbon; then X^- is lost (fast).



(the negative charge of the σ^- -complex is shared by the two *ortho* carbons and the *para* carbon).

- An electron-withdrawing group ($-\text{NO}_2$, $-\text{CN}$, $-\text{COR}$) at the *ortho* or *para* position stabilises the complex (the charge can sit on it) and increases the rate; one at the *meta* position cannot. At ordinary temperature

and pressure S_N2Ar takes place only if an EWG is at the *o/p* positions.

- The rate also increases with the $-I$ effect of the halogen (it makes the carbon more positive for the slow addition step; $C-X$ breaks only in the fast step): $Ar-F > Ar-Cl > Ar-Br > Ar-I$ — the reverse of alkyl halides.

S_N2 versus S_N2Ar

S_N2 at an alkyl carbon is much faster than S_N2Ar (one step against two, and no aromaticity to lose). In a molecule having both $Ar-X$ and $ArCH_2-X$, a nucleophile replaces the benzylic X first.

Example 1.24 Arrange in decreasing order of reactivity towards aqueous $NaOH$: (a) 4-nitrochlorobenzene, (b) 2,4-dinitrochlorobenzene, (c) 2,4,6-trinitrochlorobenzene.

Solution. Each *o/p* nitro group stabilises the Meisenheimer complex further. 4-Nitrochlorobenzene needs 443 K, the dinitro compound 368 K, and picryl chloride reacts with warm water.

Answer: $c > b > a$

Example 1.25 Predict the products: (a) 1-chloro-2,4-dinitrobenzene with hydrazine; (b) 1-chloro-3-nitrobenzene with $PhSNa$; (c) 1,2-dichloro-4-nitrobenzene with aqueous $NaOH$.

Solution. (a) Both nitro groups are *o/p* to Cl : S_N2Ar with NH_2NH_2 . (b) The nitro group is *meta* to Cl : it cannot hold the negative charge, so no reaction under ordinary conditions. (c) Only the Cl at C-1 is *para* to NO_2 , so only it is replaced.

Answer: (a) 2,4-dinitrophenylhydrazine (2,4-DNP, Brady's reagent); (b) no reaction; (c) 2-chloro-4-nitrophenol (after acidification)

Example 1.26 1-(Chloromethyl)-5-fluoro-2,4-dinitrobenzene is treated with 2 equivalents of $PhSNa$. Give the product.

Solution. PhS^- replaces the benzylic Cl by S_N2 (fast), and the F , which is *ortho* to the 4- NO_2 and *para* to the 2- NO_2 , by S_N2Ar (F is the best leaving group for S_N2Ar).

Answer: 2,4-dinitro-5-(phenylthio)benzyl phenyl sulfide: both Cl and F are replaced by PhS

Electrophilic substitution in haloarenes

Halogen is deactivating ($-I$ effect wins) but *ortho/para* directing ($+R$ effect places electron density at *o/p*): reactions are slower than for benzene; the *para* product is usually major (less steric hindrance).

Reaction	Reagent	Products from C_6H_5Cl
Halogenation	Cl_2 , anhyd. $FeCl_3$	1,2- and 1,4-dichlorobenzene
Nitration	conc. HNO_3 + conc. H_2SO_4	1-chloro-2- and 1-chloro-4-nitrobenzene
Sulphonation	conc. H_2SO_4 , Δ	2- and 4-chlorobenzenesulphonic acid
F-C alkylation	CH_3Cl , anhyd. $AlCl_3$	2- and 4-chlorotoluene
F-C acylation	CH_3COCl , anhyd. $AlCl_3$	2- and 4-chloroacetophenone

Reactions with metals

Wurtz-Fittig: $Ar-X + R-X + 2Na \xrightarrow{\text{dry ether}} Ar-R + 2NaX$; **Fittig:** $2 Ar-X + 2Na \xrightarrow{\text{dry ether}} Ar-Ar + 2NaX$ (e.g. biphenyl).

Example 1.27 Suggest reagents for converting (a) aniline into fluorobenzene, (b) chlorobenzene into 4-chloroacetophenone, (c) bromobenzene into toluene?

Solution. (a) Diazotise and use the Balz–Schiemann reaction. (b) Friedel–Crafts acylation; Cl is *o/p* directing and *para* is major. (c) Wurtz–Fittig with CH_3Br .

Answer: (a) NaNO_2/HCl at $0-5^\circ\text{C}$, then HBF_4 and heat; (b) $\text{CH}_3\text{COCl}/\text{anhyd. AlCl}_3$; (c) CH_3Br , Na, dry ether

1.14 Polyhalogen compounds

Important polyhalogen compounds

- **Dichloromethane** CH_2Cl_2 : solvent (paint remover, propellant, metal cleaning); harms the central nervous system; converts to CO in the body.
- **Chloroform** CHCl_3 : solvent; was an anaesthetic. Air and light oxidise it to the very poisonous **phosgene**:
$$2\text{CHCl}_3 + \text{O}_2 \xrightarrow{\text{light}} 2\text{COCl}_2 + 2\text{HCl}$$
It is stored in closed dark-coloured bottles filled to the top (and 1% ethanol is added, which converts any phosgene into harmless diethyl carbonate).
- **Iodoform** CHI_3 : yellow solid with a characteristic smell; antiseptic (releases I_2). Formed in the iodoform test.
- **Carbon tetrachloride** CCl_4 : solvent, fire extinguisher (formerly), manufacture of freons. Depletes the ozone layer; may cause liver cancer.
- **Freons** (chlorofluorocarbons, e.g. CCl_2F_2 , freon-12): refrigerants and aerosol propellants; unreactive and non-toxic, but in the stratosphere UV releases Cl radicals that destroy ozone.
- **DDT** (*p,p'*-dichlorodiphenyltrichloroethane): insecticide (malaria mosquitoes); very stable, fat-soluble, not metabolised quickly, so it accumulates in food chains; banned in many countries.

Example 1.28 Why is chloroform stored in dark bottles filled to the brim? Calculate the percentage of chlorine in chloroform (C 12, H 1, Cl 35.5).

Solution. To exclude light and air, which oxidise it to phosgene COCl_2 . $M(\text{CHCl}_3) = 12 + 1 + 3(35.5) = 119.5$;
$$\% \text{Cl} = \frac{106.5}{119.5} \times 100 = 89.1\%$$

Answer: Phosgene formation is prevented; Cl = 89.1%