JEE MAIN · PAPER 1 · CHEMISTRY

16 Organic Compounds Containing Halogens

Formula & concept sheet

Alkyl and aryl halides: classification, the polar C—X bond and physical trends, every method of preparation, nucleophilic substitution (S_N1, S_N2) and elimination (E1, E2) with their stereochemistry and the factors that decide between them, reactions with metals, why haloarenes are unreactive, their special reactions, and the polyhalogen compounds. Each idea is explained first, then the reactions as drawn schemes and tables.

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READ ALONGSIDE NCERT XII · Haloalkanes and Haloarenes

HOW TO USE THIS SHEET

CHAPTER 16

Organic Compounds Containing Halogens

NCERT XII · Haloalkanes and Haloarenes

Covers: classification and nomenclature · preparation from alcohols, alkenes, by halogen exchange (Finkelstein, Swarts), from arenes and diazonium salts (Sandmeyer, Gattermann, Balz-Schiemann) · S_N1 and S_N2, stereochemistry · E1 and E2, Saytzeff and Hofmann · Grignard, Wurtz, Wurtz-Fittig, Fittig · haloarene reactivity, Dow process · chloroform, iodoform, CCl_4, freons, DDT.

1 Classification, the C–X bond and physical properties

- **Haloalkanes** $R-X$ have X on an sp^3 carbon and are 1°, 2° or 3° by the carbon carrying X; **allyl** halides ($C=C-C-X$) and **benzyl** halides ($Ar-C-X$) have X on an sp^3 carbon next to a π system; **vinyl** and **aryl** halides have X on an sp^2 carbon (haloarenes). Dihalides: **gem** (same carbon), **vic** (adjacent carbons).
- The $C-X$ bond is polar ($\delta+$ on C, $\delta-$ on X) because X is more electronegative. Down the group the bond gets **longer and weaker**: length $C-F < C-Cl < C-Br < C-I$, enthalpy $C-F > C-Cl > C-Br > C-I$; so reactivity $RI > RBr > RCl > RF$ and iodide is the best leaving group.

PHYSICAL PROPERTIES

PROPERTY	TREND AND REASON
boiling point	$RI > RBr > RCl > RF$ (larger, more polarisable halogens, stronger dispersion forces); rises with the chain length; branching lowers it (less surface); higher than the parent alkane
density	$RI > RBr > RCl$; CH_2Cl_2, $CHCl_3$, CCl_4 and bromo/iodo compounds are denser than water
solubility	insoluble in water (cannot break water's H-bond network), soluble in organic solvents
dipole moment (D)	CH_3Cl 1.86 > CH_3F 1.85 > CH_3Br 1.81 > CH_3I 1.62 (bond length offsets charge)
dichlorobenzenes	*p*-isomer has the highest melting point (symmetry packs better in the crystal) but the lowest solubility; boiling points are close

KEY IDEA

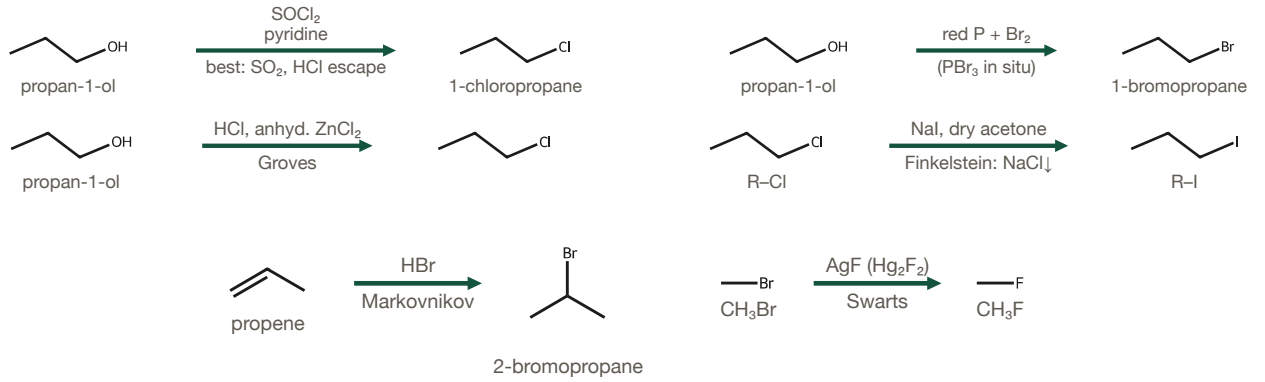
The reactivity of $R-X$ is set by two things: the strength of the $C-X$ bond (leaving-group ability, $I^- > Br^- > Cl^- > F^-$) and the stability of the carbon centre (carbocation for S_N1, access for S_N2). Aryl and vinyl halides fail on both counts.

QUICK CHECK

Arrange by boiling point: CH_3CH_2Cl, CH_3CH_2Br, CH_3CH_2I, $CH_3CH_2CH_2Cl$ and by $C-X$ bond enthalpy: CH_3F, CH_3Cl, CH_3Br.

Answer: b.p. (K): C_2H_5Cl 285 < C_2H_5Br 311 < C_3H_7Cl 320 < C_2H_5I 345. Bond enthalpy: $CH_3F > CH_3Cl > CH_3Br$.

2 Preparation of haloalkanes and haloarenes



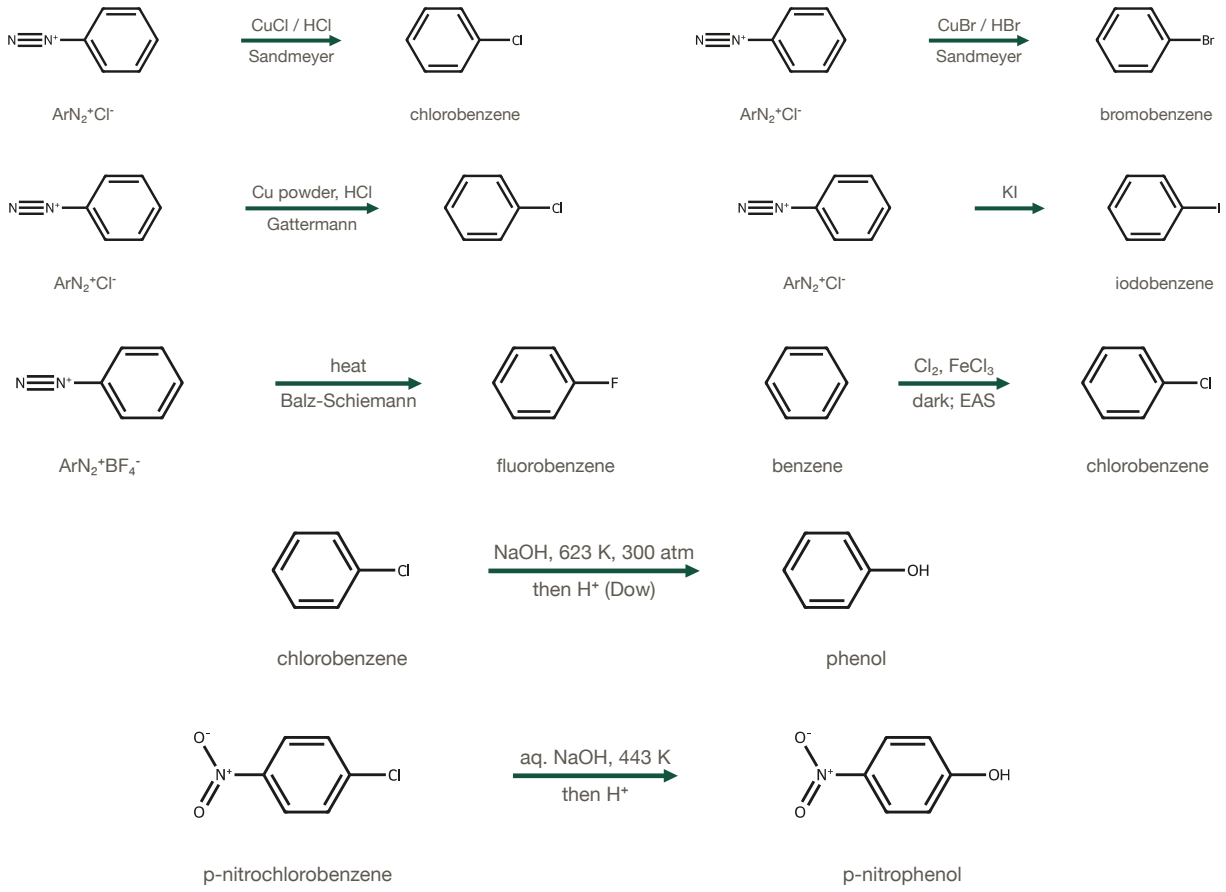
preparation of haloalkanes from alcohols and alkenes, and halogen exchange

PREPARATION OF HALOALKANES (ALL NCERT METHODS)

FROM	REAGENT AND EQUATION	REMARK
alcohol + HCl	$\mathrm{ROH + HCl \xrightarrow{anhyd\cdot ZnCl_2} RCl + H_2O}$ (Groves)	3° alcohols react even without $\mathrm{ZnCl_2}$; $\mathrm{ZnCl_2}$ is the Lucas reagent
alcohol + PCl5	$\mathrm{ROH + PCl_5 \longrightarrow RCl + POCl_3 + HCl}$	gaseous HCl and liquid $\mathrm{POCl_3}$ to separate
alcohol + PCl3	$\mathrm{3\,ROH + PCl_3 \longrightarrow 3\,RCl + H_3PO_3}$	red P + $\mathrm{Br_2}$ or $\mathrm{I_2}$ gives $\mathrm{PBr_3/PI_3}$ in situ
alcohol + SOCl2	$\mathrm{ROH + SOCl_2 \xrightarrow{pyridine} RCl + SO_2 + HCl}$	best method: both by-products are gases
alkene + HX	$\mathrm{CH_3CH{=}CH_2 + HBr \longrightarrow CH_3CHBrCH_3}$ (Markovnikov); with peroxide the anti-Markovnikov $\mathrm{CH_3CH_2CH_2Br}$	HI and HBr add easily, HCl needs a catalyst
alkene + X2	$\mathrm{CH_2{=}CH_2 + Br_2 \longrightarrow BrCH_2CH_2Br}$ (vicinal dibromide, anti addition)	bromine test: reddish-orange colour discharged
alkane + X2, light	$\mathrm{CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl}$	mixture of products, poor for a single one
Finkelstein	$\mathrm{RCl + NaI \xrightarrow{dry\ acetone} RI + NaCl}$	NaCl/NaBr precipitate in acetone and drive the reaction
Swarts	$\mathrm{CH_3Br + AgF \longrightarrow CH_3F + AgBr}$	also $\mathrm{Hg_2F_2}$, $\mathrm{CoF_2}$, $\mathrm{SbF_3}$ for fluorides
iodoform route	$\mathrm{CH_3CH_2OH + 4\,I_2 + 6\,NaOH \longrightarrow CHI_3 + 5\,NaI + HCOONa + 5\,H_2O}$ (haloform)	yellow ppt

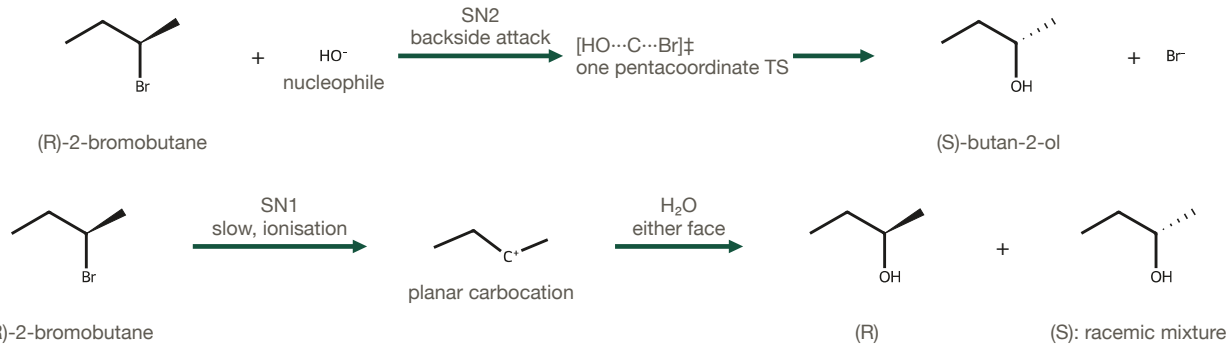
PREPARATION OF HALOARENES

METHOD	EQUATION AND CONDITIONS
electrophilic substitution	$\mathrm{C_6H_6 + Cl_2 \xrightarrow{anhyd\cdot FeCl_3,\ dark} C_6H_5Cl + HCl}$; $\mathrm{C_6H_6 + Br_2 \xrightarrow{FeBr_3} C_6H_5Br + HBr}$; toluene gives *o* and *p* isomers (separated by fractional distillation)
Sandmeyer	$\mathrm{C_6H_5N_2^+Cl^- \xrightarrow{CuCl/HCl} C_6H_5Cl + N_2}$; $\mathrm{CuBr/HBr}$ gives bromide; $\mathrm{CuCN/KCN}$ gives benzonitrile
Gattermann	$\mathrm{C_6H_5N_2^+Cl^- \xrightarrow{Cu,\ HCl} C_6H_5Cl + N_2}$ (copper powder instead of Cu(I) salt; lower yield)
iodide	$\mathrm{C_6H_5N_2^+Cl^- + KI \longrightarrow C_6H_5I + KCl + N_2}$ (no catalyst needed)
Balz-Schiemann	$\mathrm{C_6H_5N_2^+BF_4^- \xrightarrow{heat} C_6H_5F + BF_3 + N_2}$
not possible	phenol with HX or $\mathrm{PCl_5}$ gives no useful aryl halide: the $\mathrm{C{-}O}$ bond has double-bond character by resonance; iodination of benzene needs an oxidant ($\mathrm{HIO_3}$, $\mathrm{HNO_3}$) to remove HI



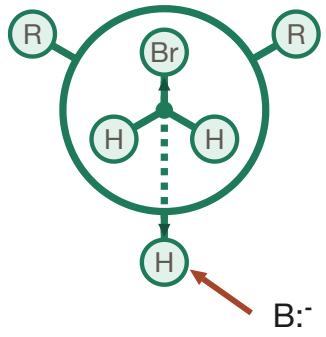
haloarenes from benzenediazonium chloride (Sandmeyer, Gattermann, Balz-Schiemann) and from benzene; Dow process

3 Nucleophilic substitution: SN2 and SN1



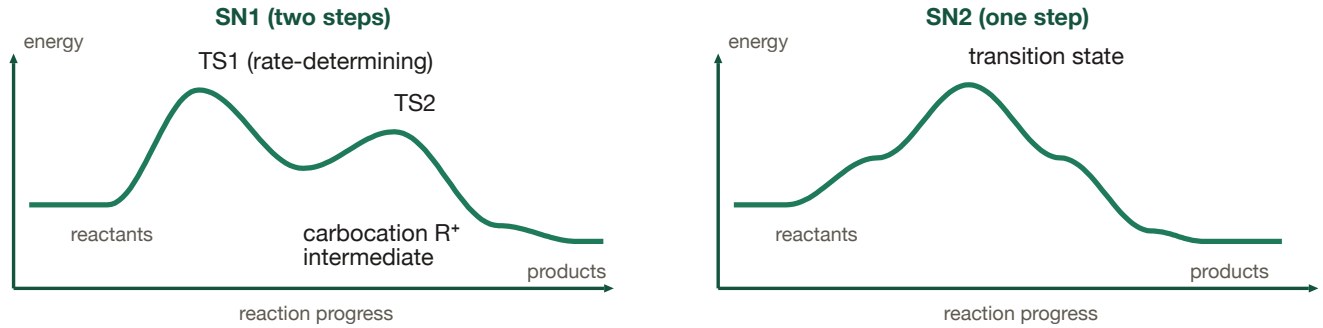
SN2 inverts the configuration (Walden inversion): (R)-2-bromobutane gives (S)-butan-2-ol; SN1 goes through the planar carbocation and gives a racemic mixture

180°: H and Br anti-periplanar



E2 needs the leaving group and the β-hydrogen anti-periplanar

S_N2 AND S_N1 IN ONE LINE EACH S_N2: one step; the nucleophile attacks from the side opposite to the leaving group, through a pentacoordinate transition state; rate $= k[\mathrm{RX}][\mathrm{Nu}^-]$; inversion. S_N1: slow ionisation to a planar carbocation, then fast attack from either face; rate $= k[\mathrm{RX}]$; racemisation (often with some excess inversion because the leaving group still shields one face); rearrangement of the carbocation is possible.



SN1 has an intermediate and two transition states; SN2 has a single transition state

SUBSTITUTION VERSUS ELIMINATION: WHAT DECIDES

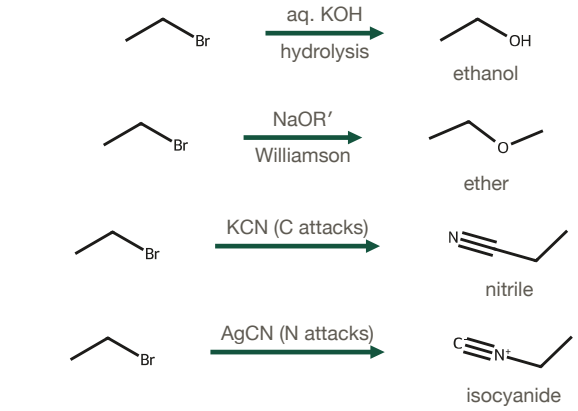
FACTOR	S_N2	S_N1	E2	E1
rate law	$k[\mathrm{RX}][\mathrm{Nu}]$	$k[\mathrm{RX}]$	$k[\mathrm{RX}][\mathrm{B}]$	$k[\mathrm{RX}]$
substrate	$\mathrm{CH_3X} > 1^\circ > 2^\circ$; allyl, benzyl fast; neopentyl very slow	$3^\circ > 2^\circ$; allyl, benzyl, $(\mathrm{C_6H_5})_2\mathrm{CHX}$, $(\mathrm{C_6H_5})_3\mathrm{CX}$ fastest	$3^\circ > 2^\circ > 1^\circ$	3° (same as S_N1)
reagent	strong, high-concentration nucleophile	weak nucleophile (water, alcohol)	strong base: alc. KOH, NaOEt; bulky $(\mathrm{CH_3})_3\mathrm{CO}{-}\mathrm{K}^+$ gives Hofmann product	weak base, heat
solvent	polar aprotic (DMSO, DMF, acetone) speeds up	polar protic (water, alcohols, HCOOH) stabilises ions	ethanol (alcoholic)	polar protic
stereochemistry	inversion	racemisation	anti-periplanar H and X	planar cation
rearrangement	no	yes (hydride, methyl shift)	no	yes
product	substitution	substitution (+ alkene)	alkene (Saytzeff: more substituted)	alkene (Saytzeff)

READING THE TABLE

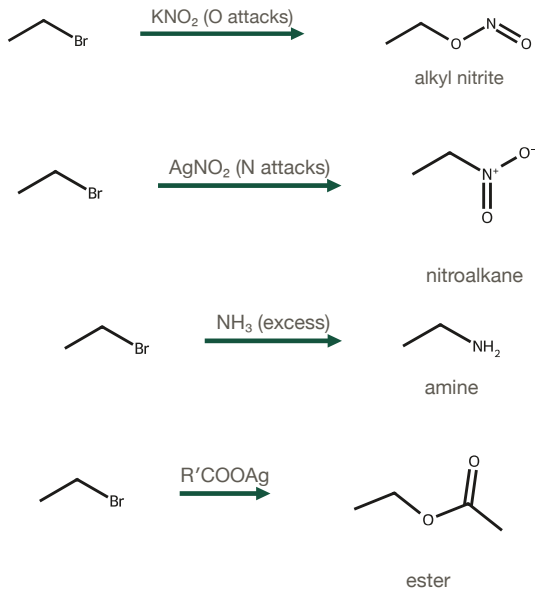
- **Aqueous KOH** gives substitution (alcohol; OH^- is heavily solvated by water); **alcoholic KOH** gives elimination (alkene). A 3° halide with a strong base eliminates.
- **Saytzeff rule**: the more substituted (more stable) alkene is the major product of dehydrohalogenation, e.g. 2-bromobutane gives but-2-ene (major) and but-1-ene.
- **Ambident nucleophiles**: KCN (ionic, C attacks) gives nitrile, $AgCN$ (covalent, N attacks) gives isocyanide; KNO_2 gives nitrite (O attacks), $AgNO_2$ nitroalkane (N attacks).

TRAP

2° halide with a strong, unhindered nucleophile at high concentration goes S_N2; the same halide in a polar protic solvent without a strong nucleophile goes S_N1. Optical activity: S_N2 gives one inverted product; S_N1 gives a (mostly) racemic mixture. Vinyl and aryl halides do neither.

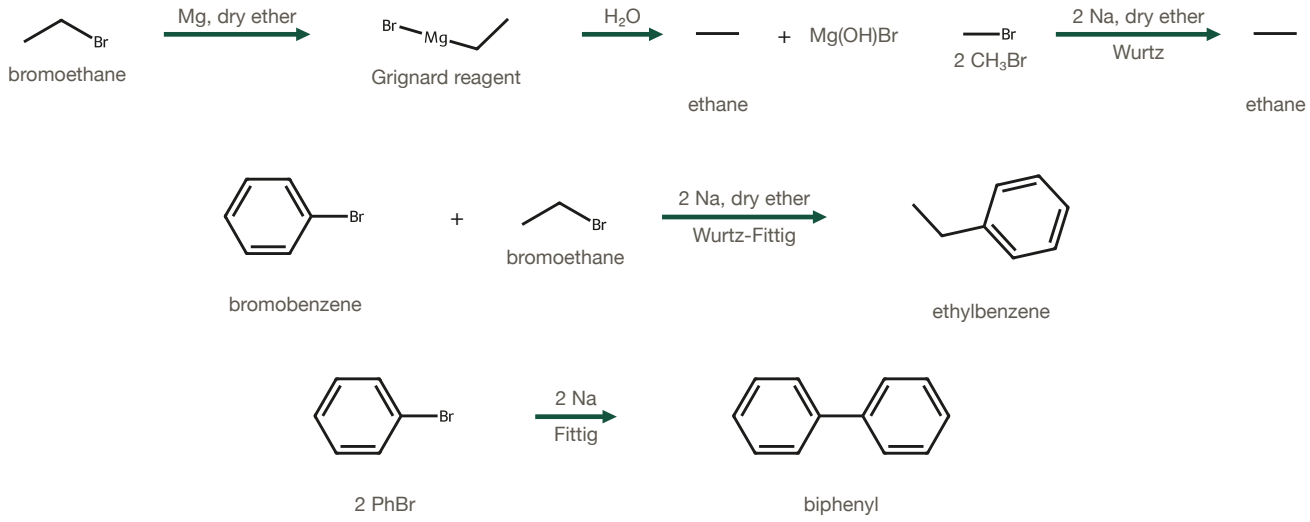


nucleophilic substitution products of bromoethane (1)



nucleophilic substitution products of bromoethane (2)

4 Reactions with metals and the Grignard reagent

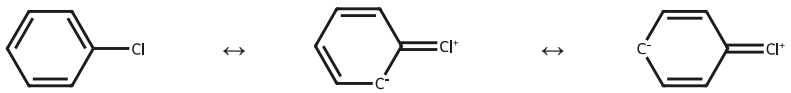


organometallic and coupling reactions of halides: Grignard reagent, Wurtz, Wurtz-Fittig and Fittig

ORGANOMETALLIC AND COUPLING REACTIONS

REACTION	EQUATION	NOTES
Grignard reagent	$\mathrm{RX + Mg \xrightarrow{dry\ ether} RMgX}$	reactivity of RX: $\mathrm{RI > RBr > RCl}$; strictly dry ether
destroyed by active H	$\mathrm{RMgX + H_2O \longrightarrow RH + Mg(OH)X}$; same with ROH, $\mathrm{NH_3}$, $\mathrm{RC{\equiv}CH}$ ($\mathrm{RMgX + R'C{\equiv}CH \longrightarrow RH + R'C{\equiv}CMgX}$)	a way to make alkanes and acetylide Grignards
Wurtz	$\mathrm{2\,RX + 2\,Na \xrightarrow{dry\ ether} R{-}R + 2\,NaX}$	even-carbon alkanes; unsymmetrical gives a mixture
Wurtz-Fittig	$\mathrm{ArX + RX + 2\,Na \xrightarrow{dry\ ether} Ar{-}R + 2\,NaX}$	alkylbenzene; also gives biaryl and R−R as by-products
Fittig	$\mathrm{2\,ArX + 2\,Na \xrightarrow{dry\ ether} Ar{-}Ar + 2\,NaX}$	biphenyl from bromobenzene
reduction	$\mathrm{RX + 4\,[H] \xrightarrow{LiAlH_4} RH + HX}$ (also $\mathrm{Zn/H^+}$, $\mathrm{Zn{-}Cu}$ couple)	alkane of the same carbon number
with alkynides	$\mathrm{RX + R'C{\equiv}C{-}Na^+ \longrightarrow R{-}C{\equiv}C{-}R' + NaX}$	chain extension of terminal alkynes

5 Haloarenes: why they are unreactive and how they do react



chlorobenzene ↔ ortho ↔ para

so C–Cl in chlorobenzene (1.69 Å) is shorter than in $\mathrm{CH_3Cl}$ (1.77 Å)

the lone pair of chlorine delocalises into the ring, so the C–Cl bond has partial double-bond character (shorter, stronger, hard to break)

FIVE REASONS ARYL HALIDES RESIST NUCLEOPHILIC SUBSTITUTION

- **Resonance**: the lone pair of X delocalises into the ring, so $\mathrm{C{-}X}$ has partial double-bond character (shorter, stronger).
- **Hybridisation**: the sp^2 carbon is more electronegative and holds the bond tighter than sp^3.
- The phenyl cation is not resonance stabilised, so no S_N1.
- The ring blocks the backside approach, so no S_N2; the electron-rich ring also repels the nucleophile.

WHY IT WORKS

Chlorine pulls electrons through the σ bond ($-I$, deactivating) but donates a lone pair into the ring ($+M$), which raises the electron density at the ortho and para positions. So haloarenes are slower than benzene in electrophilic substitution yet direct **ortho/para**: chlorobenzene with $\mathrm{Cl_2/FeCl_3}$ gives mainly the para (and ortho) dichlorobenzene; nitration, sulphonation and Friedel-Crafts also go o/p.

REACTIONS OF HALOARENES

REACTION	CONDITIONS AND PRODUCT
Dow process	$\mathrm{C_6H_5Cl + 2\,NaOH \xrightarrow{623\ K,\ 300\ atm} C_6H_5ONa + NaCl + H_2O}$; $\mathrm{H^+}$ then gives phenol
nitro activation	$\mathrm{-NO_2}$ at ortho or para (not meta) makes substitution easy: p-nitrochlorobenzene with NaOH at 443 K, 2,4-dinitro at 368 K, 2,4,6-trinitro with warm water, each giving the phenol after acidification
mechanism	addition-elimination: $\mathrm{OH^-}$ adds to the ring carbon bearing Cl, giving a resonance-stabilised carbanion (Meisenheimer complex, negative charge delocalised onto the o/p nitro groups), then $\mathrm{Cl^-}$ leaves
Wurtz-Fittig, Fittig	see section 4 (ArX with Na)

TRAP

Nitro groups activate haloarenes towards nucleophiles only at **ortho and para**; a meta nitro group does not help. And they are $-I, -M$ groups that **deactivate** the ring for electrophiles. Do not confuse the Dow process (high T and p) with the easy hydrolysis of nitro-substituted chlorobenzenes.

QUICK CHECK

Which is hydrolysed fastest by aqueous NaOH: chlorobenzene, p-nitrochlorobenzene, m-nitrochlorobenzene, 2,4-dinitrochlorobenzene?

Answer: 2,4-dinitrochlorobenzene $>$ p-nitrochlorobenzene $>$ m-nitro (no resonance help) $\approx$ chlorobenzene.

6 Polyhalogen compounds and environmental effects

POLYHALOGEN COMPOUNDS

COMPOUND	USES	HAZARD AND FACTS
CH_2Cl_2 (methylene chloride)	solvent, paint remover, propellant, metal cleaning	harms the CNS; harmful in air
$CHCl_3$ (chloroform)	solvent, formerly an anaesthetic	slowly oxidised by air and light to poisonous **phosgene** $COCl_2$: $2\,CHCl_3 + O_2 \xrightarrow{h\nu} 2\,COCl_2 + 2\,HCl$; stored in dark, filled, closed brown bottles (a little ethanol stops it); liver damage
CHI_3 (iodoform)	antiseptic (liberates iodine)	yellow solid, characteristic smell; made by the haloform reaction
CCl_4 (carbon tetrachloride)	refrigerant and aerosol-propellant manufacture, solvent, fire extinguisher (earlier)	damages the liver; contributes to ozone depletion; not hydrolysed by water
freons (CFCs), CCl_2F_2	refrigerants, air conditioning, aerosol propellants	in the stratosphere $Cl\cdot$ radicals destroy ozone: $Cl\cdot + O_3 \longrightarrow ClO\cdot + O_2$ and $ClO\cdot + O \longrightarrow Cl\cdot + O_2$ (chain); the ozone hole
DDT	insecticide against malaria and typhus vectors (2,2-bis(4-chlorophenyl)-1,1,1-trichloroethane)	not biodegradable, accumulates in fatty tissue, harms birds and fish; banned in many countries

KEY IDEA

Halogenated compounds persist: CCl_4 and freons release chlorine atoms high in the atmosphere, and DDT passes up the food chain. Chloroform must be kept from light and air to avoid phosgene. Iodoform formation (CHI_3, yellow precipitate with $I_2/NaOH$) is also the test for CH_3CO^- and $CH_3CH(OH)^-$ groups.

QUICK CHECK

Why is chloroform stored in dark brown, full bottles?

Answer: Light and air oxidise it to poisonous phosgene, $COCl_2$; a full bottle leaves no air.

7 Worked examples

ORDER OF S_N2 RATE

Order CH_3Br, CH_3CH_2Br, $(CH_3)_2CHBr$, $(CH_3)_3CBr$ towards OH^- (S_N2) and towards H_2O (S_N1).

S_N2: $CH_3Br > 1^\circ > 2^\circ > 3^\circ$ (steric hindrance); S_N1: the reverse, $3^\circ > 2^\circ > 1^\circ > CH_3Br$ (carbocation stability)

STEREOCHEMISTRY

(R)-$CH_3CH(Br)C_2H_5$ with $NaOH$ gives 100% (S)-alcohol by S_N2; by S_N1 with H_2O the product has 40% ee. % inversion and % retention?

S_N2: 100% inversion. S_N1: ee $= \%\text{inv} - \%\text{ret} = 40$ and the sum is 100: 70% inversion and 30% retention

DEHYDROHALOGENATION

Major product of 2-bromobutane with alcoholic KOH and with $(CH_3)_3CO^-K^+$.

alcoholic KOH: but-2-ene (Saytzeff, more substituted); bulky tert-butoxide: but-1-ene (Hofmann, less hindered H removed)

REAGENT CHOICE

Prepare ethyl iodide from ethyl chloride, and ethyl isocyanide from ethyl bromide.

$C_2H_5Cl + NaI \xrightarrow{\text{dry acetone}} C_2H_5I + NaCl$ **(Finkelstein);** $C_2H_5Br + AgCN \longrightarrow C_2H_5NC + AgBr$

CONVERSION

Convert benzene to phenol in two ways through a halogen compound.

(i) $C_6H_6 \xrightarrow{Cl_2/FeCl_3} C_6H_5Cl \xrightarrow[\text{then } H^+]{NaOH,\ 623\ K,\ 300\ atm} C_6H_5OH$ **(Dow); (ii)** $C_6H_6 \rightarrow C_6H_5NO_2 \rightarrow C_6H_5NH_2 \rightarrow C_6H_5N_2^+ \rightarrow C_6H_5OH$ **(diazonium hydrolysis)**

CARBYLAMINE LINK

Why does $AgCN$ with an alkyl halide give an isocyanide?

$AgCN$ is largely covalent: the lone pair on N (not C) is available, so the N attacks the carbon; ionic KCN attacks through C to give the nitrile

8 Last-minute checklist

BEFORE YOU ANSWER

Primary, secondary or tertiary? Strong or weak nucleophile or base? Protic or aprotic solvent? Aqueous or alcoholic KOH? Is the halogen on an sp^3 carbon at all?

- $C-X$: length $F < Cl < Br < I$, enthalpy opposite; reactivity $RI > RBr > RCl$; boiling points $RI > RBr > RCl$, branching lowers; p-dichlorobenzene highest m.p.
- Make R−Cl: $SOCl_2$ (best), PCl_5, PCl_3, $HCl/ZnCl_2$; R−I: Finkelstein; R−F: Swarts; ArX: Sandmeyer (Cu(I)), Gattermann (Cu), KI, Balz-Schiemann; not from phenol.
- S_N2: inversion, $k[RX][Nu]$, $CH_3 > 1^\circ$; S_N1: racemisation, $k[RX]$, 3°, benzyl, allyl; E2 anti-periplanar, Saytzeff, bulky base gives Hofmann; aq. KOH substitutes, alc. KOH eliminates.
- KCN nitrile, AgCN isocyanide, KNO_2 nitrite, $AgNO_2$ nitro; Grignard needs dry ether and is destroyed by active H; Wurtz, Wurtz-Fittig, Fittig use Na in dry ether.
- Haloarenes: partial double bond, sp^2, no S_N1/S_N2; o/p nitro activates (addition-elimination, Meisenheimer); Dow process; EAS slow but o/p; $CHCl_3$ to phosgene; freons deplete ozone; DDT persists.

Now test it. Practise this chapter with past-paper and bank questions on Prep Vault. **Practice this chapter →**