

Haloalkanes & Haloarenes

Replacement of H atom(s) in an aliphatic or aromatic hydrocarbon by halogen atom(s) gives alkyl halide (haloalkane) ~~and~~ or aryl halide.

$R-X$ ($sp^3 C$)	vs	$Ar-X$ ($sp^2 C$)	\leftarrow alkyl vs
			\leftarrow aryl halide

Some Useful Halocompounds

- * Chloramphenicol : antibiotic (typhoid)
- * Thyroxine : I-hormone (anti-goiter)
- * Chloroquine : anti-malarial drug
- * Halothane : surgical anaesthetic

Classification

(a) By no. of halogen atoms :

mono, di, tri, tetra, ~~hexa~~ ... polyhalo.

(b) By hybridisation of C - X bond :

* $sp^3 C - X$: alkyl, allyl, benzyl halides

* $sp^2 C - X$: vinyl, aryl halides

Alkyl halides are 1deg, 2deg or 3deg depending on whether the C carrying X is 1deg, 2deg or 3deg C.

Gem-dihalide : both X on same C ; vic : adj. C.

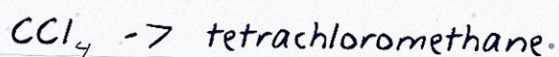
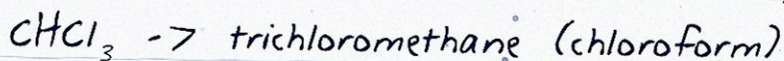
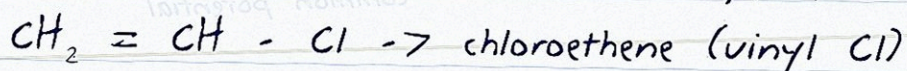
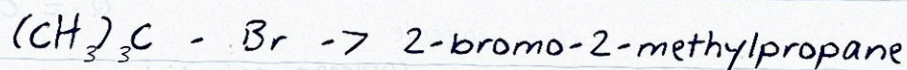
Nomenclature & C-X Bond

IUPAC Nomenclature

Alkyl halides : halosubstituted hydrocarbons.

Locate X with lowest locant ; ortho / meta / para
= 1,2 / 1,3 / 1,4 in IUPAC system.

Examples :



Nature of C - X Bond

X is more electronegative than C, so C - X is

polar : $\text{C}^{\delta+} - \text{X}^{\delta-}$ (C : partial +ve charge).

Down the group : size of X increases

\Rightarrow bond length increases : $\text{C-F} < \text{C-Cl} < \text{C-Br} < \text{C-I}$

\Rightarrow bond enthalpy decreases : $\text{C-F} > \text{C-Cl} > \text{C-Br} > \text{C-I}$

\Rightarrow dipole moment : $\text{CH}_3\text{-Cl} (1.86 \text{ D}) > \text{CH}_3\text{-I} (1.64 \text{ D})$

C-F: 139 pm

C-I: 214 pm

\leftarrow longer

$\leftarrow \Rightarrow$ weaker

\leftarrow R-I, best

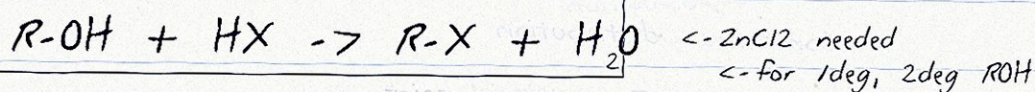
Best leaving group : $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$

(weaker C - X \Rightarrow easier cleavage in subst.)

Preparation of Haloalkanes

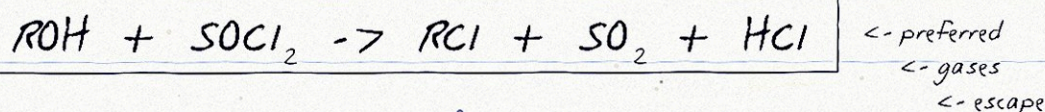
1. From Alcohols

Replace -OH of ROH by X using HX, PX₃, PX₅ or SOCl₂ (thionyl chloride).



Reactivity of ROH with HX : 3deg > 2deg > 1deg

Tertiary ROH + conc. HCl react at room temp, no catalyst needed. *

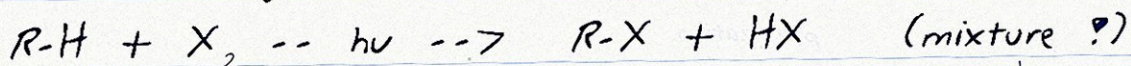


PBr₃, PI₃ : made in situ from red P + Br₂ / I₂.

For R - F : Swarts rxn (R-Cl/Br + ~~KF~~ AgF / SbF₃)

2. From Hydrocarbons

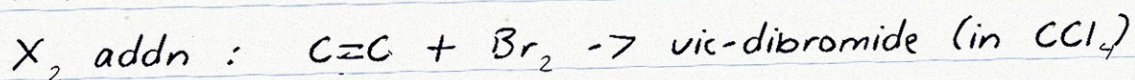
(a) Free radical halogenation of alkane :



Gives isomeric mono- + polyhalides ; poor yield.

(b) From alkenes :

* H-X addition : follows Markovnikov rule



Decolourisation of Br₂ = test for C=C bond.

Halogen Exchange & Haloarenes

3. Halogen Exchange (Finkelstein)

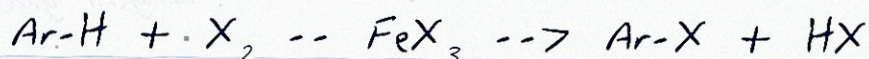
Alkyl iodides made from R-Cl / R-Br with NaI in dry acetone (Finkelstein reaction).



Swarts rxn : R-Cl/Br + AgF / Hg₂F₂ / SbF₃
 → R-F (best route to alkyl fluorides).

Preparation of Haloarenes

(i) Electrophilic substitution :

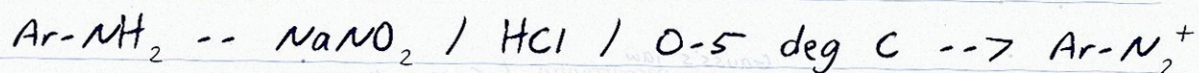


Lewis acid (Fe / FeCl₃) needed ; only Cl, Br.

o- & p- isomers separated by m.p. difference.

Iodination needs HNO₃ (oxidiser) to remove HI formed (the rxn is reversible).

(ii) Sandmeyer reaction :



Then with Cu₂X₂ / HX : → Ar-X + N₂(g)

For Ar-I : Ar-N₂⁺ + KI → Ar-I (no Cu needed)

Why no direct ArOH → ArX ? C-O in phenol has partial double-bond char ⇒ too strong to break.

Physical Properties

Colour & Smell

Pure R-X : colourless ; R-Br & R-I darken in light.

Many volatile halides have a sweet smell.

Melting & Boiling Points

CH_3Cl , CH_3Br , $\text{C}_2\text{H}_5\text{Cl}$ \rightarrow gases at RT

Higher members : liquids / solids.

B.p. of R-X $>$ parent R-H of similar mass

(dipole-dipole + van der Waals forces).

b.p. : R-I $>$ R-Br $>$ R-Cl $>$ R-F	larger X $\leftarrow \Rightarrow$ more e- $\leftarrow =$ bigger vdW
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Among isomers : b.p. decreases with branching

(2-bromo-2-methylpropane : lowest of three).

Dihalobenzenes : b.p. of o, m, p almost equal. *

But m.p. of ~~ortho~~ para- \gg ortho / meta (symmetry fits crystal lattice better).

Solubility & Density

R-X : slightly soluble in water (can't H-bond well)

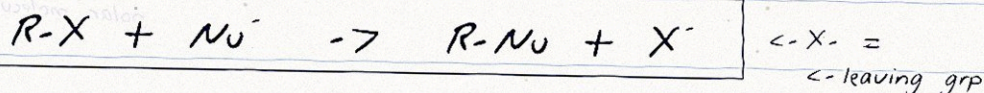
but freely soluble in organic solvents.

R-Br, R-I, polychloro cpds : denser than water.

Density increases with no. of X and mass of X.

Nucleophilic Substitution

Nu⁻ attacks the C carrying dt ; X⁻ leaves.



SN2 Mechanism (bimolecular)

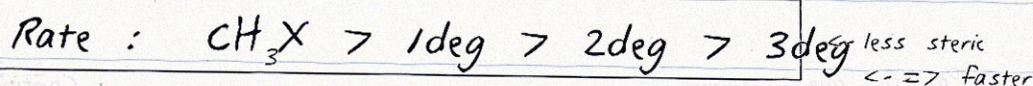
Rate = $k [R-X] [Nu^-]$ (2nd order kinetics)

Nu attacks from ~~front~~ back side, X leaves;

single step, no intermediate, transition state

with 5-bonded C \Rightarrow inversion of configuration

("umbrella" / Walden inversion).



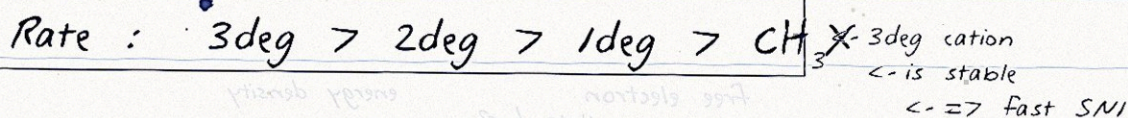
SN1 Mechanism (unimolecular)

Rate = $k [R-X]$ (1st order ; only [R-X] matters)

Step I (slow) : $*R-X \rightarrow R^+ + X^-$

Step II (fast) : $R^+ + Nu^- \rightarrow R-Nu$

Done in polar protic solvent (H₂O, ROH, AcOH).



Allyl / benzyl halides : resonance-stabilised
carbocation \Rightarrow react fast by SN1.

Stereochemistry of NS Reactions

Optical Activity

Compound rotating plane-polarised light is optically active. Measured by polarimeter.

(+) dextro = clockwise ; (~~+~~ -) laevo = anti-clockwise

Chirality

Asymmetric C (stereocentre) : 4 different groups attached. Mirror image NOT superimposable \Rightarrow molecule is chiral \Rightarrow optically active.

e.g. butan-2-ol : chiral ; propan-2-ol : achiral.

Enantiomers & Racemic Mixture

Enantiomers : non-superimposable mirror images.

Same physical props except rotation : equal & opposite in sign.

Racemic mix : (+) + (-) = zero rotn

\leftarrow denoted
 \leftarrow (+-) or dl

Outcome at Stereocentre

Retention : config preserved (no bond broken).

Inversion : config flipped (S_N2 reaction).

Racemisation : 50:50 mix of (+) & (-) (S_N1 rxn).

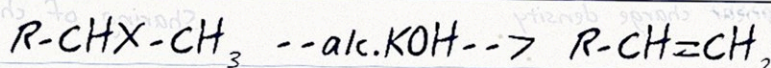
S_N1 carbocation is planar (sp^2) \Rightarrow attack both faces.

Elimination & Reactions with Metals

Beta-Elimination (E1 / E2)

$R-X$ with beta-H + alc. KOH (alc. KOH, heat) :

loses H^+ from beta-C and X from alpha-C \Rightarrow alkene.



\leftarrow dehydro-
 \leftarrow halogen.

Zaitsev / Saytzeff rule : preferred alkene is the one with MORE alkyl groups on $C=C$ atoms (more substituted = more stable). *

e.g. 2-bromopentane \rightarrow pent-2-ene (major) + pent-1-ene (minor).

Substitution vs Elimination

- * aq. KOH \rightarrow substitution (R-OH)
- * alc. KOH \rightarrow elimination (alkene)
- * bulky base \rightarrow elimination favoured
- * 1deg R-X \rightarrow SN2 ; 3deg R-X \rightarrow SN1 or E1

Reaction with Metals

Grignard : $R-X + Mg \xrightarrow{\text{dry ether}} R-MgX$ *

C-Mg bond polar covalent ; Mg-X bond ionic.

Wurtz : $2 R-X + 2 Na \xrightarrow{\text{ether}} R-R + 2 NaX$

Doubles the number of C atoms. Avoid moisture !

Reactions of Haloarenes

Low Reactivity Towards Nu-Sub

Ar - X is much less reactive than R - X because :

(i) Resonance gives C-X partial double bond char.

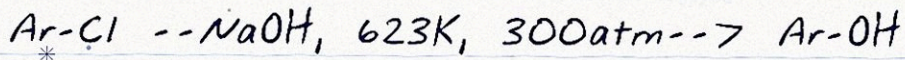
(ii) sp^2 C holds X tighter ; C-X bond shorter

(Ar : 169 pm vs R : 177 pm).

(iii) Phenyl cation NOT stabilised by resonance.

(iv) Nu- repelled by electron-rich arene ring.

Nu-Sub : Replacement by -OH



<- harsh
<- conditions

Activated by $-\text{NO}_2$ at o- / p- positions

(stabilises carbanion intermediate by resonance).

m- NO_2 gives NO activation \rightarrow negative charge

doesn't reach the meta- NO_2 in resonance forms.

Electrophilic Substitution

Halogen is slightly deactivating but o-/p-directing :

* $-\text{I}$ effect \Rightarrow e- withdrawal (deactivation)

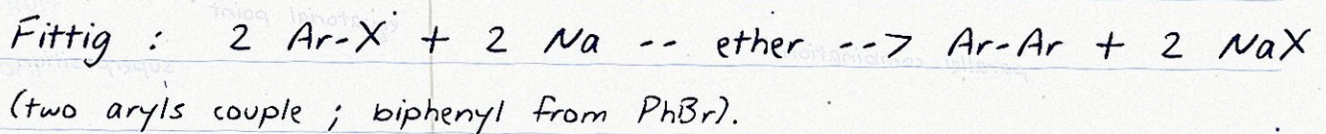
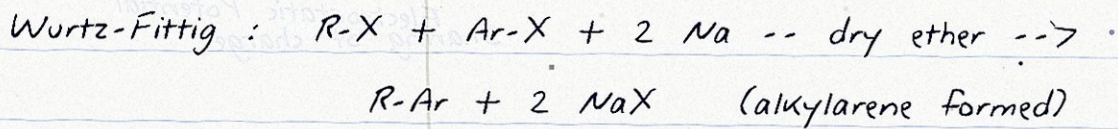
* $+\text{R}$ effect \Rightarrow e- release at o- & p-

Result : ortho / para products form preferentially

but rxn is slower than for benzene itself.

Wurtz-Fittig & Polyhalogen Cpds

Reactions of Ar - X with Metals



Important Polyhalogen Compounds

* CH_2Cl_2 (DCM, methylene chloride) :

paint remover, aerosol, drug-mfg solvent.

Harms CNS ; eye / skin contact = burns.

* $CHCl_3$ (chloroform) : solvent for fats,

iodine, alkaloids. Once used as anaesthetic.

Oxidised by air + light to $COCl_2$ (phosgene)

stored in dark, full bottles (no air space).

* CHI_3 (iodoform) : earlier antiseptic ;

antiseptic action is from free I_2 it releases.

* CCl_4 : feedstock for CFCs ; once a

cleaning fluid. Damages liver, ozone-depleting.

* Freon-12 (CCl_2F_2) : refrigerant, aerosol

propellant. Diffuses to stratosphere & DESTROYS

O_3 by radical chain rxn (ozone depletion?)

* DDT : 1st chlorinated insecticide (Paul Muller,

1939). Stable, fat-soluble \Rightarrow bioaccumulates. Banned.