

- empirical $\rightarrow$ molecular $\rightarrow$ structural $\rightarrow$ displayed $\rightarrow$ skeletal

alkanes $- \text{C}_n\text{H}_{2n+2}$ alkenes C_nH_{2n} arenes C_6H_6

halogenoalkanes $- \text{C}_n\text{H}_{2n+2}\text{X}$ alcohols R-OH aldehydes R-CHO

ketones $\text{R}_2\text{C=O}$ carboxylic acids R-COOH esters R-COO-R'

amines R-NH_2 nitriles R-CN amide R-CONH_2

- functional group - group responsible for chemical characteristics

- isomerism - structural - position

- functional group

- chain

- stereo - geometrical - cis/trans E/Z (must be about C=C)

- optical - chiral centre C , enantiomers

- racemic mixture 50% to 50%

- Alkanes - generally unreactive - low ΔE so non-polar

- combustion + halogenation with $\text{Cl}_2/\text{Br}_2/\text{F}_2$

$\hookrightarrow$ homolytic free radical substitution

initiation: $\text{Cl}_2 \xrightarrow{\text{h}\nu} 2\text{Cl}^\bullet$ propagation: $\text{Cl}^\bullet + \text{CH}_4 \rightarrow \text{CH}_3^\bullet + \text{HCl}$

$\text{CH}_3^\bullet + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl}^\bullet$

termination: $\text{Cl}^\bullet + \text{Cl}^\bullet \rightarrow \text{Cl}_2$

$\text{CH}_3^\bullet + \text{CH}_3^\bullet \rightarrow \text{C}_2\text{H}_6$

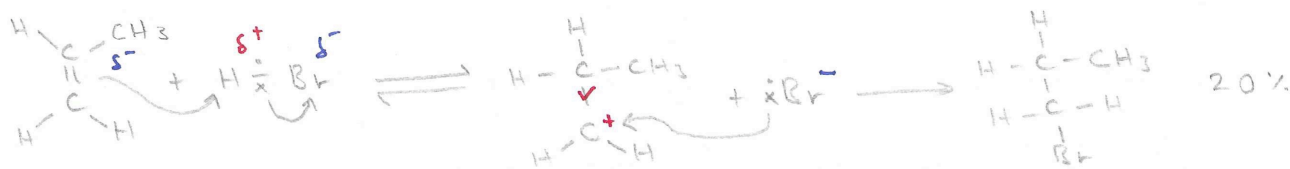
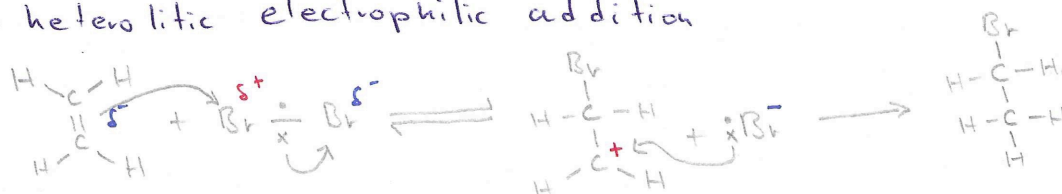
$\text{Cl}^\bullet + \text{CH}_3^\bullet \rightarrow \text{CH}_3\text{Cl}$

multisubstitution if $[\text{Cl}] \uparrow$ $[\text{CH}_4] \downarrow$

- Alkenes - e^- density around C=C

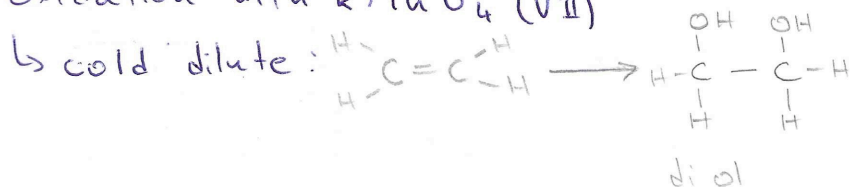
HX or X_2 (aq)

$\hookrightarrow$ heterolytic electrophilic addition



- +ve inductive effect - alkyl groups are e^- releasing $\therefore$ stabilise carbocation in intermediate
- results in regio selectivity (Markovnikov rule)

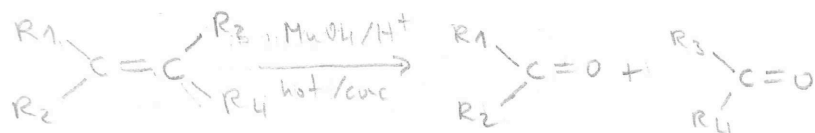
↳ oxidation with $KMnO_4$ (VII)



acidic: $MnO_4^- \longrightarrow Mn^{2+}$
purple $\longrightarrow$ colourless

alkaline: $MnO_4^- \longrightarrow MnO_2$
dark green $\longrightarrow$ dark brown

↳ hot acidified concentrated: reflux!



no further reaction with ketone

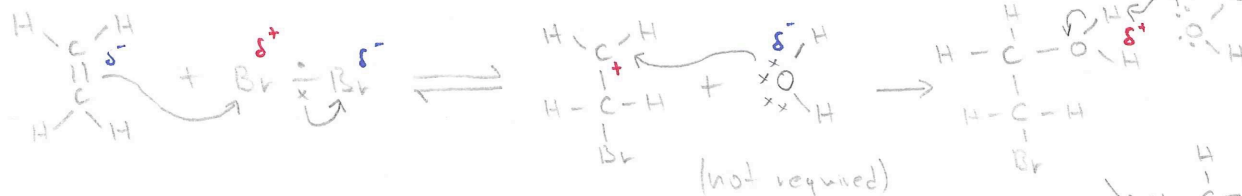
↳ cracking - heat in absence of O_2
with zeolite catalyst

- alkane $\longrightarrow$ alkene + alkane

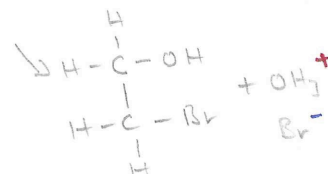
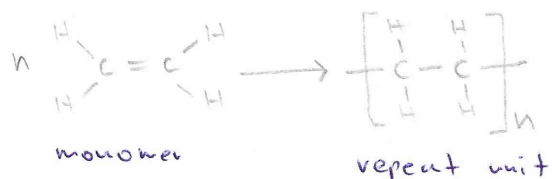
↳ hydrogenation - addition of H_2 - nickel catalyst $140^\circ C$

↳ hydration - addition of H_2O (aq) - H_3PO_4 conc catalyst $330^\circ C$ 6 MPa

↳ alkene + $Br(aq) \longrightarrow$ bromo alcohol brown $\longrightarrow$ colourless

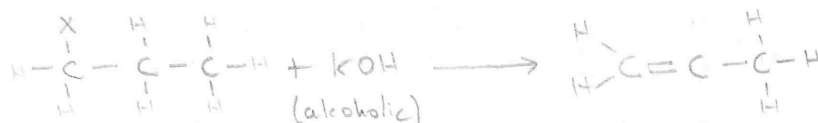


↳ addition polymerisation:



- Halogeno alkanes - polar primary 1° , secondary 2° , tertiary 3°
- reactivity increases going down the group since $BE \downarrow$

↳ electrophilic elimination:



sometimes not possible since 2nd C can't lose the H to form $C=C$

- CFCs - chemically inert - non flammable - non toxic

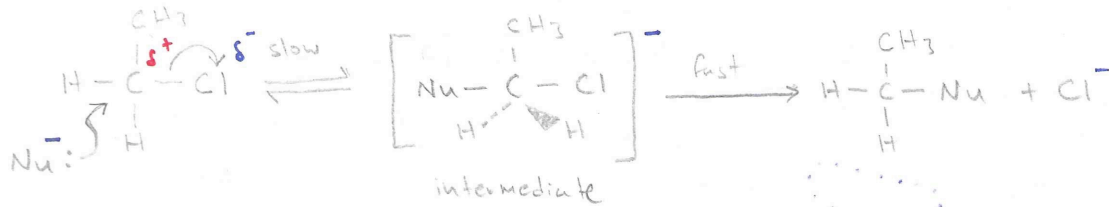
- used as aerosol propellants + solvents + refrigerants

- O_3 layer - absorbs UV - UV breaks $C-Cl$ in CFC giving $Cl^\bullet$ which reacts with 10^6 O_3 molecules

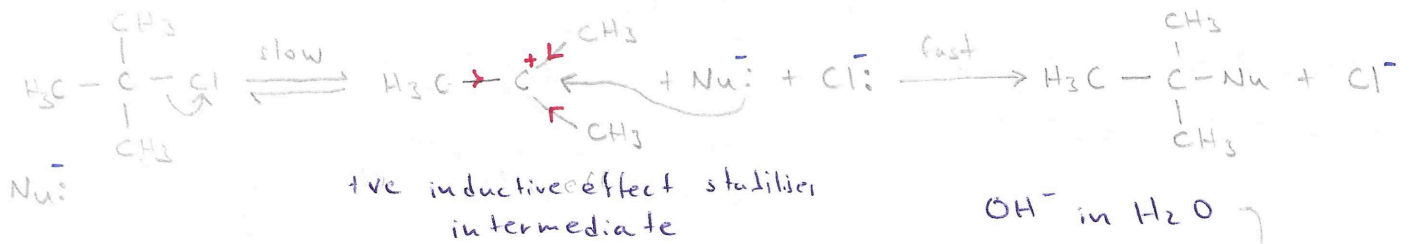
- solution - HFC + HFE - hydro fluoro ethers / carbons higher bond strength $C-F$

- Halogenoalkanes

↳ bimolecular nucleophilic substitution - S_N2 - only 1° halogenoalkanes



↳ monomolecular nucleophilic substitution - S_N1 - only 3° halogenoalkanes



↳ 2° go by mix of S_N1 and S_N2

OH^- in H_2O
 CN^- in $EtOH$
 NH_3 in $EtOH$
 $NH_3(g)$
 OH^- in $EtOH$ - elimination

substitution

- Alcohols - H bonds so $\uparrow$ bp + mix with H_2O

↳ substitution to give halogenoalkane

use: halogen gas, PCl_3 , PCl_5 , $SOCl_2$

white stony fumes

↳ test for OH use PCl_5 $R-OH + PCl_5 \xrightarrow{rtp} R-Cl + HCl + POCl_3$

↳ alcohol + Na - similar to $H_2O + Na$ but less vigorous

- releases $H_2(g)$ and sodium alkoxide (basic salt)

ethanol + Na $\rightarrow$ H_2 + sodium ethoxide

↳ oxidation - 1° and 2° only oxidised 3° not

- done by $K_2Cr_2O_7$ acidified with dil H_2SO_4 heated

$Cr_2O_7^{2-} \rightarrow Cr_2O_3$
 orange green

1° alcohol: alcohol $\rightarrow$ aldehyde $\rightarrow$ carboxylic acid

2° alcohol: alcohol $\rightarrow$ ketone

3° alcohol: not oxidised

alcohol vapour passed over

↳ dehydration - elimination reaction with Al_2O_3 hot or H_2SO_4

- alcohol $\xrightarrow{Al_2O_3}$ alkene + H_2O

- Carboxylic acids - made by oxidising 1° alcohols or nitriles from ketones

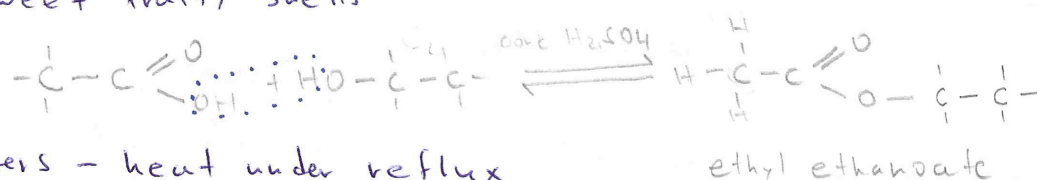
↳ with alkalis give H_2O + salt

carbonates give CO_2 + H_2O + salt

↳ reduced with $LiAlH_4$ in dry ether at rtp adds H : reduction

$LiAlH_4$ reacts violently with water

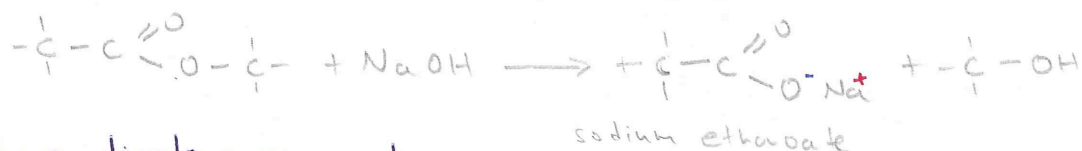
- Esterification - alcohol + carboxylic acid $\xrightleftharpoons{\text{H}_2\text{SO}_4 \text{ conc}}$ ester + H_2O
- under reflux with strong acid catalyst
 - H_2SO_4 also removes H_2O shifting the equilibrium
 - sweet fruity smells



↳ hydrolysis of esters - heat under reflux with acid or base

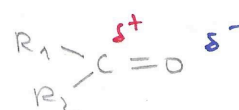
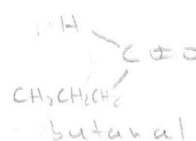
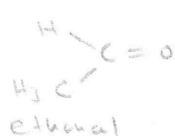
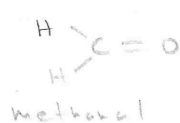
↳ acid: dynamic eqb in reverse giving alcohol + acid

↳ alkali: fully hydrolysed - acid reacts with alkali to give salt of carboxylic acid

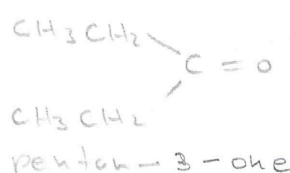
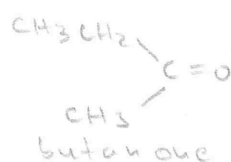
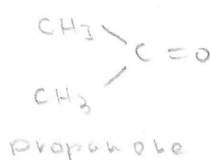


- Carbonyles - large dipole = very polar

↳ aldehydes - al



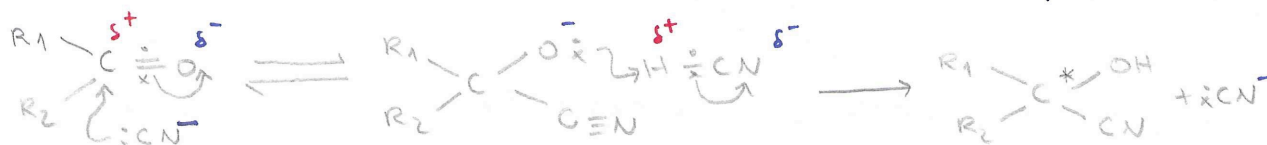
↳ ketones - one



↳ when preparing aldehydes 1^o alcohol oxidised and product immediately distilled off to avoid further oxidation

↳ can be reduced with LiAlH_4 in dry ether

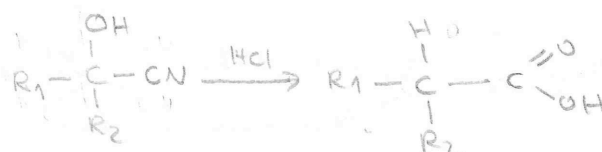
↳ nucleophilic addition of HCN - CN^- nucleophile attacks $\text{C}=\text{O}$



- nitrile refluxed with dil HCl produces carboxylic acid

but there is 1 more C in the chain

- all ways 2-hydroxy nitrile formed

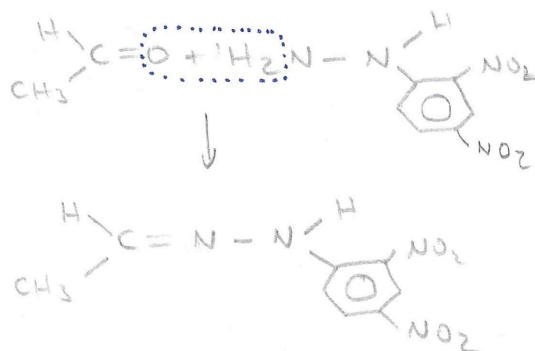


trigonal planar

so CN^- approaches from top or bottom giving a 50%:50% racemic mixture

- Testing carbonyles

↳ 2,4-DNPH (2,4-di nitro phenyl hydrazine)



- test for both aldehyde + ketones

- add 2,4-DNPH solution gives orange ppt

- recrystallise ppt and measure mp used to find identity of carbonyl

- condensation reaction

↳ Tolls reagent - test for aldehyde - aqueous AgNO_3 in excess NH_3

(warm)

- Ag^+ acts as mild oxidising agent aldehyde $\rightarrow \text{COOH}$

$\text{Ag}^+ \rightarrow \text{Ag}$ - mirror on test tube

↳ Fehlings solution - test for aldehyde - alkaline Cu^{2+} solution

(warm)

- Cu^{2+} act as mild oxidising agent aldehyde $\rightarrow \text{COOH}$

$\text{Cu}^{2+} \rightarrow \text{Cu}^+$ blue $\rightarrow$ red/orange (braguel)

↳ tri-iodomethane - iodo form - test for $\text{R}-\text{C}(=\text{O})\text{CH}_3$ or $\text{R}-\text{C}(\text{OH})(\text{H})\text{CH}_3$



antiseptic smell

mp = 119°C

- alkaline solution of I_2

- with $\text{R}-\text{C}(\text{OH})(\text{H})\text{CH}_3$ first oxidised to $\text{R}-\text{C}(=\text{O})\text{CH}_3$