REVISION ORGANIC CHEMISTRY

naming

① longest carbon chain (meth/eth/prop/but)

② type of bonding (ane/ene/yne)

③ functional group → (functional group) alcohols (class)
- -OH, -ol (hydroxyl)
- $-C(=O)-$, ketone (-one)
- $-NH_2$, amino- (amino)
- $-COOH$, carboxyle -oic acid
- -CHO (end of chain), -al
- $-C(=O)-O-R$, ester -oate.

④ numbers for position

homologous series [series of cpds in the SAME family, differ by a common structural unit]

· same general formula · similar chem properties · grad. physical prop.

classification of alcohols/halogenoalkanes/amines

primary: ONE -R group (alkyl like $CH_3$ or $CH_2$)

e.g. $R-CH_2-OH$ $R-CH_2-Br$ or $R-NH_2$

secondary: TWO -R groups

$R-CH(R)-OH$ $R_1-CH(R)-Br$ $R-NH-R'$

tertiary: 3 R-groups

$R_1-C(R_2)-OH$ ...

some org. compds

$H-CH_2-CH_2-NH_2$ aminoethane

$H-CH(NH_2)-CH_2-H$ 2-amino propane

$H-CCl_2-CH_2-H$ 1,1-dichloroethane

$H-CH_2-CHO$ (aldehyde) ethanal

$H_3C-C(=O)-CH_3$ (ketone) propanone

$C_2H_5-COOH$ (carboxylic acid) propanoic acid

$H_3C-COO-C_2H_5$ (ester) ethyl ethanoate

$CH_3-CONH_2$ (carboxamide) ethanamide

$C_2H_5-CONH_2$ propanamide

$H_3C-C\equiv N$ (nitrile) ethanenitrile

$H_5C_2-C\equiv N$ propanenitrile

$H-CH_2-O-CH_2-H$ (ester) methoxymethane ... ethoxyethane...

benzene ring ($C_6H_5-$)

chloro benzene

benzene – AROMATIC, UNSATURATED Hydrocarbon

① CC bond lengths equal

② enthalpy of hydrog. less exo than expected → more stable [chem property]

③ ↛ decolourize bromine

## structural formulas / isomers

- same MOLECULAR formula + diff STRUCTURAL formula
- may have diff PHYSICAL prop / similar CHEM prop.

about painkillers....

→ all have –OH phenol group OH → ester group (C(=O)–O–R)

→ some have CARBOXYL GROUP = C(=O)–OH → carboxyamide (NH–C(=O))

## bpts / properties

↑ length ↑ bpt but at decreasing rate

↑ branches → reduce SA contact ↓ bpt

} same for volatility

? solubility in water = polarity? — if chain gets longer ↓ solubility

## alkanes

✓ unreactive ✓ go thru combustion (I c : C and CO)

✓ substitution in UV light ✓ chlorination of methane

about methane.. free radical substitution

① $Cl_2 \rightarrow Cl\cdot + Cl\cdot$ (UV!!) (→ homol) — init

② $CH_4 + Cl\cdot \rightarrow CH_3\cdot + HCl$ — propog.

③ $CH_3\cdot + Cl_2 \rightarrow CH_3Cl + Cl\cdot$ — propog. v. 2

TTT: any free radicals react.

Cl–Cl → photochemical homolytic fission.

## alkenes

✓ more reactive ✓ addition reactions ✓ halogen halide ✓ polymerization (heat & pressure)

$+H_2$ = hydrogenation (OILS; heat and Nickel)

$+Br_2$ bromination (TEST 4 ALKE)

$+H_2O$ hydration [ALCOHOL] (ALCOHOLS; heat & conc $H_3PO_4$)

## alcohols

✓ combustion ✓ oxidation

3 $CH_3CH_2OH + Cr_2O_7^{2-} + 8H^+ \rightarrow 3CH_3CHO + 2Cr^{3+} + 7H_2O$

$H-C(H)(H)-C(H)(H)-OH \xrightarrow[Cr_2O_7^{2-}+H^+]{[O]} H-C(H)-C(=O)-H$ (ethanal) $\xrightarrow{[O]} H-C(=O)-O-H$ (ethanoic acid)

primary – ONE additional carbon → aldehydes (C=O, H) → carboxylic acids (C(=O)–OH)

secondary – TWO c's → ketones (C=O)

$H-C(CH_3)(H)-OH \rightarrow C-C(=O)-CH_3$

GENERAL idea: $CH_3CH_2OH + [O] \xrightarrow[H^+]{Cr_2O_7^{2-}} CH_3CHO + H_2O$

distillation: separation of aldehyde / carboxylic acid based on different boiling points

reflux: intense distillation which recondenses vapours (carboxylic acid)

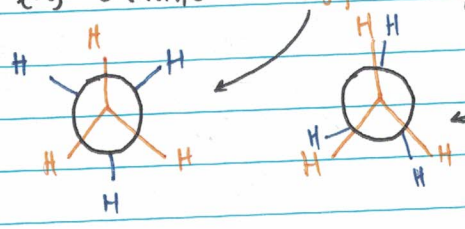
# stereoisomerism (revision notes)

- same molecular/structural/chemical formula
- different spatial (3D arrangement)

THERE ARE 2 TYPES:

**conformational**
↳ free rotation about sigma (σ) bonds
↓
↳ differ in arrangement of atoms around 1 bond (single)
↳ atoms are CONSTANTLY moving (rapidly) ∴ can't identify separate

e.g. Ethane: staggered & eclipsed (two extreme conformations)



(least stable bc H-H proximity is repulsive — same charges repel)

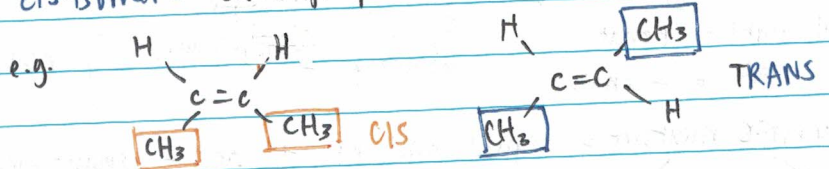
**configurational**
↳ restricted rotation ∵ π bonds
↳ cis-trans, E Z, optical isomerism

configurational isomers ONLY interconverted by breaking of covalent bonds
2 TYPES: ① cis-trans, E/Z & ② optical isomers

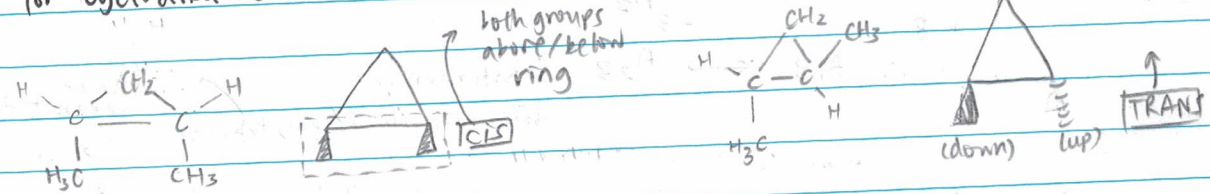
① cis-trans & E-Z

alkenes + cycloalkanes → restricted rotation due to C=C (π) double bond
↳ two different groups attached to double-bond C=C
↳ sideways overlap above + below plane.

cis isomer — same group same side trans: same grp, opp sides.

e.g. 

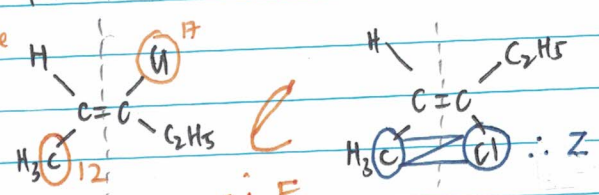

↳ for cycloalkanes... restricted rotation due to RING.




EZ: double bonded carbon with THREE/FOUR different groups

① atom w/ higher atomic number on C has priority
② if atoms have same atomic number, compare to NEXT atom

prioritize



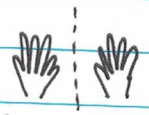

BTW!

⇒ LIGHT: cis-trans isomers have a photochemical transformation in ↳ rhodopsin in the eye, pigment

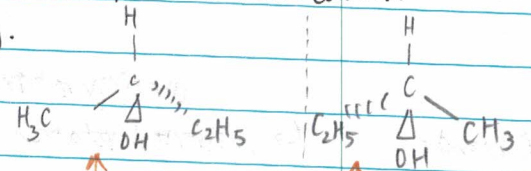
⇒ HYDROGENATION: cis fats → trans fats

## Optical isomerism

- must have CARBON bonded to 4 DIFFERENT functional groups / atoms
  - ↳ ie assymetric / chiral carbon.



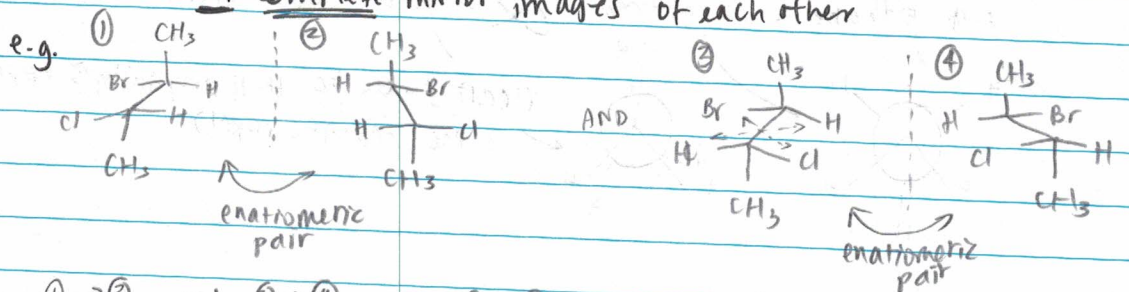
e.g.




- exists as a mirror image of itself
- but is non-superimposable
- pairs are called enantiomers

- diastereomers have different configurations at SOME chiral centres
  - → non-superimposable
  - BUT NOT complete mirror images of each other

e.g.

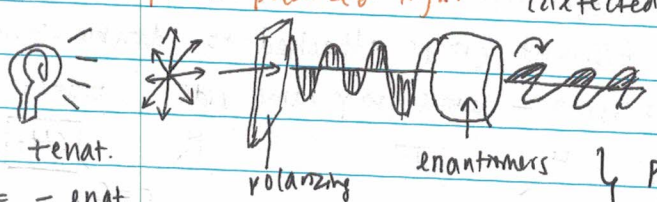



① → ③ and ② → ④ and ② → ③ and ① → ④ are diastereomers.

- properties of optical isomers

✓ same physical properties

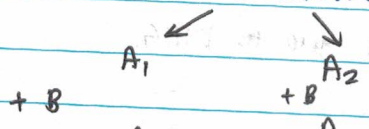
EXCEPT effect on plane polarized light (can rotate plane of polarised light) (detected by polarimeter)




↳ POLARIMETER.

- rotated to the right = +enat.
  - left = − enat.

IF... in racemic mixture = equal amt of + and − enantiomers ∴ NO effect
∴ optically inactive




∴ $A_1B \longleftrightarrow A_2B$

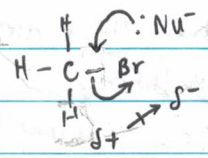
diastereomers ∴ can be separated!
diff properties (phy + chem)
↳ reverse −B ∴ get $A_1$ / $A_2$

process called resolution.

substitution / condensation

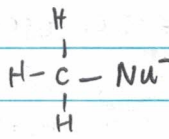
more reactive than alkanes because they have polar bonds / are asymmetrical

**SUBSTITUTION** of halogeno alkanes

e.g. 

∴ nucleophyles / attracted to lack of e⁻ in C as Br pulls!

have e⁻ RICH to donate (2x) to

∴ carbon 

[usually $OH^-$ solution]

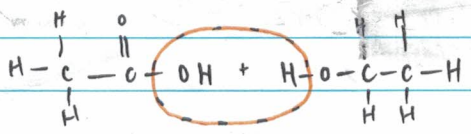
$H_2SO_4 + HNO_3 \rightarrow H^+ + NO_2^- + HSO_4 + H_2$

**SUBSTITUTION** of benzene

- has high e⁻ density  + $Cl_2$ , $Cl^+$ produced  + HCl (in presence of $AlCl_3$)

 + $HNO_3$ $\xrightarrow[50^\circ C]{H_2SO_4}$  + $H_2O$ (nitrobenzene)

**CONDENSATION** alcohol + acid / esterification



→ methyl → methanoate

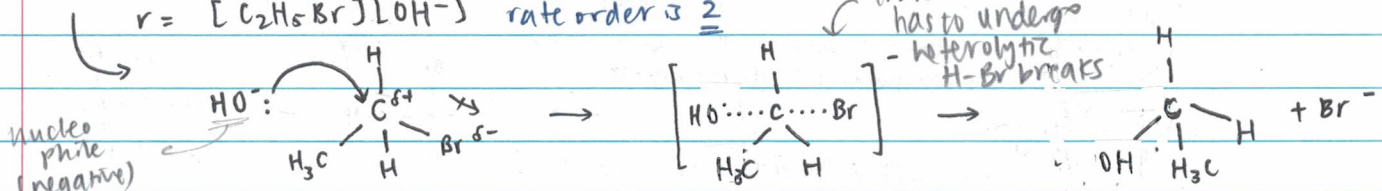
→ ester (-oate.)

**NUCLEOPHYLLIC SUBSTITUTION**

$S_N2$ happens with PRIMARY halogenoalkanes → bimolecular

e.g. $C_2H_5Br + OH^- \rightarrow C_2H_5OH + Br^-$

$r = [C_2H_5Br][OH^-]$ rate order is 2



nucleophile (negative)

transition has to undergo - heterolytic H-Br breaks

C-Br bond length is longer than C-H / C-C bond length. ∴ Br gets pushed OUT.

OH better than water as it is -ve ion ∴ greater attraction of the charge

NEED - nonpolar solvent, should NOT have $H^+$ produced (or OH will react)

- aprotic (DOES NOT have OH or NH bonds or provide $H^+$/protons)

$Sn1$ happens with TERTIARY → uni molecular

e.g. $C(CH_3)_3Br + OH^- \rightarrow C(CH_3)_3OH + Br^-$

$r = [C(CH_3)_3Br]$

no space for OH to rush out Br

∴ must wait for Br to leave group

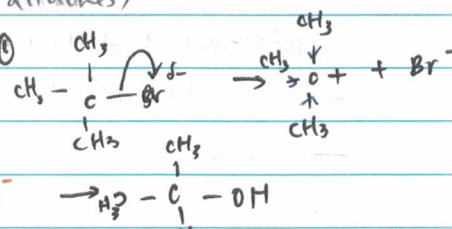
carbons BLOCK $OH^-$ from attacking ∴ must happen in TWO steps

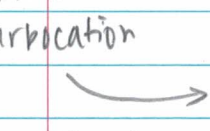
↳ official name = STERIC hinderance

① $C(CH_3)_3Br \xrightarrow{slow} C(CH_3)_3^+ + Br^-$ (C-Br breaks first → heterolytic fission → carbocation)

② $C(CH_3)_3^+ + OH^- \xrightarrow{fast} C(CH_3)_3OH$ (it attaches)

BC ① is slower, it is rate determining

actual mech. 

this is a carbocation → 

POSITIVE INDUCTIVE EFFECT

$CH_3$ pushes their electrons towards the centre one to stabilise it

NEED - polar, protic solvents

that's why $CH_3$ doesn't have that many e⁻ to stabilise it!)

solvents...

$SN_2$ : APROTIC, LESS POLAR
↳ or will react with $OH^-$
↳ unable to form H bonds↑

$SN1$ : PROTIC, POLAR... they support ① → they attract $Br^-$ to some tertiary halogenoalk
↳ can form H bond
↳ this prevents $OH^-$ attacking the halogenoalk in the first place but once $Br^-$ is out, then $H^+$ will $Br^-$ and OH is free!

FACTORS affecting nucleophyllic substitution

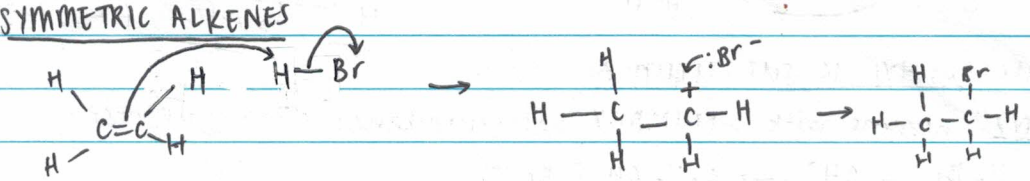
① nature of nucleophile → $e^-$ density higher
· better if anion (like $OH^-$, not water) over neutral.

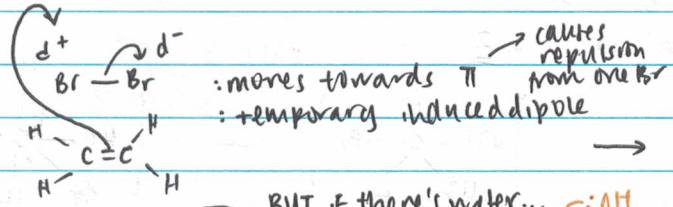
② nature of halogen
C–F bond is really strong (diff in $e^-$) ∴ REACT slowest!

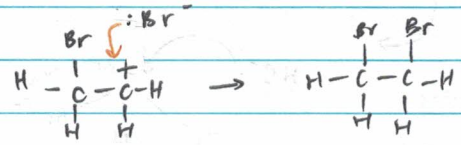
③ tertiary faster than secondary. ($SN1 > SN2$ bc less activation $e^-$)
faster

electrophillic addition

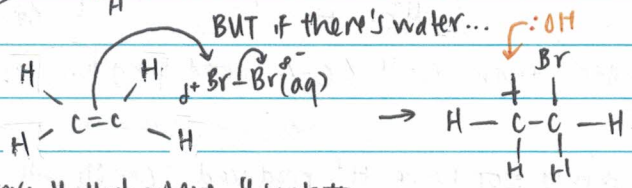
SYMMETRIC ALKENES





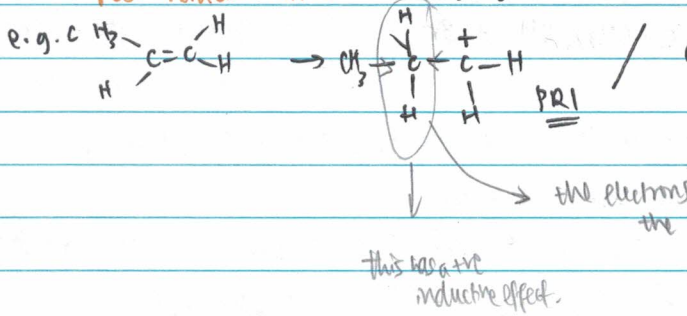



BUT if there's water...



(2bromoethanol)

markov: H attach where H bonds to
· tertiary has 3 Cs attached - tend to push $e^-$ to C atoms = stabilise the charge
pos inductive effect : MOST stable choice has most C atoms. whenever H+ doesn't go, put +

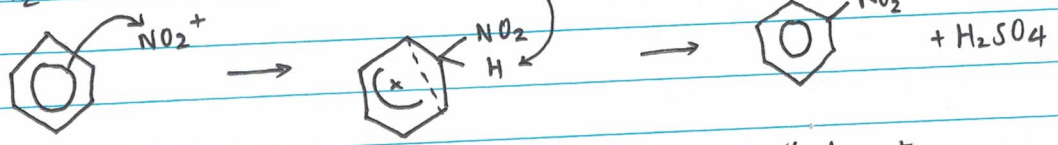
e.g. 


reductions of alcohols — dry ether
— carboxylic acids — $LiAlH_4$ → primary alcohols
— Ketones — $NaBH_4$, heat → tertiary alcohols

electrophyllic substitution

NITRATION OF BENZENE

① $H_2SO_4 + HNO_3 \rightleftharpoons H_2O + NO_2^+ + HSO_4^-$ ← electrophile.



1. $NO_2$ attracted to π bond, 2. the charge spread w/ the rest
3. loses $H^+$ (proton) so bond is reformed. 4. catalyst regenerated.

② $H^+ + HSO_4^- \rightarrow H_2SO_4$

REDUCTION OF CARBONYL COMPOUNDS (reverse of alcohol oxidation)

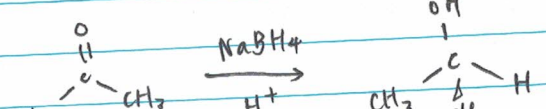
· $LiAlH_4$ (strong Red agent) → primary, in dry ether + HEAT (accessin P.Table)
catalyst
↳ must be in protic solvent to react w/ water

$CH_3COOH \xrightarrow{[4H^-]} CH_3CHO \xrightarrow{[+H^-]} CH_2OH$

carboxylic aldehyde primary alcohol

RMB: NA is less reactive & less strong

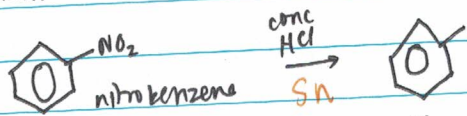
OR ... · $NaBH_4$ (protic, but CAN'T work on carboxylic) ↳ +HEAT



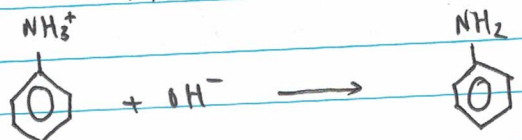
ketone secondary alcohol

$2[H] + (CH_3)_2CO \rightarrow (CH_3)_2CHOH$

REDUCTION OF NITROBENZENE

① 
nitrobenzene phenylammonium ] in presence of tin as reducing agent.

$+7H^+ + 6e^- \rightarrow$

② 
phenylamine

synthesis routes.

· series of chem steps → work molecule backwards → retrosynthesis analysis