10: Organic Chemistry $\rightarrow$ the Chemistry of Carbon
a.k. a fake biology

Homologous Series

- Definition: a series of compounds of tho same family, with the same general formula and differ from ane another by a common structural unit.
- varying carbon backbone iengths, from $C_{1}$ to $C_{\infty}$, increasing by $\mathrm{CH}_{2}$
- Similar chemical properties as same functional groups presents
- There is a gradual and progressive change in physical properties
- E.g Boiling Points $\rightarrow$ as the size of a molecule increases, the ste of a random instantaneous dipole increases, hence the strength of LDFs increase as you ascend a homologous series. Therefore, more energy is required to break the stronger intermolecular forces

Identifying Compounds

- identify longest carbon chain first [ eeg $\mathrm{CH}_{3} \mathrm{CH}\left(\mathrm{CH}_{3}\right) \mathrm{CH}_{2} \mathrm{CH}_{3}$, longest chain is 4 C and I meohyl, $\therefore$ it is something-butane]
- Bonding $\rightarrow$ all single bonds $\rightarrow$-ane, andouble $=$ - ene, one triple $-y n-$.
- Check functional group [see detailed list on next page]
(i) alkene $\mathrm{C}=\mathrm{C} \rightarrow$-ene
(2) alkane $\mathrm{C}-\mathrm{C} \rightarrow$-ane
(3) Alcohol $\mathrm{C}-\mathrm{OH} \rightarrow-\mathrm{Oi}$
(4) CarboxylicAad $\mathrm{C}=\mathrm{O}-\mathrm{O}-\mathrm{H} \rightarrow$ Whic-oic acid
(5) Haloalkave $\quad \stackrel{r}{c}-\mathrm{C}-\overbrace{i 0}^{\circ}: \rightarrow$ iodo/bromo/chbrolfluoro-
(6) aldehyde $\mathrm{C}-\mathrm{H}$ [atchainend] $\rightarrow-a l$
(7) Ketone $0^{0} c c_{i 1}^{i}-c-c$ [anotatend] $\rightarrow$-one
(8) Amide $\mathrm{H}^{\prime \prime} \mathrm{C}-\mathrm{N}-\mathrm{H} \rightarrow$-amide [itatend]
(9) Amino $\underset{\substack{-1 \\-1 \\ N_{1}}}{\substack{1 \\ H} \text { amino- }}$
- Put numbers $a \rightarrow$ ea alcohols $\rightarrow$ position of $\mathrm{OH} \rightarrow$ popan-1-01, allcene), position of $C=C$, prop-1-ene haloallcanes $\rightarrow$ position of halogen ( $)$ ), 1-bromopropane
Example:


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Functional Groups

1) Alkane-Alkene $\mathrm{EC}=\mathrm{C}-] \rightarrow$ aikenyl
2) Alkyne $[-C \equiv C-] \rightarrow$ alkynyl
3) Alcohol $[\mathrm{C}-\mathrm{OH}]$-hydroxyl
4) Ether $\left[R-O-R^{\prime}\right] \rightarrow$ oxy (alkane), where allcane is $R^{\prime}$ e.g ethooxyethane
5) Ketone $\left[\begin{array}{c}i \\ -C\end{array}\right]$-none
6) Aldehyde $[-\mathrm{C}=\mathrm{O}]-\mathrm{O}]$
7) carboxylicacid [C"OOH]
8) ester $[-\stackrel{i}{C}-Q-c-]$
9) nitrile $[-C \equiv N]$ [alkane inducing last carbon - nitrile]
10) amine $\left[\mathrm{C}^{\prime \prime 0}-\mathrm{N}_{21 \mathrm{H}}^{\prime 4}\right]$ [allcane-anamide] e.g propanamide
11) Arene [ $\left.\hat{\mid}^{R}\right][R$-benzene], e-g methyl benzene

Homologous series differ by a $\mathrm{CH}_{2}$

Alkanes

- comprised purely of $c-c$ and $c-1+$ bonds
- only react in presence of energy source because of relatively high bond enthalpies
- Non polar because of low electronegativity difference.
- Low reactivity due to inability to attract other species, no double bonds or - vel/ + ves
- Undergo combustion, cracking + halogenation

Combustion,

- The $\mathrm{C}=\mathrm{O}$ bonds in $\mathrm{CO}_{2}$ and $\mathrm{O}-\mathrm{H}$ bonds in $\mathrm{H}_{2} \mathrm{O}$ are stronger than $\mathrm{C}-\mathrm{H}$ and $\mathrm{C}-\mathrm{C}$ bonds in alkanes, hence $-\Delta H, \therefore$ exothermic and releases energy $\rightarrow$ used as fuel source
- Complete or Incomplete [because of insufficient $\mathrm{O}_{2}$ ]

$$
\begin{aligned}
& \rightarrow \mathrm{CH}_{4}+2 \mathrm{O}_{2} \rightarrow \mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O} \text { [complete] } \\
& \rightarrow \mathrm{CH}_{4}+\frac{3}{2} \mathrm{O}_{2} \rightarrow \mathrm{CO}+2 \mathrm{H}_{2} \mathrm{O} \text { [incomplete] }
\end{aligned}
$$

$$
\begin{aligned}
& \text { binds to haemoglo bin to reduce a ability to abhor } \mathrm{OO}_{2}
\end{aligned}
$$

Halogenation

- occurs by free radical substitution
(i) Initiation
$\mathrm{Cl}_{\text {I }}^{\sim} \mathrm{Cl} \stackrel{\mathrm{U}}{\longrightarrow} 2 \mathrm{Cl}^{\circ}$ [homolyticfission $\rightarrow$ electrons in covalent bond equary shared]

$$
\mathrm{Cl}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{Cl}^{\circ}
$$

(2) Propagation = forming more radicals
(1) $\mathrm{Cl}^{\circ}+\underset{\text { H }}{\mathrm{H}} \underset{+}{\mathrm{C}}-\mathrm{H} \rightarrow$

$$
\mathrm{Cl}+\mathrm{CH}_{4} \rightarrow{ }^{\circ} \mathrm{CH}_{3}+\mathrm{HCl}
$$

(2)
 chloromeshane
(3) Termination $\rightarrow$ two radicals react




Theoretically, can go further.
Note: The haloalkanes are more reactue
 than alkanes due to the polandy of the $C-X$ bond, where $X=$ halogen


$$
\text { Overall }=\mathrm{CH}_{4}+\mathrm{Cl}_{2} \rightarrow \mathrm{CH}_{3} \mathrm{Cl}+\mathrm{HCl}
$$

Nucleophillic Substitution,

- Nucleophile = an electron rich species, such as a Lewu Base or Ligand, attracted to + ven nuclei
- Attracted to $f^{+}$on a polar bond. $E, g$..
- Hats aNudeophile donates a stared pair of electrons it to the C-F bond, whose electrons (both) move to the $\delta^{-}$atom. This forms an intermediate in the slow step with or half-brolcen hat f formed bonds to the halogen and nucloophile. A covalent bond is formed between the coven nucloophile and C, specifically, a dadivecovalent bond.

Diagram of a substitution by $\mathrm{OH}^{-}\left[S_{N}{ }^{2}\right.$ Mech $]$.


What has been explained relates to $5-(2)$ - bimolecular slowstep substitution nuclesphillic
However, what if we have loads of stabilisers? Consider the structures of haloalkans


Alkyl groups have an inductive effect, where electrons move and can stabilve any + charges

Note: Sol faster than $S_{N}$ 2, need procic solvent to stabilise carbocation

Tertiary Structures

- most likely to undergo SNDI, because morestable br it

?? astr!! $\because$ to collide mosh NH
Secondary haloalicanes can undergo $S_{N}$ or 2 . Todetermive, change [nucleophile), if rate change) $S_{N} 2$ used. It not; $S_{N}$. "Use aproticsolvent to favor $S_{N} 2$, because it creates aprotic solvents [ethoxyethane] favours it. Protic solvents such as water a eohanol support bread own into carhocations, dissociate int. $\delta+$ and $\delta$, later stabilles $+v e C$ on carbocadion
(Rates of Reaction
The rate of reactions moth halo alkanes vary worth the alkanes identity. For examples: I\& $\mathrm{Br}<\mathrm{Cl}$ ? F . This is became $C-I<C-\mathrm{Br}<C-C l<C-F$ in terms of bond enthalpy. A lower bond enthalpy to be broken requires los energy, ret generating a relatively lower $E_{a,}$ : $\uparrow$ rate of nucloophillic substitution.
The electron density of the nudleophile also affects the rate. Telection density, greater attractive force between nucleophile and $\delta^{+}$carbon, $\therefore$ irate of reaction. T moth anions, as it is a negatively charged molecule /ion. Thisis why $\mathrm{OH}^{-}$is a better nudeophib than $\mathrm{H}_{2} \mathrm{O}$ because it ha a higher electron density
hasa
$S_{N} 2$ is also generalys sower than $S_{N} 1$, hecave it is a bimolecular RDS, unlike $\int_{N}$ I.
$\sqrt{\text { Protic Us Aprotic }}$
Aprotic for $S_{N^{2}} \rightarrow$ this is because protic solvents, i. e polar solvents, will solvate the nudleophile, rendenng it unable to attack tho species Also, because soprodic, no $\delta$ - or
- ves to stabilise charge on carbocation, : unlikely to move through SN!
$\therefore \int_{N}{ }^{2}$. Aprotic solvade metal cation, $T \therefore$ incleophile is unsolvaded, increasing trade
- unsaturated hydrocarbons containing a $C=C$ bond
- $C \frac{\pi}{\sigma} C$, each $C$ is $s p^{2}$ hybridised
- More reactive than alkanes because of the double bond, whose constituent sc bond can easily be broken to crease 2 new bonding positions
- Distinguishing alkanes from alkenes $\rightarrow$ burn them, alkene produces a smoky flame, indicades an unsaturaded molecule OR try decolourising bromine, happerforasleenes, not alkanes

Hydrogenation [addition reaction]

- alkenes react with $\mathrm{H}_{2}(\mathrm{~g})$ at $T \uparrow 150^{\circ} \mathrm{C}$ in the presence of a nidcel catalyst to formakaney

but (1)ene + hydrogen gas $\rightarrow$ butane

$$
\mathrm{CH}_{3} \mathrm{CH}_{3} \mathrm{CHCH}_{2}+\mathrm{H}_{2} \rightarrow \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{3}
$$

- used to break do wo oils containing many unsaturaded hydrocarbon into saturaded compound j with higher b.p andm.p. Allows for margarine 10 be solid at room temperature

Halogenation, [addition reactor]

- react um diatomic halogens to produce dihalogenocompands
- occur at $r$. temperature, decolourises one halogen: tests for presence of $C=C$
$\theta$


$$
\begin{aligned}
& \mathrm{CH}_{3} \mathrm{CH} \mathrm{CH}_{2}+\mathrm{Br}_{2} \rightarrow \mathrm{CH}_{3} \mathrm{CHBr} \mathrm{CH}_{2} \mathrm{Br} \\
& \text { prop(i)ene }+ \text { bromine } \rightarrow 1,2 \text { dibromopropane }
\end{aligned}
$$

Addition Reacconons wo Hydrogen Halides) [hydrohalogenanon]

- react to form haloalkanes, a from tempera five
- reactivity 1 a yardesend gray IV VI, becave of decreasing $H-X$ bond enthalpy, IE a, $\uparrow$ rate of reaction
(Hydration? addition reaction)
- reaction with H,O Oof form alton wing concentrated HCL


Overall $=\mathrm{C}_{2} \mathrm{H}_{4}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}$

- need steam as well, ethanol needed as a probic solvent

Polymerisation

- a series of addition reactor between identical avenges
- alkene called the monomers
$n\left[\begin{array}{cc}H & H \\ 1 & 1 \\ c & C \\ 1 & 1 \\ 1+ & 1+\end{array}\right] \rightarrow-\left(\begin{array}{ccc}H & H \\ 1 & 1 \\ C & -C \\ 1 & 1 \\ 1+1 & n \\ n\end{array}\right) \rightarrow$ number of repeating units
$n$ ethenes polyethene (polythene)

$n$ propenes
polypropene
- Polychloroethene [PVC] $\rightarrow\left[\begin{array}{ccc}H \\ i & & 1 \\ C & - & C_{1}^{1} \\ i & 1 \\ C i\end{array}\right]$

- Electiophile: an elecorondeficient species that can accept election pairs [Lewis Adj]
- Why do alkenes undergo electrophilic advior addison?
(1) Catoms are $s p^{2}$ hy bridued, here trigonal planar shape worth $120^{\circ}$ bond angles formed. This creates an openstructureatich makes it easy for electrophiler to attack
(2) $\pi$ bond =area of electron density above and below the internudear axis, hence less associated wion the nucleus, $\therefore$ weak and easily broken in addition reactions
(3) Electron in $\pi t$ bond attract elactrophiles

With a halogen
induced

$\mathrm{Br}_{2}$ becomes polarised by $e^{-}$repulsion from $\pi$ band, reeling in heterolyoic fission b form $\mathrm{Br}_{+}^{+}$and $\mathrm{Br}^{-}$.
The $B_{1}{ }^{+}$is attracted took $\pi$ bond
 and attack it to form a carbocation.
The step is slow and the unstable carbocation reacts cion $\mathrm{Br}^{-}$to form 2, $3^{3}$ dibiomo butane

With hydrogen halide


Asymmetric Alkenes
egg 1)



จ)
propene


- There are 2 theorerencal products.
- Consider propene + hydrogen bromide
- It depends on if the attacking electrophile

- We look for the most stable carbocation, primary \& secondary < tertiary
- More alkyl groups, greater positive inductive effect by morning electrons to stabilise the positive charge. $\therefore 2$ more stable as it is a secondary carbocasion, morestable than the primary $\rightarrow$ this is the major product, due to lower $E_{a}$
- Markounizovs' rule states that the H will bond to the carbon moth the mat hydrogen bonded to it [ergo, the adjacent one will be stabilued by more allyl groups]
- Formal Definition: The most electropositive atom of the reacting species bonds to least highly Substituted carbon atom in the alkene [least valially 1]
- i - induc due effect, e.g double inductive effect
- Note: write equation in structural form $\left[\mathrm{CH}_{3} \mathrm{CH}_{\mathrm{H}}\left(\mathrm{B}_{3}\right) \mathrm{CH}_{2}\right]$
(Interhalogenic compounds)
- $\mathrm{Br}^{\prime}-\mathcal{\delta}^{-} \rightarrow$ bromofluoride - because $\delta^{-}$
- $\mathrm{Br}^{\delta^{-}}-I^{\delta-} \rightarrow$ iodine bromide


Alcohols
$\rightarrow \mathrm{C}_{n} \mathrm{H}_{2 n+1} \mathrm{OH}$
$\rightarrow$ OH -functional group
$\rightarrow$ The - O-H bond is polar and increases the solute of alcohols, ethanol for instance in soluble in water of all proportions. However, solubility of alcohobdecreasey as you move down the chain, as larger proportion is non-polar
Combustion
$\rightarrow$ Alcohol used as afvel, as it combusts plentifully
$\rightarrow$ Low probability of incomplete combustion because O is available from the OH

$$
\text { e.g } \mathrm{C}_{3} \mathrm{H}_{7} \mathrm{OH}+\frac{4}{2} \mathrm{O}_{2} \rightarrow 3 \mathrm{CO}_{2}+4 \mathrm{H}_{2} \mathrm{O}
$$

$\rightarrow \Delta H$ becomes mares. hermit to mere as you descend the series as more moles of $\mathrm{CO}_{2}$ produced

RECALL





$$
\text { Tertiary Alcohol : } R-C_{C}^{i}-R \rightarrow 2 \text {-methyl poppon-2-01 }
$$



Oxidation

- Alcohols can be oxidised to aldehydes, Ketones or carboxylic acids
$\rightarrow$ Tertiary Alcohols cannotbe ondised because of the lack of individual Hatorms bonded to the C which is connected to The OH , hence it is difficult for it to be oxidised
$\rightarrow$ Need acidified potassium dichromade [VI], which is reduced from $\mathrm{Cr}_{r}{ }^{6+}$ to $\mathrm{Cr}^{3+}$ gain
to ede the electrons need produced by the oxidation of the alcohol


$\rightarrow$ a leiblig condenser placed above the set up
$\rightarrow$ Aldehydes formed would vapountedue to the loss of a one It-bond, but would condense and fall back down, keeping it in contact with the oxidising agent for a prolonged period of time to increase $P$ (secondoxidadron).

Distillation
$\rightarrow$ We use this it we only want the aldehyde
$\rightarrow$ As the aldehy de hos a lower bp than the alcohol, it evaporates, hen they move through a leibig condenser at the adjacent side

Note: The orange to greencolour change is only seen if an oxidation occurs, notseen in tertiary alcohols

To test for aldehydes, add Fehling's solution, it oxidises a ldehy de to Ketones, turning the solution red-brown from blue blue to red-brown

Interestingly, isomers of carbotylic acid u are ester.

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Esterification

- a condensation reaction between a carboxylic acid and alcohol
- The $\mathrm{OHs}_{s}$ bond to form an ester linkage and release $\mathrm{alt}_{2} \mathrm{O}$
- It is an equilibrium, hence $\mathrm{H}_{2} \mathrm{SO}_{4}$ used to shift equilibrium to the right [catalyst]
- esters formed have low m. p and bp, hence can be seperated by distillation
$\rightarrow \mathrm{H}_{2} \mathrm{SO}_{4}$ used as dehydiraning agent to shift equilibrium + lowers $E_{A} \therefore$ catalyst
Example: ethanol + propanok acid


I FP: Add $\mathrm{NaOH} / / \mathrm{NaCO}_{3}$ to react with excess acid
Esters


- Nomenclature $\rightarrow$ if alcohol + acid $\rightarrow$ ester, ester is alchol, acid E.g ethanol + propanok acid $\rightarrow$ ethyl propanoate
- Low m.p and beep becauseno free hydroxyl groups, hence cannot form H -bond, and are insoluble in protlcsolvents
- used as perfumes, solvents and artificial flavouring

Reduction Reactions
$\rightarrow$ we need a reducing agent, e.g $\mathrm{NaBH}_{4}$, sodium tetrahydrido borate, which forms highly unstable If ions that act as aredvcing agent
$\rightarrow$ The It's undergo a nucle ophillic addition react on with the electron deficient cart on of a species
$\rightarrow \mathrm{NaBH} 4$ can be used in prone soivenls but cannot reduce carboxylic acids
$\rightarrow$ Li \&AlH4 is stronger, as it dissociates into more It ions, but must be loptdry as $\mathrm{H}^{-}(\mathrm{aq})+\mathrm{H}, \partial(\mathrm{I}) \Rightarrow \partial \mathrm{H}^{-}(\mathrm{aq})+\mathrm{H}_{2}(\mathrm{~g})$ : Hence, only aprodic solven) e.g eathers
$\rightarrow$ Consider the reduction of butanal

$\rightarrow \therefore$ aldehydes $\rightarrow$ primary alcohols
$\rightarrow$ Consider the reduction of propanone


$\rightarrow \therefore$ ketone $\rightarrow$ secondary alcohol
$\therefore$ We can generalise the reductions as follows
aldehyde $\frac{\mathrm{NaBH}_{4}}{\mathrm{H}^{+} \text {(aq) }}$ primary alcohol
Ketone $\xrightarrow[1 t^{+}]{\mathrm{NaBH}}$ secondary alcohol
$\rightarrow$ Carboxylic acids are more complex, they too are reduced to primary alcohols carbotysiic acid er $\xrightarrow[H^{2}(\text { aaa })]{\mathrm{LiAll}_{4} \text { in ether }}$ primary alcohol
(Benzene Rings,
Cyclic Compounds
$\rightarrow$ We have a lot ot cyclic compounds in chemistry, such as cy clo hexene.


$$
\mathrm{C}_{6} \mathrm{H}_{10}
$$

$\rightarrow$ Benzene is a prince example, it is an aromatic Char de locallued e-] unsaturated hydrocarbon.
$\rightarrow$ Kekule thought benzene had this structere
$\rightarrow$ In fact, this theory has been falsified because
 of the 4 prices of evidence here
(1) Low reactivity $\rightarrow$ with bromine, only bromobenzene, no 1,2 bromobenzene, unlike what is expected of a compound with 3 daub 6 bonds. Dibromobenzene unstable as only 4 positions $\downarrow$
(2) Bond length $\rightarrow$ all the $C-C$ and $C=C$ bond lengths were 0.140 nm , a value between $\sqrt{5} 0.154 \mathrm{~nm}[C-C]$ and $C=C$ ©. $134[C=C]$, indicating resonance, as it varies the number of electrons in covalent bond), varying their strengths and therefore, their lengths
(3) Enthalpy of hydrogenation


This was expected to be $3(-120)$, as you need to break $3 x$ as many bonds. It was morestable by about 152 kJ mol !
This energy is the amount by which one internav energy of the benzene is reduce. This energy would have to be supplied to overcome Hen ctabilit. of $f$. H. Hone it irduhhod rasnnourn annas

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(4) Isomers $\rightarrow$ only one isomer exists per compound, e.g 1,2 dibromobenzene
$\rightarrow 1$ is omer for every disubstituted benzene
Note: Addihon reactions not favoured because it disrupts the aromaticning of benzene [cloud/ring of delocalsed electron/ $\pi$ bond conjugation]; and resonance energy would be needed. Additionally, the lack of an aromatic ring decreases the stability of benzene. Hence, substituinons prefered, to as they preserve the aromothcring. Benzene is $s p^{2}$ hybridised
Electrophilic Addition Substitution\} ~
$\rightarrow$ Benzene is attractive to electrophiles because of its aromatic ring
$\rightarrow$ High Ea as the first step disrupts the $\in \delta$ bond conjugation [aromaticring].
Energy


Where $E$ is the electrophile
$O+E$


Consider the nitration [add $\mathrm{NO}_{2}$ ] of benzene
(1) We form $\mathrm{NO}_{2}$ by reacting $\mathrm{HNO}_{3}$ and $\mathrm{H}_{2} \mathrm{SO}_{4}$

(2) $N O_{2}$ then is reacted with benzene at no more than $50^{\circ} \mathrm{C}$, because fut the nitration occurs at $750^{\circ} \mathrm{C}$


Be wary of this; ensure the arrow from the H bond goes through the ring, no need to go through C atom.

The $1 \mathrm{NO}_{2}^{+}$ion attacks the p electrons in the aromadicring, hence an electron is Used by the ring to form a covalent bond to one $\mathrm{NO}_{2}{ }^{\top}$. Simultaneowly, the double bond $N^{ \pm}=0$, splits to $N^{+}-0^{-}$. The fond delocalisation of electrons is now brolcen and a positive charge is distributed amongst the benzene, forming a carbocadion. A bond to hydrogen is subsequently broicen, releasing a proton and the aromatic ring is restored
(1) $\mathrm{H}_{2} \mathrm{SO}_{4}$ - catalyst. It generated can react isth hydrogensulfat ion [ $\mathrm{HSO}_{4}^{-}$] to reform $\mathrm{H}_{2} \mathrm{SO}_{4}$
(2) $\mathrm{HNO}_{3}$ - source of $\mathrm{NO}_{2}+$
(3) $50^{\circ} \mathrm{C}$. $\uparrow$ rate, but no higher as it facilitates further nitration

Similar Reaction

- given $\mathrm{AlCl}_{3}$, fond $\mathrm{Cl}_{2}$, form chlorobenzene


OR , with $\mathrm{Fe}_{\mathrm{Br}_{3}}, \mathrm{Br}_{2}$ and $\mathrm{C}_{6} \mathrm{H}_{6}$, form bromobenzenp


Back to Reduction

- By a reduction reaction, phenylamine $\left[\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{2}\right]$ can be formed
$\rightarrow \mathrm{C}_{6} \mathrm{H}_{6}+\mathrm{HNO}_{3} \rightarrow \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NO}_{2}+\mathrm{H}_{2} \mathrm{O}$
then, under reflux in aboiling water bath


Overall


The NaOH neutralises any remaining $H^{+}(u q)$.


Configurational isomers interconvert between each other by breaking and reforming $a$ bond

Cis/trans
$\rightarrow$ exist where there is estrictectrotadion around atoms
$\rightarrow$ egg always in alkenes becave of double bond

We only use cis/ trans for rings systems, otherwise use E/Z or optical

- Alkenes
$\rightarrow$ Why? $\pi+\sigma$ bonds make up the $C=C$ hond, the $\pi$ is formed from an overlap of 2 porbituls which need to be on the same plane to combine. A bond rotation breaks the sc bond, hence there is restricted rotation around atoms, $\therefore$ cis-drar


Note: cis alkenes have higher b. ps becave of inductive effects on same toplbottom, granting poland, th p

- Cyclic Compounds [specifically disubstitutedones, eg I, Ldichorocyciohexane]
$\rightarrow$ Why? Rotation restricted because $C-C$ bonds are part of a ring system e.g [note, all triton on same plane]

(ElL isomerism)
$\rightarrow$ like cisprans, when we have atomic rotationow restriction
$\rightarrow$ but when $C$ atoms oi $C=C$ bonded to more than 2 different molecules egg

$\rightarrow$ Using the Cahn Ingid Prelog rues of priority, we decide whether we have a E or $Z$
(1) Identify heaves ATOM bonded to a side $C=C$. So it is clearly $I_{1}$, as $\operatorname{Mr}(I)>\operatorname{Mr} \sqrt{\text { ACDYNOTR }}$
(2) Now, check RHS, $\operatorname{Mr}(\mathrm{Br})>\operatorname{Mr}(C)$, so it is Br

- $\underset{\rightarrow}{\vec{~}} \rightarrow$ reverse of it's cis implication, so trans 2 diff sides, Unlike the 3 bits on the $E$
- $Z_{\rightarrow} \rightarrow$ same plane, unlike the 2 bits on the $Z$
- $Z$ and $E$ are written in brackets. Hence, the example would simply be
(E)-1-iodo; 2-bromo pent-1-ene
$E v_{5} Z$
$\rightarrow$ different physical properties, e.g be, solubility, m.p.
$\rightarrow$ differentchemical propprdes ar different passible reactionscan occur
Optical Isomers
- Enantiomers
$\rightarrow$ Definition: isomers that are non supirimposable mirror images of one another
$\rightarrow$ a chiral carbon is required
$\rightarrow$ A chiral carbon is a carbon bonded to 4 different atoms or groups, also called asynnethc
$\rightarrow$ Lenantiomers per optically active molecule
$\rightarrow$ We draw them as tetathedrons, with the chiral carbon at the centre.
$\rightarrow$ If asked for both enantiomers, write as the following


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$\rightarrow$ a mixture containing a $50-50$ mix of each enantiomer is a racemic mixture, and is optically inactive
$\rightarrow$ Identifying chiral carbons. Draw the enantiomers of $\mathrm{C}_{4}+\mathrm{d} / \mathrm{H}_{q} \mathrm{Br}$
Rotations in opposite directions with equal magnitudes
We need an isomer of loo bromobutare that has a chiral carbon


$\downarrow$ Yes!

 all different groups, hence optically active!
Noto: the wedges and dashes must be used!
Something interesting [not in syllabus]

- Distinguishing $R$ and S optical isomers
- Look at The heaviest atonded heaviest atomsbonded in order and number them. If $1 \rightarrow 4$ go cloclcuse, it is $R$, if and clockcuise then $S$


Plane polarised Light
$\rightarrow$ a transverse wave $\$$ of light
$\rightarrow$ normal light vibrates on ion every plane, but plane polarved light moves perpendicular to the wave. Polane Polanied (PP) light generated by shining light through polarising filter
$\rightarrow$ Enantiomersrotate plane polarised light, if plane planned light passed through, the plane of polarization is rojrated in oppositedirecsorn

$$
\begin{aligned}
& \text { [polarimeter] } \\
& \text { analyser that determines } \\
& \text { polarvingfitter } \\
& \text { in } 1 \mathrm{~cm}_{\mathrm{m}}{ }^{-3} \text { chiral companion range. }
\end{aligned}
$$

$\rightarrow$ if we have a cacemate, there is no net rotation as both chiral compounds rotate clackule and anti-clocccwise, cancelling each other out, $\therefore$ not optically active
$\rightarrow$ Note: naturally occuring chiral compounds are optically active, only I type of enantiomer
$\rightarrow$ clockwise $[+$ soangle $]$ is an $R$ isomer, anti is an $S$
Comparing properties of enantiomers
(1) Chemical
$\rightarrow$ different reactivities, and because biological systems [eeg enzymes] are chiral, it has significant impacts. E.y thalidomide Elisten to "We Didn't Start the Fire," ], I at enantomer reduced morning sickness, another caused birth defects
$\rightarrow$ To produce a single enantrmer, asymmetuc synthesis is used, a process using a chiron catalyst
(2) Physical -also differ

Effect
$\rightarrow$ Distinct chemical and physical properties allowfor seperation
$\rightarrow$ Hence, 2 enantomen in a racemade can be seperated by "resolution,"
$S_{N}$ and $S_{N} 2$ w.r.t stereoisomers
(S ND)
$\rightarrow$ it is stereospecific, causes an inversion of spatiovarrangement of atoms around a Catom
$\rightarrow$ Called stere specific because the spahav arrangement of atoms in reactants determines 3D configuration of the products
$\rightarrow$ This is because bond formation is before bond cleavage in the transition stade, oo no loss of stereochemistry
S NI
$\rightarrow$ non stereospecific as there are 2 possible bonding sites on carbocation intemediade because it is plariar

$\rightarrow$ hence an $S_{N}$ I mechanism produces a racemixate, as a mix of optically active 1 isomers are produced.

Question Tips

1) Structure of benzene $-C_{s}$ are $s p^{2}$ hybndised, $120^{\circ}$ angles, hexagonal, resonance, all equal ( -Cbond), bond order of 1.5

Every Organic Reaction
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- Free Radical Substitution
$\rightarrow$ UV light

$$
\begin{aligned}
& \mathrm{CH}_{4}+\mathrm{Cl}_{2} \rightarrow \mathrm{CH}_{4}+2 \mathrm{Cl} \rightarrow \text { prop initiation } \\
& \mathrm{CH}_{4}+\mathrm{Cl}^{\circ} \rightarrow{ }^{\circ} \mathrm{CH}_{3}+\mathrm{HC} \rightarrow \text { propagation } \\
& \left.{ }^{\circ} \mathrm{CH}_{3}+\mathrm{Cl}_{2} \rightarrow \mathrm{CH}_{3} \mathrm{Cl}+\mathrm{Cl}^{\circ}\right\} \text { termination } \\
& { }^{\circ} \mathrm{CH}_{3}+\mathrm{Cl}^{\circ} \rightarrow \mathrm{CH}_{3} \mathrm{Cl} \rightarrow \text { teri }
\end{aligned}
$$

Electrophillic Addition

- Hydrogenation $\rightarrow 150^{\circ} \mathrm{C}$, Nickel Catalyst, $\mathrm{H}_{2}$ (g)
$\rightarrow$ alkene to alkane
- Reactions with interhalogeno compounds/ halogens [halogenation] / hydrogen halogen halide Chydrohalogenadion
- Hydration $\rightarrow \mathrm{H}_{2} \mathrm{SO}_{4}$ and $\mathrm{H}_{2} \mathrm{O}$


- Be careful with Markounikor's rule

Nucloophillic Substituovon

- $S_{N}$ if ternary, $S_{N} 2$ it primary, both for secondary $\left[\right.$ prot ic $=S_{N^{\prime}}$, aprodic $\left.=S_{N^{2}}\right]$
- No conditions
- Convert halogen alkanes into alcohols moth a O-H nucleophile

Alcohol Oxidadon
$\rightarrow$ All require $\mathrm{K}_{2} \mathrm{Cr}_{2} \mathrm{O}_{7}$ and $\mathrm{H}_{2} \mathrm{SO}_{4}$ ar f $[$ acidified potassium dichromade (VI)]
$\rightarrow$ alcohol $\left(1^{\circ}\right) \rightarrow$ aldehyde $\rightarrow$ carboxylicacid dusilatron reflux
$\rightarrow$ alcohol $\left(2^{\circ}\right) \longrightarrow$ ketone
$\rightarrow$ alcohol $\left(3^{\circ}\right) \rightarrow$ no reaction, no its $b$ be last as part of oxidation

22 Reductions.
$\rightarrow$ With LiBH 4 and a $\mathrm{H}_{2} \mathrm{O} /$ prosodic solvent

1) Ketone $\rightarrow$ secondary alcohol
2) primary aldehyde $\rightarrow$ primary alcohol
$\rightarrow$ With $\mathrm{NaAlHy}_{4}$ and aprome solvent (because otheruse Lions gone)
3) carboxyelic acid $\rightarrow$ primary alcohol?
$\rightarrow$ Nitrobenzene to phenylamine


Esterification)
$\rightarrow$ alcohol+carbooylic acid
$\rightarrow \mathrm{H}_{2} \mathrm{SO}_{4}$ catalyst+ dehydrating agent [shifts equilibrium]
Electro phillis substitution

- Production of nitrobenzene
$\rightarrow \mathrm{H}_{2} \mathrm{O}_{4}$ and $\mathrm{HNO}_{3}$ at $50^{\circ} \mathrm{C}$, ali conc

