OCR (A) Chemistry A-level

Module 6: Organic Chemistry and Analysis

Notes

by Amie Campbell

25.1 introducing benzene

- Benzene is a colourless, sweet smelling, flammable liquid
- Found in crude oil/cigarette smoke
- Carcinogen (causes cancer)
- Kekule model: 6 membered ring of carbon atoms joined by alternate single/double bonds
- Evidence against Kekule: lack of reactivity (doesn't undergo electrophilic addition reactions/decolourise bromine under normal conditions), lengths C-C bonds (saw all bonds were the same length using X-ray diffraction, in between length of single/double bond), hydrogenation enthalpies (less exothermic than predicted compared to cyclohexene)
- Delocalised model:
    - Planar, cyclic, hexagonal hydrocarbon with 6 carbons + 6 hydrogens
    - Carbon uses 3 of 4 electrons to bond to 2 other carbons and 1 hydrogen
    - 1 electron in p-orbital at right angles to plane
    - P orbitals overlap sideways above + below plane of carbon atoms, forming a ring of electron density
    - Overlapping creates system of π-bonds, spreading across all 6 carbons in ring
    - Electrons in π-bonds are delocalised
- One substituent group=monosubstituted
- Alkyl groups, halogens & nitro groups=prefixes to benzene
- When attached to chain with 7+ carbons, benzene=substituent, use prefix phenyl
- Exceptions: benzoic acid (benzenecarboxylic acid), phenylamine and benzaldehyde (benzenecarbaldehyde)

25.5 electrophilic substitution reactions of benzene

- Nitration: if temp over 50°C, further substitution may occur→ dinitrobenzene produced
- Halogen carrier can be iron metal and halogen, which react to make $FeCl_3$
- Phenylethanone is used in the perfume industry
- Comparison of reactivity to alkenes:
    - π-bond in alkene contains localised electrons→area of high electron density
    - This induces a dipole in non-polar bromine molecule (one is made slightly positive, the other slightly negative)
    - Slightly positive Br enables bromine molecule to act as an electrophile
    - Benzene doesn't react unless a halogen carrier is present because it has delocalised π-electrons, with electron density less around any 2 carbons than a C=C bond

- Insufficient π-electron density around any 2 carbons to induce dipole in non-polar molecule, preventing a reaction taking place

25.3 the chemistry of phenol

- Contain hydroxyl group bonded directly to an aromatic ring
- Simplest of phenols=phenol C_6H_5OH
- Used in production of disinfectants, detergents, plastics, paints and aspirin
- Used to be made by: $C_6H_6 + H_2SO_4 + 2NaOH \rightarrow C_6H_5OH + Na_2SO_3 + 2H_2O$ (multi stage process)
- Now made by: $C_6H_6 + C_3H_6 + O_2 \rightarrow C_6H_5OH + CH_3COCH_3$ (multi step). Propanone (acetone) also produced- useful but less in demand than phenol. 86% yield
- Future: $C_6H_6 + N_2O \rightarrow C_6H_5OH + N_2$. 95% yield, N_2O=waste product from production nylon & greenhouse gas so can't be released to atmosphere, making this process useful
- Less soluble in water than alcohols due to non-polar ring
- When phenol dissolves, it dissociates to phenoxide ion and a proton. Partially dissociates producing proton so classed as a weak acid (same with any phenols)
- More acidic than alcohols, less than carboxylic acids (can be seen by comparing Ka values, increase with acidity). Alcohols don't react with strong bases(NaOH)/weak (Na_2CO_3) bases, phenols react with only strong bases, only carboxylic acids are able to react with weak bases
- Test for whether carboxylic acid/phenol: react with Na_2CO_3, carboxylic acid will produce CO_2 (use lime water test)
- Compared reactivity to benzene:
  - Phenol can be nitrated with dilute nitric acid rather than concentrated HNO_3 + conc H_2SO_4
  - Lone pair of electrons from oxygen p-orbital of OH group is donated into π-system, increasing electron density of benzene ring, which attracts electrophiles more strongly than benzene
  - Aromatic ring is therefore more susceptible to electrophilic attack. For bromine, electron density in phenol is enough to polarise molecule so no halogen carrier is needed

25.4 directing groups

- Second substitution=disubstitution
- Names for substitution on different carbons: ortho=2, meta=3, para=4
- All 2,4 directing groups are activating (except halogens), all 3 directing groups are deactivating

- OH + NH_2= 2,4 directing & NO_2=3 directing
- Making TNT:
    - toluene (methylbenzene)→ 2-nitrotoluene (50°C, H_2SO_4/HNO_3)
    - 2-nitrotoluene→ 2,4-dinitrotoluene (70°C since 1st NO_2 deactivates ring)
    - 2,4-dinitrotoluene→ 2,4,6-trinitrotoluene (extreme conditions since 2nd NO_2 deactivates even further)

26.1 carbonyl compounds

- Methanal (formaldehyde) used in solution to preserve biological specimen
- Propanone (acetone) used as industrial solvent/nail-varnish removers
- Octanal: in citrus oils, used in perfumes/flavouring. Crested auklets emits tangerine perfume in breeding season
- Ketones don't undergo oxidation (this is why Tollen's reagent test works to distinguish them)
- Carbon-oxygen double bond made up of a π-bond and a σ-bond, same as alkene C=C, but C=C bond is nonpolar and C=O bond is polar
- Oxygen is more electronegative than carbon so double bond lies closer to oxygen, making oxygen end slightly negative & carbon end slightly positive
- Polarity of C=O allows carbonyl compounds to react with nucleophiles (attracted to δ+ carbon), resulting in addition across the bond (nucleophilic addition)
- Mechanism for reaction with $NaBH_4$:
    - Lone pair from $:H^-$ is attracted and donated to δ+ carbon in C=O bond
    - Dative covalent bond is formed between H^- and carbon
    - π-bond in C=O breaks by heterolytic fission, forming -ve charged intermediate
    - Oxygen donates a lone pair to hydrogen in a water molecule
    - Intermediate has been protonated to form an alcohol
- Mechanism for reaction with $NaCN/H^+$:
    - Lone pair on $:CN^-$ is attracted and donated to δ+ carbon in C=O, forming dative covalent bond
    - π-bond in C=O breaks by heterolytic fission, forming a -ve charged intermediate
    - Intermediate protonated by donating lone pair electrons to a H ion

26.2 identifying aldehydes and ketones

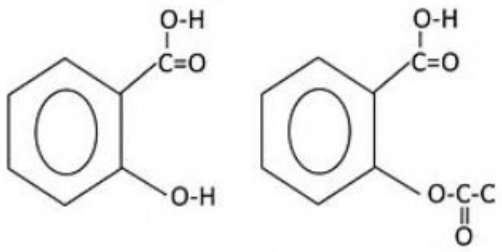
- Test for carbonyl group:
    - 2,4-dinitrophenylhydrazine (2,4-DNP) is usually dissolved in methanol and sulfuric acid to make a pale orange solution called Brady's reagent. Solid 2,4-DNP is very hazardous- friction/a sudden blow can make it explode

- Add excess ($5cm^3$) 2,4-DNP and a few drops of the compound. If no crystals form, add a few drops of H_2SO_4.If a yellow/orange ppt forms, it is a carbonyl compound
- 2 H's on NH_2 group & O in carbonyl are removed to make water and a C=N bond is formed

- Test for aldehyde:
  - Tollen's reagent has short shelf life
  - To make Tollen's: add 3cm $AgNO_3$ to a test tube, add NaOH until a brown ppt (Ag_2O) forms, add dilute ammonia solution until ppt dissolves to clear solution.
  - Test tollen's with an equal volume of the compound & leave in beaker of warm water at 50℃ for 10-15mins. Aldehydes form a silver mirror, ketones do not
- Identification by mpt
  - Ppt from 2,4-DNP test is filtered to separate solid ppt from solution
  - Solid is recrystallised to get pure sample
  - Mpt is measured, recorded + compared to data base to identify compound

26.3 carboxylic acids

- Found in: medicines, fruit juices, vinegar, rhubarb leaves
- Used in synthesis e.g. aspirin from salicylic acid



Salicylic acid Aspirin

- C=O and O-H bonds are polar so can they form hydrogen bonds with water. Soluble up to 4 carbons, but as the number of carbons increases, solubility decreases because non polar chain has a greater effect on overall molecule polarity
- Dicarboxylic acids dissolve readily in water & are solids at room temp
- Weak acids

26.4 carboxylic acid derivatives

- ester= R-COOR, acyl chloride= R-COCl, acid anhydride= R-COOC(R)O, amide= $R\text{-}CONH_2$
- Name of an ester: --thyl --oate (--thyl from alcohol) (--oate from carboxylic acid)
- To make an ester in a lab: use equal volumes of carboxylic acid/alcohol, add few drops of concentrated H_2SO_4 & place tube in 80°C water for 5mins. Pour into beaker with

aqueous sodium carbonate (neutralises acids in mixture). You get oily drops of ester on surface (don't inhale smell-some are poisons/carcinogens)

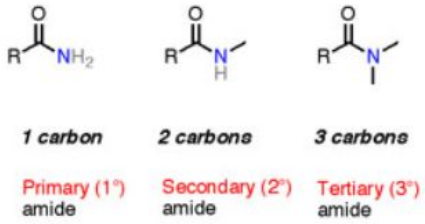
- Hydrolysis-the chemical breakdown of a compound in the presence of water or in aqueous solution
- In acid hydrolysis, the ester is broken down by water with the acid acting as a catalyst

27.1 amines

- Derivatives of ammonia with one or more H's replaced by carbon chain/ring
- primary/secondary/tertiary depending on number of alkyl/aryl groups attached to N
- serotonin= neurotransmitter, controls: appetite, sleep, memory, learning, temperature regulation
- Pseudoephedrine: active ingredient in decongestant medicines e.g. nose drops. Works by shrinking nasal membranes & inhibiting nasal secretion
- Naming primary amines: if NH_2 is at end of the chain add amine as suffix & if not at end, use prefix amino- with a number to indicate position (e.g. 2-aminobutane)
- Naming secondary/tertiary amines: if they have the same alkyl group- use di-/tri- to indicate number of groups on N (e.g.dimethylamine) & for different groups, it is an N-substituted derivative of the larger group (e.g. N-ethyl-N-methylpropylamine)
- Most amines come from breakdown of proteins so make up smell of decomposing organisms (e.g. putrescine/cadaverine)
- Behave as bases: lone pair on N can accept a proton to form a dative covalent bond
- mauveine= first chemically produced dye which paved way for many dyes used today, it was based upon the structure of phenylamine

27.2 amino acids, amides and chirality

- General formula ***α***-amino acids= $RCH(NH_2)COOH$ (all common amino acids in body are ***α***)
- Less common amino acids have NH_2 connected to ***β***(3rd)/***γ***(4th) carbon
- Have acidic COOH and basic NH_2 groups so have similar reactions to carboxylic acids/amines
- Amides are produced by reaction of acyl chlorides with ammonia/amines. Common in nature. Can be primary/secondary/tertiary R-CONHR



- Optical isomerism is found in molecules with a chiral centre (carbon atom attached to 4 different atoms/groups of atoms)
- Optical isomers/enantiomers= non super-imposable mirror images (2 per chiral centre)
- Sugars, proteins and nucleic acids all contain chiral carbon atoms & so do all ***α***-amino acids except glycine
- Chiral carbon shown by * & optical isomers drawn showing 3D tetrahedral arrangement
- Optical isomers react differently with our receptors→ different taste/smell sensations e.g. two isomers of leucine are bitter/sweet

27.3 condensation polymers

- Condensation polymerisation: the joining of two monomers with loss of a small molecule (usually water)
- poly(lactic acid) and poly(glycolic acid) are biodegradable polymers (used as dissolvable stitches) & lactic acid is derived from maize→ more sustainable
- Terylene is used in plastics/clothing. Polyesters can be used as electrical insulation
- Different types of nylon can be made with different carbon chain lengths & it is used as high strength fibre for ropes/parachutes

28.1 Carbon-carbon bond synthesis

- Formation of nitriles from: haloalkanes or aldehydes/ketones
- Reaction of aldehydes/ketones with HCN: HCN is far too poisonous to use & increased reaction rate can be obtained by presence CN^- ions→ a mixture of sodium cyanide and sulfuric acid is used
- A species of millipede stores 2-hydroxy-2-phenylethanenitrile in one of its body segments & releases it when attacked, mixes with an enzyme producing HCN and benzaldehyde

28.2 further practical techniques

- Filtration under pressure:
    - To separate solid product from solvent/liquid
    - Apparatus: buchner funnel, buchner flask, pressure tubing, filter paper, filter/vacuum pump

      1. Connect pressure tubing to vacuum outlet & to buchner flask
      2. Fit buchner funnel to flask with a tight fit (use buchner ring/rubber bung)
      3. Switch on vacuum pump/tap & check for good suction by placing hand on funnel
      4. Place filter paper in funnel & press down with the same solvent as used preparing solid. Should see it being sucked down
      5. Slowly pour reaction mix into centre of filter paper & rinse beaker with solvent

6. Rinse crystals in funnel with more solvent & leave on suction to dry for few mins

- Recrystallisation:
  - To remove impurities in solid after filtration

    1. Pour chosen solvent into conical flask. If flammable, warm over water bath, if not or if water is used, use bunsen to warm

    2. Put impure sample in 2nd beaker & slowly add solvent until it dissolves (add minimum volume needed)

    3. Allow to cool, crystals should form & when no more do, filter crystals under reduced pressure to obtain dry, crystalline solid
- Melting point determination:
  - To determine if compound is pure
  - Melting range: difference in temperature between starting/finishing melting (should be 1/2°)
  - An impure sample has lower melting point than a pure sample
  - Before: ensure sample is completely dry + free flowing, rotate end glass capillary tube in bunsen until sealed, allow to cool, fill with crystals (by forcing solid in)
  - Using electrically heated apparatus: place tube into sample hole + thermometer (0-300°) in thermometer hole, use rapid heating setting + observe through magnifying window, record melting point, allow apparatus to cool, do again but as melting point is approached raise temp slowly to get accurate measurement
  - Using oil bath/Thiele tube: set up oil bath/thiele tube, insert thermometer through cork for Thiele tube/ clamp thermometer and capillary with end dipping into oil for oil bath, use micro burner to heat slowly, record mpt, repeat for accurate value

28.8 further synthesis routes

- Target molecule= molecule you are trying to obtain

29.1 chromatography and functional group analysis

- Used to separate individual components from a mixture of substances
- Stationary phase: doesn't move (usually solid/liquid supported on a solid)
- Mobile phase: moves (normally liquid/gas)
- Can be used in analysis of: drugs, plastics, flavourings, air samples
- TLC:
  - Quick, inexpensive, indicates how many components in a mixture
  - TLC plate: usually plastic/glass coated w/ thin layer solid adsorbent substance (often silica). adsorbent= stationary phase

- Different components have different affinities for adsorbent and bind with different strength to surface, meaning separation is achieved
- Adsorption: process by which silica holds different substances in mixture to surface
- Carrying out: draw a baseline with pencil, spot a small amount of solution on baseline with a capillary tube, prepare tank (small beaker with watch glass on top), pour solvent to depth below base line, place TLC plate in, leave solvent to rise up until 1cm from top, remove plate + mark solvent front with pencil, allow plate to dry, draw circles around visible spots/hold UV lamp over then circle/spray with locating agent (e.g. iodine or for amino acids use ninhydrin) to show spots
- Analysed by calculating retention factor (distance moved by component ÷ solvent)
- Can run alongside pure sample to identify visually

- Gas chromatography:
  - To separate/identify volatile organic compounds
  - Stationary phase=high boiling point liquid adsorbed onto inert solid support
  - Mobile phase= inert carrier gas (e.g. helium/neon)
  - Small amount of mixture is injected into gas chromatograph and is carried by mobile gas through capillary column where it slows down as it interacts with liquid stationary phase
  - More soluble in liquid stationary phase→ moves more slowly through capillary column→ larger retention time
  - Each component=peak on gas chromatogram. Retention time can be compared to known values & peak integrations (area) used to determine concentrations
  - To test for concentration: prepare standard solution of known concentration, obtain a gas chromatogram, plot a calibration curve of peak area vs conc, obtain gas chromatogram of compound being tested under same conditions, use calibration curve to obtain concentration
- Test for carboxylic acid: add aqueous sodium carbonate & you will get effervescence
- Test for phenol: at room temperature bromine is decolourised and a white ppt is formed

29.2 Nuclear magnetic resonance (NMR) spectroscopy

- Nuclear spin: nucleus has nuclear spin, significant if there is an odd number of nucleons
- Resonance: with a strong magnetic field + radio frequency radiation, nucleus rapidly flips between 2 spin states
- Frequency required is proportional to magnetic field strength & they have a large cylinder storing electromagnet, cooled by liquid helium

- Found in hospitals as MRI scanners
- Frequency shift is measured on a scale (chemical shift), the units are parts per million (ppm)
- Tetramethylsilane (TMS) $(CH_3)_4Si$: standard reference chemical against which all shifts are measured
- C/H arrangements are mapped without carrying out conventional test/destroying compound
- The sample is dissolved in solvent + placed in NMR sample tube with a small amount of TMS. This is placed in spectrometer, spun to even out imperfections, the spectrometer is zeroed against TMS standards & the sample is given a pulse of radiation with a range of frequencies and a constant magnetic field. Absorptions are detected + are displayed on computer
- Sample can be recovered by evaporation of the solvent
- Deuterated solvent: where ^1H is replaced by ^2H, produces no NMR signal. $CDCl_3$ commonly used, will produce peak in C-13 NMR but computers usually filter this out

29.3 carbon-13 NMR spectroscopy

- provides: number of carbon environments (number of peaks) & types of carbon environment (chemical shift)
- Chemical shifts may be out of range due to: solvent, concentration, substituents
- Two symmetrical carbons are equivalent + have same environment→ contribute to same peak
- Carbons nearer an oxygen atom will be shifted more to left

29.4 proton NMR spectroscopy

- Provides: number of proton environments (number of peaks), types of proton environments (chemical shift), relative numbers each type proton (from integration traces/ratio of areas), number of nonequivalent protons adjacent to given proton (from spin-spin splitting pattern)
- Factors including solvent, conc, substituents can mean peak moves outside range
- Equivalent protons will absorb same shift, increasing peak size
- Measured area under each peak as integration trace shown as extra line/printed number
- Spin-spin coupling: splitting of a main peak into sub-peaks
- For a proton with n protons on adjacent carbon, number of sub-peaks is n+1
- Splitting pattern=singlet/doublet/triplet/quartet etc
- OH and NH protons usually not involved in spin-spin coupling→ chemists use proton exchange to identify them: NMR spec run as normal, small volume of deuterium oxide (D_2O) is added, mixture is shaken & second spectrum run. Deuterium replaces OH/NH

protons (e.g. $CH_3OH + D_2O \rightleftharpoons CH_3OD + HOD$), deuterium doesn't absorb chemical shift range so OH peak disappears

29.6 combined techniques

- Elemental analysis (empirical formula)→ mass spectra→ infrared spectra→ NMS spectra