

# [Organic chemistry al notes flashcard](https://assignbuster.com/organic-chemistry-al-notes-flashcard/)

Topic Acid-Base Theory (Unit 1) Acid-Base Theory (Unit 2) Isomerism (Unit 1) Isomerism (Unit 2) Nomenclature Reaction Mechanism (Unit 1) – Introduction to Mechanism Reaction Mechanism (Unit 2) – Nucleophilic substitution Reaction Mechanism (Unit 3) – Nucleophilic substitution Reaction Mechanism (Unit 4) – Nucleophilic substitution Reaction Mechanism (Unit 5) – Nucleophilic substitution Reaction Mechanism (Unit 6) – Nucleophilic substitution Reaction Mechanism (Unit 7) – Elimination Reaction Mechanism (Unit 8) – Elimination Reaction Mechanism (Unit 9) – Nucleophilic addition Reaction Mechanism (Unit 10) – Nucleophilic addition Reaction Mechanism (Unit 11) – Nucleophilic addition Reaction Mechanism (Unit 12) – Nucleophilic addition Reaction Mechanism (Unit 13) – Nucleophilic addition Reaction Mechanism (Unit 14) – Nucleophilic addition Reaction Mechanism (Unit 15) – Electrophilic addition Reaction Mechanism (Unit 16) – Electrophilic addition Reaction Mechanism (Unit 17) – Electrophilic substitution Reaction Mechanism (Unit 18) – Electrophilic substitution Reaction Mechanism (Unit 19) – Electrophilic substitution Reaction Mechanism (Unit 20) – Radical reactions Amino acids Oxidation and Reduction Uses of compounds with different functional groups Structure determination (Unit 1) Structure determination (Unit 2) Structure determination (Unit 3) Structure determination (Unit 4) Organic synthesis Organic Laboratory Technique (Unit 1) Organic Laboratory Technique (Unit 2) Organic Laboratory Technique (Unit 3) Organic Laboratory Technique (Unit 4)

Reference Reading from Solomons, Organic Chemistry 6th edition 90-93, 96-101 102-118, 320, 433-434, 795-796, 903-905, 970-972 59-61 178-185, 188, 193-198, 200 41-47, 65-75, 128-137, 284-286, 288-289, 415-417, 615-617, 705-706, 792-793, 797-800, 899-900 87-90, 94-96 224-233, 238-252, 256-259 260 913-914 438-443 923-924, 926-927, 966 260-262, 265-268, 300, 302-305 308, 312, 318-319, 443-444 719 470-472, 716-719, 729-734, 759-761 708-711 805-817, 820-824 919-921 711, 825-827, 918 327-333 336-339, 346-351, 422-425 617-618, 655-658 658-664, 930-931, 974 930-931, 974 334-335, 366-379, 393-397 1146-1148 165-166, 473-475, 690-691, 915-916 295-297 359-360, 742 541-547 169-171 Summary of Organic Reactions (I. Alkanes) Page 1 I. A. B. Alkanes Cracking very long alkane ???? > long alkane + short alkene heat , catayst Combustion y y CxHy + (x + 4 ) O2(g) > xCO2(g) + 2 H2O(l) C. Chlorination Chain initiation (chain initiating step) Cl Cl h? Cl + Cl Cl· radical is generated. Chain propagation (chain propagating step) H Cl H C H H Cl H + H C H H Cl· radical is consumed. H Cl Cl C H H Cl + Cl H C H H Cl· radical is regenerated. Chain termination (chain terminating step)

Cl + Cl H Cl C H H H C H H C H H H Cl Cl Cl H C H H H H C C H H H H + Energy radical is destroyed. A mixture of products would be obtained. Summary of Organic Reactions (II. Alkenes and alkynes) Page 2 II. A. 1. Alkenes and alkynes Addition reactions Reaction with bromine in CCl4 Br2 + R C C R R in CCl4 R in dark Br Br C R R R C R 1, 2-dibromoalkane Note : Test for C= C or C? C bond Br OH C R R R 2. Reaction with bromine water Br2(aq) + R C C R R R in dark R C halohydrin Note : Test for C= C or C? C bond H Br H C C H major product 3. Reaction with hydrogen bromide H C H H H C C C H + H Br H H H 2-bromopropane Br H H H C C C H minor product H H H 1-bromopropane

H H propene Note : Follows Markownikov’s orientation OH S O C R R 4. Reaction with conc. sulphuric(VI) acid conc. H2SO4(l) + R C C R R R O H R C R O alkyl hydrogensulphate(VI) Note : A reversible reaction OH O H S O C R R O + H2O(l) H R C R OH C R R + H2SO4(aq) R C R alcohol alkyl hydrogensulphate(VI) Note : Laboratory preparation of alcohol 5. Reaction with water CH2 CH2 + H2O ethane H3PO4 300 ? C CH3 CH2 OH ethanol Note : Industrial preparation of alcohol 6. Catalytic hydrogenation of oil Note : hardening of oil Summary of Organic Reactions (II. Alkenes and alkynes) B. Ozonolysis of alkene CH3 CH3CHCH CH2 3-methylbut-1-ene (1) O3, CH2Cl2, -78 ?

C (2) Zn / H2O CH3 O CH3CH C H 2-methylpropanal + O H C H methanal Page 3 Note : Can be used to determine the structure of the alkene with characterization of the derivatives of carbonyl compounds formed. C. Oxidation cleavage of double bond CH3CH2 CH3CH2 C C CH3 CH3 (1) KMnO4, OH-, hot (2) H+ O CH3CH2 C CH2CH3 + pentan-3-one CH3 O CH3CH C OH + CO2 2-methylpropanoic acid + H2O O H3C C CH3 3-ethyl-2-methylpent-2-ene CH3 CH3CHCH CH2 3-methylbut-1-ene propanone (1) KMnO4, OH-, hot (2) H+ Note : The outcomes are different from the ones from ozonolysis. a) Reaction with cold acidic or alkaline permanganate solution H H H C C H ethane H H cold KMnO4(aq) H3O+ or OHH C C H O O H H ethane-1, 2-diol D.

Oxymercuration of alkyne H R C C terminal alkyne H HgSO4(aq) H2SO4(aq) R C O H Markovinkov orientation C H keto-enol tautomerization H R C C O H methyl ketone H Summary of Organic Reactions (II. Alkenes and alkynes) E. Polymerization of alkenes Chain initiating step O O R R C O O C Diacylperoxide heat O 2 R C O 2R + 2 CO2 alkyl radical Page 4 Chain propagating step H R H C C H H H H R C C H H H H R C C H H H C H C H H H H H H R C C C C H H H H etc. long chain polymer Chain terminating step H H R (CH2 CH2)n C C H H H H C C H H (CH2 CH2)n R combination H H H H R (CH2 CH2)n C C C C H H H H (CH2 CH2)n R H H R (CH2 CH2)n C C H H H H C C H H (CH2 CH2)n R isproportionation H H R (CH2 CH2)n C oxidation product C H H H H C C H H reduction product (CH2 CH2)n R Summary of Organic Reactions (III. Aromatic hydrocarbons) Page 5 III. A. 1. Aromatic hydrocarbons Substitution reactions of benzene Nitration conc. HNO3(aq) conc. H2SO4(l) 55°C benzene nitrobenzene NO2 Note : No reaction if conc. H2SO4(l) is not added. X 2. Halogenation X2 FeX3 or AlX3 benzene halobenzene 3. Sulphonation conc. H2SO4 heat benzene O O S O H NaOH(s) 350°C O O S O H benzenesulphonic acid O-Na+ OH H3O+ benzenesulphonic acid sodium phenoxide / sodium phenolate phenol Note : Industrial preparation of phenol R 4. Alkylation RX and AlX3 benzene lkylbenzene B. Oxidation of alkylbenzene R 1) KMnO4, OH-, heat 2) H3O+ alkylbenzene O C OH benzenecarboxylic acid Summary of Organic Reactions (IV. Halogeno-compounds) Page 6 IV. A. 1. Halogeno-compounds Nucleophilic substitution Reaction with sodium hydroxide R X haloalkane X NaOH(aq) heat halobenzene phenol NaOH(aq) R OH alcohol OH Note : Prolonged heating is required for the alkaline hydrolysis of halobenzene. 2. Reaction with potassium cyanide R X haloalkane KCN(aq) R CN nitrile 3. Reaction with ammonia H N H + R X H ammonia haloalkane H N R + R X haloalkane + R X haloalkane H N R + HX H 1° amine R N R + HX H 1° amine R N R H 2° amine R N R + HX

H 2° amine R 3° amine R R N R + R X haloalkane R N R X- R 3° amine R quaternary ammonium halide Note : A mixture of products would be obtained. 4. Reaction with alkoxide R’ O-Na+ R X + haloalkane sodium alkoxide R O R’ ether 5. Reaction with carboxylate ion O R’ C O Na sodium haloalkane carboxylate R X + + O R R’ C O ester Summary of Organic Reactions (IV. Halogeno-compounds) B. 1. Elimination reaction Reaction with alcoholic sodium hydroxide to form alkene X H C R C R NaOH(alc. ) R C C R R R haloalkane R R alkene Page 7 2. Reaction with alcoholic sodium hydroxide to form alkyne X X C H H 1, 2-dihaloalkane alkyne R C R boiling NaOH(alc. ) R C C R

Summary of Organic Reactions (V. Hydroxy compounds) Page 8 V. A. 1. a) Hydroxy compounds Reactions of alcohols Formation of halide by halogenating agent R OH alcohol PCl5 / PCl3 / SOCl2 R Cl chloroalkane b) by heating with halide salt in acidic medium + R OH Na X , conc. H2SO4(l) heat alcohol R X haloalkane 2. Formation of alkoxide 2 C2H5OH(l) + 2 Na(s) > 2 C2H5O-Na+(alc. ) + H2(g C2H5OH(l) + NaOH(s) d C2H5O-Na+(alc. ) + H2O(l) 3. Oxidation of alcohols H R C O H H 1° alcohol R R C O H H 2? alcohol R R C O H R 3? alcohol [O] Resistant to oxidation [O] [O] O R C H [O] O R C O H carboxylic acid aldehyde O R C R ketone 4. Dehydration of alcohols H H H C C H conc.

H SO 2 4 H O heat H ethanol H H H C C H ethene 5. Esterification O R OH + R’ C OH carboxylic alcohol acid O conc. H2SO4(l) R’ C O R heat ester + H2O Summary of Organic Reactions (V. Hydroxy compounds) 6. Triiodomethane formation H H R C C H O H H alcohol with 1-hydroxyethyl group NaOH(aq) + I2(aq) O R C O – Page 9 I + H C I I carboxylate iodoform ion (yellow ppt. ) Note : Details : 1. 2. Test for the presence of 1-hydroxyethyl group. Shorten the carbon chain by 1 C. H H R C C H O H oxidation + I2 + 2 OH- H R C C H + 2 I- + 2 H2O O H methyl ketone O I + H C I I H alcohol with 1-hydroxyethyl group O H R C C H methyl ketone H NaOH(aq) + I2(aq) R C O- arboxylate iodoform ion (yellow ppt. ) 7. a) Distinction between primary, secondary and tertiary alcohols With potassium dichromate(VI) H R C O H H 1° alcohol R R C O H H 2? alcohol R R C O H R 3? alcohol [O] Resistant to oxidation [O] [O] O R C H [O] O R C O H carboxylic acid aldehyde O R C R ketone b) Lucas’ test H R C OH H 1° alcohol H conc. HCl(aq) ZnCl2(aq) no reaction H conc. HCl(aq) ZnCl2(aq) R C R R conc. HCl(aq) ZnCl2(aq) R C R Cl fast reaction R C OH R 2° alcohol R R C OH R 3° alcohol Cl slow reaction Note : 3? alcohol will turn cloudy quickly, 2? alcohol will turn cloudy slowly but 1? alcohol will not turn cloudy at all. Summary of Organic Reactions (V.

Hydroxy compounds) B. 1. Reactions of phenol Reaction with sodium OH Na O-Na+ + H2 Page 10 phenol sodium phenoxide / sodium phenolate 2. Reaction with sodium hydroxide OH NaOH(aq) O-Na+ + H2O phenol sodium phenoxide / sodium phenolate Note : Phenol is soluble in sodium hydroxide solution. O or O R ester C O R 3. Esterification OH O R C Cl O phenol R C O C 4. Reaction with bromine OH Br2(aq) Br OH Br phenol Br 2, 4, 6-tribromophenol (a white ppt. ) Note : A test for phenol. Summary of Organic Reactions (VI. Carbonyl compounds) Page 11 VI. A. 1. Carbonyl compounds Nucleophilic addition Reaction with hydrogen cyanide O R C R O H C N + HCN R C R 2.

Reaction with sodium hydrogensulphate(IV) R R O C + Na HSO3 + – H O C SO3-Na+ white precipitate CH3/H CH3/H Note: 1. 2. Sensitive to steric hinderance and reacts with aldehyde and methyl ketone only. Can be used to purify aldehyde or methyl ketone. B. 1. Addition-elimination (condensation) Reaction with hydroxylamine O R C R + H N OH H R R oxime (white ppt. ) C N OH + H2O hydroxylamine Note : 1. 2. A test for aldehyde or ketone. Identify the carbonyl compound by characterization. H H H 2. Reaction with 2, 4-dinitrophenylhydrazine R R O C + H N N O2N 2, 4-dinitrophenylhydrazine NO2 R R C N N O2N NO2 + H O 2 2, 4-dinitrophenylhydrazone (orange ppt. ) Note : 1. 2.

Test for aldehyde or ketone but no reaction with carboxylic acid and its derivatives Identify the carbonyl compound by characterization. O R C O- 3. Triiodomethane formation O H R C C H methyl ketone H NaOH(aq) + I2(aq) I + H C I I carboxylate iodoform ion (yellow ppt. ) Note : 1. 2. Test for methyl ketone. Shortens the carbon chain by 1 C Summary of Organic Reactions (VI. Carbonyl compounds) C. 1. Oxidation and reduction Oxidation of aldehyde with potassium dichromate(VI) O R C H aldehyde [O] O R C OH carboxylic acid Page 12 Note : Orange acidified potassium dichromate will turn to green chromium(III) ion. O 2. Oxidation of aldehyde with Tollens’ reagent

O R C H aldehyde R C O NH4 + Ag(s) [Ag(NH3)2]OH(aq) ammonium silver mirror carboxylate Tollen’s reagent + Note : Test for aldehyde O 3. Oxidaton of aldehyde with Fehling’s reagent O Fehling’s reagent R C H aldehyde R C O + Cu2O brick red ppt. carboxylate ion Note : Test for aldehyde 4. Resistance of ketones to oxidation O R C R [O] no reaction Note : Ketone is stable to general oxidation. O- 5. Reduction with sodium tetrahydridoborate / lithium tetrahydrioaluminate O R C R/H aldehyde or ketone O R C R/H aldehyde or ketone + LiAlH4(ether) + NaBH4(aq) R C R/H H alkoxide OR C R/H H alkoxide H3O+ H3O+ O H R C R/H H alcohol O H R C R/H H alcohol Note : LiAlH4 cannot be used in aqueous medium. O R C OI + H C I I . Haloform reaction O H R C C H methyl ketone H NaOH(aq) + I2(aq) carboxylate iodoform ion (yellow ppt. ) Note : 1. 2. Test for methyl ketone. Shorten the carbon chain by 1 C. Summary of Organic Reactions (VII. Carboxylic acids and their derivatives) Page 13 VII. A. 1. Carboxylic acids and their derivatives Formation of carboxylic acid Hydrolysis of nitrile R C N nitrile dil. H2SO4(aq) reflux O R C OH carboxylic acid Note : Complete hydrolysis of nitrile 2. Oxidation of alcohol H R C O H H 1° alcohol [O] O R C H [O] O R C O H carboxylic acid aldehyde Note : Aldehyde intermediate can be separated from the reacting mixture by distillation. O 3.

Oxidation of aldehyde O R C H aldehyde [O] R C OH carboxylic acid 4. Oxidation of alkylbenzene R 1) KMnO4, OH-, heat 2) H3O+ alkylbenzene O C OH benzenecarboxylic acid B. 1. Reactions of carboxylic acid Formation of salt O R C OH carboxylic acid NaOH(aq) O R C O-Na+ sodium carboxylate 2. Formation of acyl chloride O R C OH alcohol PCl5 / PCl3 / SOCl2 O Cl R C chloroalkane Summary of Organic Reactions (VII. Carboxylic acids and their derivatives) 3. Formation of anhydride O H C C H C OH 140°C C OH O cis-butenedioic acid H H O O + H2O O butenedioic anhydride Page 14 Note : O CH3 Intramolecular dehydration O CH3 ethanoic acid P2O5 (P4O10) O CH3 O CH3 C O C

C OH + HO C ethanoic acid ethanoic anhydride Note : O CH3 Intermolecular dehydration O + O CH3 O CH3 + NaCl C O Na + Cl C CH3 C O C 4. Formation of ester O R’ C O-Na+ sodium haloalkane carboxylate R X + O R C Cl acyl chloride O + R OH alcohol O R O R C O ester O R’ C O ester R R R C O C acid anhydride O R C OH carboxylic acid + R OH alcohol H3O+ heat O R C O ester O R C O ester R R + R OH alcohol 5. Formation of amide cold dil. H2SO4(aq) R C N or hot conc. H2SO4(l) nitrile O R C NH2 amide Note : Partial hydrolysis of nitrile. H 6. Reduction with lithium tetrahydridoaluminate O R C OH carboxylic acid (1) LiAlH4(ether) (2) H3O+ R C OH H 1° alcohol

Summary of Organic Reactions (VII. Carboxylic acids and their derivatives) C. 1. Reactions of acyl chlorides and anhydrides Reaction with water O R C Cl acyl chloride H2O(l) O Page 15 R C OH carboxylic acid + HCl O O R’ R C O C acid anhydride H2O(l) O R C OH carboxylic acid + O R’ C OH 2. Reaction with alcohol O ROH O R C Cl acyl chloride O O R C O C acid anhydride R’ R C OR ester ROH O R C OR ester + + HCl O R’ C OH 3. Reaction with ammonia O R C Cl acyl chloride O O conc. NH3(aq) O R C NH2 amide O R C NH2 amide R C O C R’ acid anhydride conc. NH3(aq) 4. Reaction with amine O R C Cl acyl chloride O O RNH2 O R R C NH N-substituted amide RNH2 O R R C NH N-substituted amide

R C O C R’ acid anhydride D. 1. Reactions of ester Acid and base-catalysed hydrolyses O R C O ester O R C O ester R NaOH(aq) heat R H3O+ heat O R C OH + R OH carboxylic acid O alcohol R C O- + R OH carboxylate alcohol ion Note : Rate of hydrolysis : alkaline medium > acidic medium > neutral medium H 2. Reduction with lithium tetrahydridoaluminate O R C O ester R (1) LiAlH4(ether) (2) H3O+ R C OH H 1° alcohol Summary of Organic Reactions (VII. Carboxylic acids and their derivatives) E. 1. Reactions of amide Hydrolysis of amide O R C NH2 amide O R C NH2 amide H3O+ reflux O R C OH carboxylic acid O R C Ocarboxylate ion Page 16 OH reflux – 2.

Dehydration of amide O R C NH2 P2O5 or (CH3CO)2O or SOCl2 R C N 3. Hofmann degradation of non-substituted amide O R C NH2 amide Br2 / NaOH(aq) R N H H 1? amine with 1 C less Note : Only applicable to non-substituted amide. 4. Reduction with lithium tetrahydridoaluminate O R C NH2 amide 1) LiAlH4 / ether 2) H3O+ H R C N H H H 1° amine Note : Amide is the only acid derivative which will not be reduced to alcohol. Summary of Organic Reactions (VIII. Nitrogen compounds) Page 17 VIII. Nitrogen compounds A. 1. Formation of amine From nitrile R C N nitrile (1) LiAlH4(ether) (2) H3O+ H H R C N H H 1° amine Note : LiAlH4 could not be used in aqueous medium. 2. From amide

O R C NH2 amide 1) LiAlH4 / ether 2) H3O+ H R C N H H H 1° amine Note : Amide is the only acid derivative which will not be reduced to alcohol. 3. 1? , 2? , 3? amines and quaternary ammonium compounds by alkylation H N H + R X H ammonia haloalkane H N R + R X haloalkane + R X haloalkane H N R + HX H 1° amine R N R + HX H 1° amine R N R H 2° amine R N R + HX H 2° amine R 3° amine R R N R + R X haloalkane R N R X- R 3° amine R quaternary ammonium halide Note : A mixture of products would be obtained. 4. Phenylamine from nitrobenzene NO2 1) Sn, conc. HCl(aq) 2) OH-(aq) NH2 B. 1. Base properties of amine Salt formation R N H H + HCl H R N H ClH Summary of Organic Reactions (VIII. Nitrogen compounds) C. 1.

Reactions of amine Reactions with ethanoyl chloride and benzoyl chloride R N H H amine R N H H amine O + CH3 C Cl ethanoyl chloride O + C Cl benzoyl chloride O H CH3 C N R N-substituted ethanamide O H C N R N-subsituted benzenecarboxamide Page 18 2. Reaction with nitric(III) acid H H aliphatic primary amine NH2 HNO2 0-5°C R N HNO2 0-5°C R+ + N2 nitrogen bubbles carbocation + N N aromatic primary amine benzenediazonium ion Note : A test used to distinguish aliphatic primary amine from aromatic primary amine. HO 3. Coupling reaction of benzenediazonium ion with naphthalen-2-ol and phenol + N N OH N N naphthalen-2-ol benzenediazonium ion + N N OH phenol benzenediazonium ion orange ppt. red orange ppt. N N OH Note : Tests for benzenediazonium ion. Indirect tests for aromatic primary amine. Summary of Organic Reactions (IX. Other reactions) Page 19 IX.

Other reactions Radical addtion of X2 to benzene H X2 uv X H X H X H X H X H X Reactions of benzenediazonium ion + N N CuCN + N N H3PO2 CN Preparation of vinyl chloride H C H C H H Cl2 Electrophilic addition H H Cl Cl alcoholic NaOH H C Cl C H H H C C H Anti-Markownikov’s addition H Cl H H C C C H minor product H H H 2-chloropropane Cl H H H C C C H major product H H H 1-chloropropane H H H C C C H + H Cl + R O O R H H propene alkyl peroxide Test for terminal alkyne R–C? CH ? Cu ( NH ) > R–C? C-Cu+(s) (red ppt. ) ??? 3 2 + R–C? CH ? Ag ( NH ) > R–C? C-Ag+(s) (white ppt. ) ??? 3 2 + Test for phenol [Fe(H2O)6]3+(aq) + from neutral iron(III) chloride C6H5O-(aq) > [Fe(H2O)4(C6H5O)2]+(aq) + 2H2O(l) from phenol purple complex Nomenclature of Organic compounds I. Nomenclature of organic compounds A. Labelling of carbon 1. 2. B. Methyl, primary, secondary and tertiary carbon ? carbon, ? carbon and ? carbon Skeletal formula / Stick formula II. III. Nomenclature of hydrocarbon A. Alkyl and aryl group Other functional group A. B. C. D. Halogeno-compounds Alkanols and phenol Aldehydes and ketones Carboxylic acids 1. E. F. G. H. Carboxylic acid derivatives – esters, acid chlorides, anhydrides and amides Nitriles Amines Amino-acids Ethers IV. V. VI. Priority of functional groups Examples Other common abbreviations Acid-Base Theory I.

Definition of acid-base A. B. C. Arrhenius definition Bronsted-Lowry definition Lewis definition Leveling effect Relative stability of the conjugate base comparing with the acid 1. Inductive effect (1) Amine vs Amide II. III. Strength of acid and base A. A. Factors determining the strength of a Bronsted-Lowry acid 2. Resonance effect a) Resonance effect on a benzene ring (1) (2) Phenol Aromatic amine 3. 4. 5. 6. Intramolecular hydrogen bond Solvation / hinderance to solvation a) Steric hinderance to solvation b) Effect of solvent Strength of the bond between the proton and the conjugate base Electronegativity of the atom a) Effect of hybridization Isomerism I.

Structural isomerism A. B. C. D. Chain isomerism Position isomerism Functional group isomerism Tautomerism / Tautomerization Diastereomerism / Geometrical isomerism 1. Physical properties of cis-/trans-geometrical isomers of 1, 2-dichloroethene 2. Physical and chemical properties of cis-/trans-geometric isomers of butenedioic acid a) Physical properties b) Chemical properties Optical isomerism / Enantiomerism 1. Physical properties 2. Optical activity a) Plane polarized light b) Measurement of optical activity by polarimeter c) Specific rotation 3. Chiral centre 4. Racemic mixture / Racemic modification / Racemic form / Racemate II. Stereoisomerism

A. B. Reaction Mechanism Page 1 Reaction Mechanism I. II. Bond breaking A. A. B. C. Bond breaking of a bond to carbon Free radical (electron deficiency) Electrophile (electron deficiency) Nucleophile (electron rich) Types of reaction 1. Substitution 2. Addition 3. Elimination Types of reactive species III. Classification of reaction A. Reaction Mechanism Page 2 IV. Nucleophilic substitution A. B. C. D. E. F. G. Nucleophilic substitution 1. Nucleophile 2. Leaving group SN2 reaction (1 step reaction) SN1 reaction (2 steps reaction) Competition between SN1 and SN2 reactions Alkanol from haloalkane (RX > ROH) 1. Alkaline hydrolysis of haloalkane 2.

Hydrolysis of haloalkane Rate of hydrolysis of haloalkane, haloalkene and halobenzene Other relevant reactions 1. Reactions of haloalkane a) Nitrile from haloalkane (RX > RCN) b) Alkylation of ammonia and amine (NH3 > RNH2) c) Use of SN2 reaction in organic synthesis 2. Reactions of alkanol a) Haloalkane from alkanol (ROH > RX) (1) Use of chlorinating and brominating reagent 3. b) Luca’s test to distinguish 1? , 2? and 3? alkanol Reactions of amine a) Action of nitric(III) acid on 1? amine (1) (2) 1? aliphatic amine 1? aromatic amine b) Laboratory preparation of phenol from benzenamine V. Elimination reaction A. Elimination reaction 1. Stability of elimination product 2. E2 reaction (not required in A-Level) 3.

E1 reaction (not required in A-Level) Competition between substitution and elimination reaction 1. Effect of temperature 2. Effect of bulkiness of the substrate and base 3. Effect of bascity of the nucleophile Conditions favouring substitution and elimination reaction Other relevant reactions 1. Reaction of haloalkanes with alcoholic sodium hydroxide to alkene, diene and alkyne 2. Preparation of vinyl chloride 3. Dehydration of alkanol B. C. D. Reaction Mechanism Page 3 VI. Nucleophilic addition (Nucleophilic addition-elimination) A. AdN reaction 1. Addition of HCN to carbonyl compound 2. Rate of nucleophilic addition a) Electronic effect (1) (2) Inductive effect (a) Effect of protonation Resonance effect 3. ) Steric effect Other relevant reactions a) Reactions of carbonyl group (1) (2) (3) (4) (5) Reduction of carbonyl compound by LiAlH4 and NaBH4 Addition of NaHSO3 to carbonyl compound Condensation reaction with hydroxylamine Condensation reaction with 2, 4-dinitrophenylhydrazine Haloform reaction / Iodoform reaction Carboxylic acid and its derivatives (a) Difference between carbonyl compound and carboxylic acid and its derivatives (b) Reactivities of carboxylic acid and its derivatives Formation of different acid derivatives (a) Use of chlorinating agent to prepare acyl chloride (b) Formation of ester (Esterification with alkanol and phenol) (c) Formation of acid anhydride (i) (ii) (iii) Through intramolecular dehydration by heating Through intermolecular dehydration by a very strong dehydrating agent From acyl chloride b) Reactions of carboxylic acid and its derivatives (1) (2) (3) (4) (d) Formation of amide (Acylation and benzoylation of amine) Reaction of ester (a) Hydrolysis of ester Reaction of amide (a) Reduction of amide and other acid derivatives (b) Hofmann degradation of amide Hydrolysis of nitrile and amide (a) Dehydration of amide Reduction of nitrile c) Reactions of nitrile (1) (2) VII. Electrophilic addition A. B. Addition of HBr to alkene 1. Markownikoff’s rule. 2. Reactivity of alkene towards electrophilic addition Other relevant reaction 1. Addition of Br2 to alkene 2. Addition of H2SO4 to alkene a) Preparation of alkanol from alkene 3.

Hydration of alkene 4. Ozonolysis of alkene 5. Preparation of ethane-1, 2-diol a) Oxidative Cleavage of double bond b) Comparision of ozonolysis and oxidative cleavage 6. Oxymercuration of alkyne Reaction Mechanism Page 4 VIII. Electrophilic substitution A. B. Representation of arenium ion Other relevant reaction 1. Sulphonation of benzene a) Preparation of phenol 2. Nitration of benzene a) Reduction of nitrobenzene 3. Halogenation of benzene 4. Alkylation of benzene (Friedel-Crafts alkylation) 5. Diazocoupling of diazonium ion a) Colour of a substance 6. Bromination of phenol Formation of free radical Free radical Substitution 1. Chain reaction e. g. hlorination of methane a) Chain initiation (chain initiating step) b) Chain propagation (chain propagating step) c) Chain termination (chain terminating step) 2. Reaction between H2(g) and Cl2(g) Free radical Addition 1. Chain reaction e. g. Polymerization of alkene 2. Anti-Markownikoff orientation IX. Free radical Reaction A. B. C. Amino acids I. Amino acids A. B. Zwitterion Polypeptides Oxidation and Reduction I. Oxidation A. B. C. Combustion of alkane Oxidation of alkanol and aldehyde Oxidation of aromatic side chain II. Reduction A. B. Reduction of nitrobenzene Catalytic hydrogenation (Hydrogenation of alkene) Uses of Different Compounds I. A. B.

Uses of halogeno-compounds Use as solvent Manufacture of polymer 1. Preparation of vinyl chloride 2. Physical properties of PVC and Teflon II. A. B. C. D. Uses of alcohols Use as solvent Alcoholic drink Blending agent Ethan-1, 2-diol III. A. B. Uses of carbonyl compounds Preparation of urea-methanal Use of propanone IV. A. B. C. Uses of carboxylic acids and their derivatives Food preservatives Manufacture of nylon and terylene Use of ester V. A. B. Uses of amines and their derivatives Azo compounds as dyes in dyeing industries Amine derivatives as drugs Determination of Structure I. Determination of empirical formula and molecular formula A. B. C.

Different kinds of formula Determination of empirical formula Determination of molecular formula Determination of degree of unsaturation Meaning of degree of unsaturation II. Degree of unsaturation A. B. III. IV. V. Sodium fusion test Test for different functional groups by wet chemistry Introduction to IR and NMR spectroscopy A. Use of infra-red (IR) spectrum in the identification of functional groups 1. More examples Organic synthesis I. II. Retrosynthetic analysis Structural analysis A. Chain length 1. 2. B. C. D. Carbon chain Nitrogen and Oxygen containing chain Degree of unsaturation Oxidation or Reduction Position of functional group III. IV.

Systematic approach to organic synthesis Examples Organic Laboratory Technique I. Purification of organic compound A. B. C. D. E. Solvent extraction Steam distillation Chromatography Recrystallization Filtration and Suction filtration II. Use of quickfit apparatus A. B. Handling of quickfit apparatus Different setup of quickfit apparatus 1. 2. Reflux setup Distillation setup III. Testing for purity A. B. Determination of melting point Determination of boiling point Nomenclature of Organic compounds I. Nomenclature of organic compounds A. Labelling of carbon 1. 2. B. Methyl, primary, secondary and tertiary carbon ? carbon, ? carbon and ? carbon Skeletal formula / Stick formula II. III.

Nomenclature of hydrocarbon A. Alkyl and aryl group Other functional group A. B. C. D. Halogeno-compounds Alkanols and phenol Aldehydes and ketones Carboxylic acids 1. E. F. G. H. Carboxylic acid derivatives – esters, acid chlorides, anhydrides and amides Nitriles Amines Amino-acids Ethers IV. V. VI. Priority of functional groups Examples Other common abbreviations Nomenclature of organic compounds Page 1 Topic Reference Reading Nomenclature of organic compounds 13 Organic Chemistry, Fillans, 3rd Edition pg. 50–65 Guidelines for systematic chemical nomenclature, HK Exam. Authority pg. 7–17 Chemical nomenclature, symbols and terminology for use in school science. g. 58–65 Unit 1 Assignment Chemistry in Context, 5th Edition, Thomas Nelson and Sons Ltd. , pg. 380–381, 400–401, 414, 428, 432, 438, 439, 446, 453, 467, 484, 498, 516–517 Reading Organic Chemistry, 6th Edition, Solomons, pg. 41-47, 65-75, 128-137, 284-286, 288-289, 415-417, 615-617, 705-706, 792-793, 797-800, 899-900 Nomenclature of organic compounds Classification of hydrocarbons Priority of functional group in IUPAC naming I. Nomenclature of organic compounds Syllabus Notes The basic idea of the IUPAC (International Union of Pure and Applied Chemistry) system of naming is that by following some rules, a name can be assigned to a molecule.

And from the assigned name, the original molecule can be reconstructed unambiguously. A given structure may have several different names but a name will only give 1 structure. H H H H For example, the structure is called H C C C C O H is called butan-1-ol or 1-butanol but no matter H H H H butan-1-ol or 1-butanol refer to the same structure. IUPAC system of naming is a kind of substitutive nomenclature. In substitutive nomenclature, hydrogen atoms in a named ‘ parent’ hydrocarbons are considered to be substituted by other groups. Actually, the IUPAC system of naming is not very strict. It is possible to have more than 1 name for a given molecule. But no matter which name is assigned, only 1 structure can be rebuilt. A.

Labelling of carbon To facilitate discussion, carbon atoms on a carbon chain can be labelled by 2 different methods. 1. Methyl, primary, secondary and tertiary carbon The first way is based on the no. of carbon atoms attached to the carbon to be concerned. If no other carbon is attached to the carbon, the carbon atom is called a methyl carbon. If 1 carbon atom is attached to the carbon, the carbon atom is called a primary carbon, 1? carbon If 2 carbon atoms are attached to the carbon, the carbon atom is called a secondary carbon, 2? carbon If 3 carbon atoms are attached to the carbon, the carbon atom is called a tertiary carbon, 3? carbon H H C H methyl carbon X CH3 H C H 1° carbon X CH3 CH3 C H 2° carbon X CH3 CH3 C X CH3 3° carbon e. g.

CH3CH2OH is called a primary alkanol since the hydroxyl group is attached to a 1? carbon. Nomenclature of organic compounds 2. ? carbon, ? carbon and ? carbon Page 2 Another way is according to the position of the carbon relative to a substituent (functional group). If the carbon is immediately next to the substituent, it is called a ? carbon. The carbon attached to the ? carbon is called a ? carbon. The carbon attached to the ? carbon is called a ? carbon. O C ? C C ? C C ? C X C ? C C ? C C ? C C carbonyl carbon B. Skeletal formula / Stick formula / Bond line formula In order to make the presentation simple, sometimes skeletal formula is used instead of the full structural formula or condensed structural formula.

In the skeletal formula, all atomic symbols of carbon and hydrogen are omitted. Skeletal formula / Stick formula / Bond line formula Skeletal formula / Stick formula / Bond line formula Full structural formula Condensed structural formula Full structural formula Condensed structural formula H H H C C H H H H3C CH3 CH3 CH3 H H C H C H H C C H CH2 CH CH2 CH CH3CH3 H H H H H C C C H H H H H CH3CH2CH3 H C C C C C C H H H HH C HH H C H C H C H H CH3 CH3CHCH3 CH3CH(CH3)CH3 H H H H H H C C C H H C C C H H H H H H H H H H C C C H C H H H O H CH3CH2CH(OH)CH3 H H C H C H H H C C H C C H CH3CHCH2 C H H O H H H H H H CH2 CH2 CH2 CH2 OH O CH3COOCH2CH3 H C C O C C H H H CH3CH CH2 CH3C(CH2)CH3 H H O

H H H C H H C C H C H H Nomenclature of organic compounds II. Nomenclature of Hydrocarbon Some examples H H H H H C C C C O H is called butan-1-ol (or 1-butanol). (a primary alcohol) H H H H Page 3 H H3C C CH2 CH3 is called 2-methylbutane (or isopentane). iso- means 1 C is attached to the next-to-end C. CH3 CH3 H3C C CH2 CH3 is called 2, 2-dimethylbutane (or tert-butylethane). CH3 CH3 H3C C CH3 is called the tert-butyl group. CH3 CH2 CH2 CH CH2 CH2 CH3 H3C CH CH3 is called 4-(1-methylethyl)heptane (or 4-isopropylheptane). CH3 NH2 is called methanamine (or methylamine). O C H benzenecarbaldehyde (or benzaldehyde) O C OH benzenecarboxylic acid (or benzoic acid)

Nomenclature of organic compounds The basis of IUPAC substitutive nomenclature is that every name consists of a root, one suffix and as many prefixes as necessary. prefix – root – suffix Page 4 Root represents the longest carbon chain containing the principal functional group as indicated by the suffix and also it should contain the largest no. of substituent. Suffix represents the functional group with the highest priority among all the functional groups present. Prefix represents other functional group and arranged in alphabetical order. Cl e. g. CH3 CH CH2 CH2 OH 3-amino-2-chlorobutan-1-ol NH2 3-amino is a prefix 2-chloro is a prefix butan- is a root -ol is a suffix The numbers are called locants used to indicate the position of the functional group.

The numbers are arranged to give (a) the lowest possible number to the group cited by a suffix (principal functional group), then (b) the lowest possible individual numbers (not sum) to those cited as prefixes. CH3 CH2 CH CH CH2 CH2 CH2 CH2 CH CH3 CH3 CH3 CH3 2, 7, 8-trimethyldecane (not 3, 4, 9-trimethyldecane) N. B. hyphen (-) is used to separate number from letter. comma (,) is used to separate number from number. Name of the first 10 straight chain hydrocarbons 1. methane (meth-) 2. ethane (eth-) 3. propane (prop-) 4. butane (but-) 5. pentane (penta-) 6. hexane (hex-/hexa-) 7. heptane (hept-/hepta-) 8. octane (oct-/octa-) 9. nonane (nona-) 10. decane (dec-/deca-)

For the parent chain containing double bond or triple bond, suffixes -ene and -yne are used respectively. C C C ethene C C C C C C C ethyne C C C propyne C C C C but-1-ene C C C C but-2-yne C hepta-1, 3-diene If the chain contains both double bond and triple bond, the name will be ended with -yne. C C C C C C C C C pent-3-en-1-yne C C C C C pent-1-en-3-yne C C hex-3-ene-1, 5-diyne N. B. -e- is omitted if it is followed by a vowel e. g. y, a, o. If both double bond and triple bond has the same lowest possible number, double bond will be given a higher priority. C C C C C C C C C pent-1-en-4-yne C C hexa-1, 3-dien-5-yne Nomenclature of organic compounds Classification of hydrocarbons Hydrocarbons Page 5 Aliphatic (Acyclic) Alicyclic (Cyclic) Aromatic yclohexane Alkane CH3 CH3 ethane Alkene CH2 CH2 ethene Alkyne CH CH ethyne benzene (Arene) Aliphatic (Acyclic) : Hydrocarbon with no ring structure. It can be further classified into straight chain and branched hydrocarbon. Alicyclic (Cyclic) : Aromatic : Hydrocarbon with ring structure. A special kind of ring compound with extra stability due to delocalization of electrons. and naphthalene are aromatic. Originally, ‘ aromatic’ means having a sweet smell since Benzene the firstly discovered aromatic compounds possess special smell. A. Alkyl, vinyl, allyl and aryl group When a hydrogen is removed from an alkane, the structure is called an alkyl group R–.

It is cited by adding -yl. H H C H methyl group When a hydrogen is removed from an alkene, the structure is called a vinyl group. It is cited by adding -enyl. H H H H C C C H prop-2-enyl group When a hydrogen is removed from an alkyne, the structure is called an allyl group. It is cited by adding -ynyl. H H C H C C prop-1-ynyl group N. B. The carbons are counted from the point joining to the main chain. When a hydrogen is removed from a benzene, the structure is called a phenyl group Ph– or phenyl group However if a phenyl group is attached to a –CH2–, it is called the benzyl group. CH2 . benzyl group Phenyl group and other substituted phenyl group (e. . chlorophenyl group) are collectively called aryl group Ar–. NH2 phenylamine (or more accurate benzenamine). Nomenclature of organic compounds III. Other functional group A. Halogeno-compounds The presence of halogen (–X) is always cited by the prefixes (fluoro-), (chloro-), (bromo-) and (iodo-). Cl H C H H chloromethane Br Br H C C H 1, 2-dibromoethane H H Page 6 B. Alkanols and phenol The presence of hydroxyl group (–OH) is cited by suffix (-ol) or prefix (hydroxy-) H H H C C OH ethanol H H OH OH H C H C H ethane-1, 2-diol H H O HO C H C OH hydroxyethanoic acid N. B. (-e-) of the root is omitted if it is followed by an vowel e. g. -o- or -y-.

When a hydrogen on the benzene is substituted by a hydroxyl group, the compound is called phenol. OH phenol O2N OH 4-nitrophenol C. Aldehydes (Alkanals) and ketones (alkanones) Aldehyde (Alkanal) contains a terminal carbonyl group It is cited by suffix (-al) or prefix (oxo-). O CH3 C H ethanal O O H C C OH oxoethanoic acid O O O C . It has the general formula O R C H . Ketone contains a non-terminal carbonyl group C . It has the general formula R C R It is cited by suffix (-one) or prefix (oxo-) if the C is counted in the root or prefix (carbonyl-) if the C is not counted in the root. O CH3 C CH2 CH2 CH3 pentan-2-one O O CH3 C CH2 C OH 3-oxobutanoic acid D.

Carboxylic acids (Alkanoic acid) Carboxylic acid contains a carboxyl group prefix (carboxy-). O CH3 C OH ethanoic acid O C OH benzenecarboxylic acid (common name : benzoic acid) O HO C CH2 O C OH . It is cited by suffix (-oic acid) or (-carboxylic acid) or by O C OH propanedioic acid. O H H HO C C N+ H Cl- (carboxymethyl)ammonium chloride H H N. B. 1. 2. locant is not necessary for dioic acid since the carboxyl groups must occupy the ends of the C chain. When suffix (-carboxylic acid) or prefix (carboxy-) is used, the C in the carboxyl group is not counted as a part of the parent chain. Nomenclature of organic compounds 1. Carboxylic acid derivatives – esters,