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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, catalyst Combustion $C_xH_y + (x + \frac{y}{4}) O_2(g) \rightarrow xCO_2(g) + \frac{y}{2} H_2O(l)$ C. Chlorination Chain initiation (chain initiating step) $Cl_2 \xrightarrow{h\nu} 2 Cl\cdot$ radical is generated. Chain propagation (chain propagating step) $Cl\cdot + C_3H_8 \rightarrow HCl + C_3H_7\cdot$ radical is consumed. $C_3H_7\cdot + Cl_2 \rightarrow C_3H_7Cl + Cl\cdot$ radical is regenerated. Chain termination (chain terminating step)

$Cl\cdot + C_3H_8 \rightarrow C_3H_7\cdot + HCl$ 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 CCl_4 $Br_2 + R_2C=CR_2 \xrightarrow{CCl_4, \text{dark}} R_2C(Br)CR_2$ 1, 2-dibromoalkane Note: Test for $C=C$ or $C\equiv C$ bond Br_2 in CCl_4 2. Reaction with bromine water $Br_2(aq) + R_2C=CR_2 \xrightarrow{\text{dark}} R_2C(OH)CR_2$ halohydrin Note: Test for $C=C$ or $C\equiv C$ bond HBr major product 3. Reaction with hydrogen bromide $H_2C=CHCH_3 + HBr \rightarrow H_3CCH_2CH_2Br$ 2-bromopropane minor product $H_2C=CHCH_3 + HBr \rightarrow H_2C(Br)CH_2CH_3$ 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 OH⁻ 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

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Diacylperoxide heat $\text{O}_2 \text{R} \text{C} \text{O} \text{2R} + 2 \text{CO}_2$ alkyl radical Page 4 Chain
 propagating step $\text{H} \text{R} \text{H} \text{C} \text{C} \text{H} \text{H} \text{H} \text{H} \text{R} \text{C} \text{C} \text{H} \text{H} \text{H} \text{H} \text{R} \text{C} \text{C} \text{H} \text{H} \text{H} \text{C} \text{H} \text{C} \text{H} \text{H} \text{H}$
 $\text{H} \text{H} \text{H} \text{R} \text{C} \text{C} \text{C} \text{C} \text{H} \text{H} \text{H} \text{H}$ etc. long chain polymer Chain terminating step $\text{H} \text{H}$
 $\text{R} (\text{CH}_2 \text{CH}_2)_n \text{C} \text{C} \text{H} \text{H} \text{H} \text{H} \text{C} \text{C} \text{H} \text{H} (\text{CH}_2 \text{CH}_2)_n \text{R}$ combination $\text{H} \text{H} \text{H} \text{H} \text{R}$
 $(\text{CH}_2 \text{CH}_2)_n \text{C} \text{C} \text{C} \text{C} \text{H} \text{H} \text{H} \text{H} (\text{CH}_2 \text{CH}_2)_n \text{R} \text{H} \text{H} \text{R} (\text{CH}_2 \text{CH}_2)_n \text{C} \text{C} \text{H} \text{H} \text{H} \text{H} \text{C}$
 $\text{C} \text{H} \text{H} (\text{CH}_2 \text{CH}_2)_n \text{R}$ isproportionation $\text{H} \text{H} \text{R} (\text{CH}_2 \text{CH}_2)_n \text{C}$ oxidation product
 $\text{C} \text{H} \text{H} \text{H} \text{H} \text{C} \text{C} \text{H} \text{H}$ reduction product $(\text{CH}_2 \text{CH}_2)_n \text{R}$ Summary of Organic
 Reactions (III. Aromatic hydrocarbons) Page 5 III. A. 1. Aromatic
 hydrocarbons Substitution reactions of benzene Nitration conc. $\text{HNO}_3(\text{aq})$
 conc. $\text{H}_2\text{SO}_4(\text{l})$ 55°C benzene nitrobenzene NO_2 Note : No reaction if conc.
 $\text{H}_2\text{SO}_4(\text{l})$ is not added. X 2. Halogenation X_2 FeX_3 or AlX_3 benzene
 halobenzene 3. Sulphonation conc. H_2SO_4 heat benzene $\text{O} \text{O} \text{S} \text{O} \text{H}$ $\text{NaOH}(\text{s})$
 350°C $\text{O} \text{O} \text{S} \text{O} \text{H}$ benzenesulphonic acid $\text{O}-\text{Na}^+$ OH^- H_3O^+ benzenesulphonic
 acid sodium phenoxide / sodium phenolate phenol Note : Industrial
 preparation of phenol R 4. Alkylation RX and AlX_3 benzene lkybenzene B.
 Oxidation of alkylbenzene R 1) KMnO_4 , OH^- , heat 2) H_3O^+ alkylbenzene $\text{O} \text{C}$
 OH benzenecarboxylic acid Summary of Organic Reactions (IV. Halogeno-
 compounds) Page 6 IV. A. 1. Halogeno-compounds Nucleophilic substitution
 Reaction with sodium hydroxide $\text{R} \text{X}$ haloalkane X^- $\text{NaOH}(\text{aq})$ heat
 halobenzene phenol $\text{NaOH}(\text{aq})$ $\text{R} \text{OH}$ alcohol OH^- Note : Prolonged heating is
 required for the alkaline hydrolysis of halobenzene. 2. Reaction with
 potassium cyanide $\text{R} \text{X}$ haloalkane $\text{KCN}(\text{aq})$ $\text{R} \text{CN}$ nitrile 3. Reaction with
 ammonia $\text{H} \text{N} \text{H} + \text{R} \text{X}$ ammonia haloalkane $\text{H} \text{N} \text{R} + \text{R} \text{X}$ haloalkane + $\text{R} \text{X}$
 haloalkane $\text{H} \text{N} \text{R} + \text{HX}$ 1° amine $\text{R} \text{N} \text{R} + \text{HX}$ 1° amine $\text{R} \text{N} \text{R} \text{H}$ 2° amine
 $\text{R} \text{N} \text{R} + \text{HX}$

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 PCI5 / PCI3 / 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. $\text{H H R C C H O H} + \text{I}_2 + 2 \text{OH}^- \rightarrow \text{H R C C H} + 2 \text{I}^- + 2 \text{H}_2\text{O}$ methyl ketone $\text{O I} + \text{H C I I H}$ alcohol with 1-hydroxyethyl group O H R C C H methyl ketone $\text{H NaOH(aq)} + \text{I}_2(\text{aq}) \rightarrow \text{R C O}^-$ 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 O H H 1° alcohol $\text{H conc. HCl(aq) ZnCl}_2(\text{aq})$ no reaction $\text{H conc. HCl(aq) ZnCl}_2(\text{aq}) \text{R C R R}$ conc. $\text{HCl(aq) ZnCl}_2(\text{aq}) \text{R C R Cl}$ fast reaction R C O H R 2° alcohol R R C O H 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 $\text{OH Na O-Na}^+ + \text{H}_2$ Page 10 phenol sodium phenoxide / sodium phenolate 2.

Reaction with sodium hydroxide $\text{OH NaOH(aq) O-Na}^+ + \text{H}_2\text{O}$ 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 $\text{OH Br}_2(\text{aq}) \text{Br OH Br}$ phenol $\text{Br}_2, 4, 6$ -

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 $\text{O R C R O H C N} + \text{HCN} \rightarrow \text{R C R}_2$.

Reaction with sodium hydrogensulphate(IV) $\text{R R O C} + \text{Na HSO}_3 + - \text{H O C}$

$\text{SO}_3\text{-Na}^+$ white precipitate CH_3/H CH_3/H Note: 1. 2. Sensitive to steric

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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 $\text{O R C R} + \text{H N OH} \rightarrow \text{H R R oxime}$ (white ppt.) $\text{C N OH} + \text{H}_2\text{O}$ 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 $\text{R R O C} + \text{H N N O}_2\text{N}$ 2, 4-dinitrophenylhydrazine $\text{NO}_2 \text{R R C N N O}_2\text{N NO}_2 + \text{H O}$ 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 $\text{H NaOH(aq)} + \text{I}_2(\text{aq}) \text{I} + \text{H C I I}$ 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 $[\text{O}] \text{O R C OH}$ 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 $\text{R C O NH}_4 + \text{Ag(s)} [\text{Ag}(\text{NH}_3)_2]\text{OH(aq)}$ ammonium silver mirror carboxylate Tollen's reagent + Note : Test for aldehyde O 3. Oxidation of aldehyde with Fehling's reagent O Fehling's reagent R C H aldehyde $\text{R C O} + \text{Cu}_2\text{O}$ brick red ppt. carboxylate ion Note : Test for aldehyde 4. Resistance of ketones to oxidation $\text{O R C R} [\text{O}]$ 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 + $\text{LiAlH}_4(\text{ether}) + \text{NaBH}_4(\text{aq}) \text{R C R/H H}$ alkoxide OR C R/H H alkoxide

H_3O^+ H_3O^+ O H R C R/H H alcohol O H R C R/H H alcohol Note : LiAlH_4 cannot be used in aqueous medium. O R C O I + H C I I . Haloform reaction O H R C C H methyl ketone H $\text{NaOH}(\text{aq})$ + $\text{I}_2(\text{aq})$ 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. $\text{H}_2\text{SO}_4(\text{aq})$ reflux O R C OH carboxylic acid Note : Complete hydrolysis of nitrile 2. Oxidation of alcohol H R C O H H 1° alcohol $[\text{O}]$ O R C H $[\text{O}]$ 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 $[\text{O}]$ R C OH carboxylic acid 4. Oxidation of alkylbenzene R 1) KMnO_4 , OH^- , heat 2) H_3O^+ alkylbenzene O C OH benzenecarboxylic acid B. 1. Reactions of carboxylic acid Formation of salt O R C OH carboxylic acid $\text{NaOH}(\text{aq})$ O R C $\text{O}-\text{Na}^+$ sodium carboxylate 2. Formation of acyl chloride O R C OH alcohol PCl_5 / PCl_3 / SOCl_2 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 + H_2O O butenedioic anhydride Page 14 Note : O CH_3 Intramolecular dehydration O CH_3 ethanoic acid P_2O_5 (P_4O_{10}) O CH_3 O CH_3 C O C

C OH + HO C ethanoic acid ethanoic anhydride Note : O CH_3 Intermolecular dehydration O + O CH_3 O CH_3 + NaCl C O Na + Cl C CH_3 C O C 4. Formation of ester O R' C $\text{O}-\text{Na}^+$ 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 H_3O^+ heat O R C O ester
 O R C O ester $\text{R R} + \text{R OH}$ alcohol 5. Formation of amide cold dil. $\text{H}_2\text{SO}_4(\text{aq})$
 R C N or hot conc. $\text{H}_2\text{SO}_4(\text{l})$ nitrile O R C NH_2 amide Note : Partial hydrolysis
of nitrile. H 6. Reduction with lithium tetrahydridoaluminate O R C OH
carboxylic acid (1) $\text{LiAlH}_4(\text{ether})$ (2) H_3O^+ 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 $\text{H}_2\text{O}(\text{l})$ O R C OH carboxylic acid + HCl O O R' R C O C
acid anhydride $\text{H}_2\text{O}(\text{l})$ 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 $\text{O O conc. NH}_3(\text{aq})$ O R C NH_2 amide O R C NH_2 amide R C
 O C R' acid anhydride conc. $\text{NH}_3(\text{aq})$ 4. Reaction with amine O R C Cl acyl
chloride O O RNH_2 O R R C NH N-substituted amide RNH_2 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 $\text{R NaOH}(\text{aq})$ heat $\text{R H}_3\text{O}^+$ heat O R C
 $\text{OH} + \text{R OH}$ carboxylic acid $\text{O alcohol R C O}^- + \text{R OH}$ 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) $\text{LiAlH}_4(\text{ether})$ (2) H_3O^+ 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 NH_2 amide O R C NH_2 amide H_3O^+ reflux
 O R C OH carboxylic acid $\text{O R C Ocarboxylate ion}$ Page 16 $\text{OH reflux} - 2.$

Dehydration of amide O R C NH_2 P_2O_5 or $(\text{CH}_3\text{CO})_2\text{O}$ or SOCl_2 R C N 3.

Hofmann degradation of non-substituted amide O R C NH_2 amide $\text{Br}_2 /$

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

NH_2 amide 1) $\text{LiAlH}_4 / \text{ether}$ 2) H_3O^+ 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)

$\text{LiAlH}_4(\text{ether})$ (2) H_3O^+ H H R C N H H 1° amine Note : LiAlH_4 could not be

used in aqueous medium. 2. From amide

O R C NH_2 amide 1) $\text{LiAlH}_4 / \text{ether}$ 2) H_3O^+ 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 $\text{H N H} +$

R X H ammonia haloalkane $\text{H N R} + \text{R X}$ haloalkane + R X haloalkane $\text{H N R} +$

HX H 1° amine $\text{R N R} + \text{HX}$ H 1° amine R N R H 2° amine $\text{R N R} + \text{HX}$ H 2°

amine R 3° amine $\text{R R N R} + \text{R X}$ haloalkane R N R X- R 3° amine R

quaternary ammonium halide Note : A mixture of products would be

obtained. 4. Phenylamine from nitrobenzene NO_2 1) Sn, conc. HCl(aq) 2) OH-

(aq) NH_2 B. 1. Base properties of amine Salt formation $\text{R N H H} + \text{HCl}$ 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 $\text{O} + \text{CH}_3 \text{C Cl}$ ethanoyl chloride $\text{O} + \text{C Cl}$ benzoyl

chloride $\text{O H CH}_3 \text{C N R}$ N-substituted ethanamide O H C N R N-substituted

benzenecarboxamide Page 18 2. Reaction with nitric(III) acid H H aliphatic

primary amine NH_2 HNO_2 $0-5^\circ\text{C}$ R N HNO_2 $0-5^\circ\text{C}$ $\text{R}^+ + \text{N}_2$ nitrogen bubbles

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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 addition of X₂ to benzene H X₂ uv X H 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 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 ($NH_3 >$
 RNH_2) 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 basicity 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)
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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 LiAlH_4 and NaBH_4 Addition of NaHSO_3 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 benzylation 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 Br_2 to alkene 2. Addition of H_2SO_4 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) Comparison 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. chlorination of methane a) Chain initiation (chain initiating step) b) Chain propagation (chain propagating step) c) Chain termination (chain terminating step) 2. Reaction between $H_2(g)$ and $Cl_2(g)$ 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 Ethane-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 <https://assignbuster.com/organic-chemistry-al-notes-flashcard/>

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 <https://assignbuster.com/organic-chemistry-al-notes-flashcard/>

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.

$\text{H} \quad \text{H} \quad \text{C} \quad \text{H}$ methyl carbon $\text{X} \quad \text{CH}_3 \quad \text{H} \quad \text{C}$
 $\text{H} \quad 1^\circ \text{ carbon} \quad \text{X} \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{C} \quad \text{H} \quad 2^\circ \text{ carbon} \quad \text{X} \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{C} \quad \text{X} \quad \text{CH}_3 \quad 3^\circ \text{ carbon}$ e. g.

$\text{CH}_3\text{CH}_2\text{OH}$ is called a primary alcohol since the hydroxyl group is attached to a 1° carbon. Nomenclature of organic compounds 2. 1° carbon, 2° carbon and 3° 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 α carbon. The carbon attached to the α carbon is called a β carbon. The carbon attached to the β carbon is called a γ carbon. $\text{O} \quad \text{C} \quad \alpha \quad \text{C} \quad \beta \quad \text{C} \quad \gamma \quad \text{C} \quad \text{X} \quad \text{C} \quad \alpha \quad \text{C} \quad \beta \quad \text{C} \quad \gamma \quad \text{C} \quad \text{C}$ 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

$\text{H} \quad \text{H} \quad \text{H}$
 $\text{C} \quad \text{C} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H}_3\text{C} \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{H} \quad \text{H} \quad \text{C} \quad \text{H} \quad \text{C} \quad \text{H} \quad \text{H} \quad \text{C} \quad \text{C} \quad \text{H} \quad \text{CH}_2 \quad \text{CH} \quad \text{CH}_2 \quad \text{CH} \quad \text{CH}_3\text{CH}_3 \quad \text{H}$
 $\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{CH}_3\text{CH}_2\text{CH}_3 \quad \text{H} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{C} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{C} \quad \text{H} \quad \text{C}$
 $\text{H} \quad \text{C} \quad \text{H} \quad \text{H} \quad \text{CH}_3 \quad \text{CH}_3\text{CHCH}_3 \quad \text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_3 \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{H} \quad \text{H} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{H} \quad \text{H} \quad \text{H}$
 $\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{H} \quad \text{C} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{O} \quad \text{H} \quad \text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3 \quad \text{H} \quad \text{H} \quad \text{C} \quad \text{H} \quad \text{C} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{C} \quad \text{C}$

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 pent-3-en-1-yne C 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 cyclohexane 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-). $\text{O} \text{CH}_3 \text{C} \text{H}$ ethanal $\text{O} \text{H} \text{C} \text{C} \text{OH}$ oxoethanoic acid $\text{O} \text{O} \text{O} \text{C}$. It has the general formula $\text{O} \text{R} \text{C} \text{H}$. Ketone contains a non-terminal carbonyl group C . It has the general formula $\text{R} \text{C} \text{R}$ 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. $\text{O} \text{CH}_3 \text{C} \text{CH}_2 \text{CH}_2 \text{CH}_3$ pentan-2-one $\text{O} \text{O} \text{CH}_3 \text{C} \text{CH}_2 \text{C} \text{OH}$ 3-oxobutanoic acid D.

Carboxylic acids (Alkanoic acid) Carboxylic acid contains a carboxyl group prefix (carboxy-). $\text{O} \text{CH}_3 \text{C} \text{OH}$ ethanoic acid $\text{O} \text{C} \text{OH}$ benzenecarboxylic acid (common name : benzoic acid) $\text{O} \text{HO} \text{C} \text{CH}_2 \text{O} \text{C} \text{OH}$. It is cited by suffix (-oic acid) or (-carboxylic acid) or by $\text{O} \text{C} \text{OH}$ propanedioic acid. $\text{O} \text{H} \text{H} \text{HO} \text{C} \text{C} \text{N}^+ \text{H} \text{Cl}^-$ (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,