Umit - 11 Alkohols, phenol, and Ethens. . Introduction CHA Methane Lydrocarbon Ort CH3 OH -> Methanol -> Hydroxy group. Alcohol planal H 01-ट्रमड्छम phenal. CHEOH. L'-M CH3OCH3 - dimethylether Classification : Alcohal and phenols They one Classified as Mono, Di, Tri or polyhydric (How 5 CHOH CH2H50H Ex: CH2-OH CHOH (H) - OH HOH OH (L'OH) 011 Diny duc Monohydric ahydrig www.notesdrive Scanned by CamScanner

Monohydric alcohol further classified to hybridisation of Carbon atom to which hydroxy group is attached. ) Compound containing (Sp<sup>3</sup> - OH bond. -OH group is attached to Sp<sup>3</sup> hybridised Carbon. -> They are jurthen classified as. a) Primary, Secondary and Tertiary all alcohol. H H GH3  $\begin{array}{cccc} H - E - C - OH & 3HC - C - CH_3 & H_3C - C - CH_3 \\ \hline 1^{1^{\circ}} & 1^{1^{\circ}} & 1^{2^{\circ}} \\ H & H & OH \end{array}$ primary (1°) Secondary (2°) Tertiary (3°) [6] Allylic alcohol. H  $CH_2 = CH - C - OH$  $CH_2 = CH - CH_2 - OH$ H - C - H primary  $\frac{CH_2 - CH - C - OH}{1}$ Secondary CH3 Tertiony. www.notesdrive.

Date Page No. Benzylic alcohol UHZ H CH2-OH CH3 CH3 <u>3°</u> 2° Containing CSP<sup>2</sup> - OH bond; Compound (H2=CH-OH (Vinyllic alcohol Ethens are classified as Simple/Symmetrical and Mixed/Unsymmetrical. They For ex: O O GH, OC2H, - Symmetrica ether C2H\_OCH3 -> Unsymmetrial 

Date Page No.\_\_\_\_ Stoucture of Junctional 19687 109 1H CH30M 136 pm PI phenol Methanol. Methoxy methane -4 T The bond angle in alcohol is Slightly less than tetsahedral angle (109°-28'). why? Due to the sepulsion blue the Unshared pairs of electron of Oxygen. 5 .Ans (arbon - Oxygen bond length in phenol is less than that in methanal why? (i) due to partial double bond character ii) Sp<sup>2</sup> hybridised State of Carbon to which Oxygen is attached. [50%. S-character] Ans Q. The bond angle in Methoxymethane (ether) is slightly greater than tetsahedral angle fully? And due to bulky alkyl group. Scanned by CamScanner

Alcohols and phenols # Breparation of Alcohols.  $\bigcirc$ from alkenes By acid Catalysed hydration.  $= C = + H_2 O =$ OH - OH  $CH_3 CH = CH_2 + H_2 O - H^+ + CH_3 - CH - CH_3$  $(\cdot)$ Mechanism STEP-1 Protonation ab alkene to form Carbocation be electrophillic attack of H30<sup>+</sup>.  $\begin{array}{ccc} H_{20} + H^{+} \longrightarrow H_{30} \bullet^{+} \\ \hline H \hline \hline H \\ \hline H \hline \hline H \\ \hline H \hline \hline$ STEP-2: Nucle ophillic attack of water On Carbocation. 

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STEP-3 Deprotonation to Josm an alcohol.  $-C - C - C - C - H + H_{2}^{\circ} - - C - C - C - H_{3}^{\circ} + H_{3}$ & By hydroboration Oxidation. From 1  $CH_3 - CH = CH_2 + (H - BH_2)_2 -$ -) CH3-CH2-CH2 CH2-CH = 912  $(H_3 - CH_2 - CH_2)_3 B \leftarrow (H_3 - CH_2 - CH_2 - CH_2)_3 B \leftarrow (H_3 - CH_2 - CH_2 - CH_2)_3 B \leftarrow (H_3 - CH_2 - CH_2 - CH_2)_3 B \leftarrow (H_3 - CH_2 - CH_2 - CH_2 - CH_2)_3 B \leftarrow (H_3 - CH_2 - CH_2 - CH_2 - CH_2)_3 B \leftarrow (H_3 - CH_2 - CH_2 - CH_2 - CH_2)_3 B \leftarrow (H_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2)_3 B \leftarrow (H_3 - CH_2 - CH_2$ - (CH3-CH2-CH2) BH 3H202, 8H H20 3 CH3-CH2-CH2-OH + B(OH)3 Propane - 1- cela  $3CH_3 - CH = CH_2 \xrightarrow{B_2H_6} 3CH_3 - CH_2 - CH_2 - OH + B(OH)_3$ OH-

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Jrom Corbonyl Compounds. Reduction of aldehyde and ketone. RCHO. +H2 Pd, RCH2OH ٢ RCOR' NaBHy R - CH - R'0 OH Aldehyde -> primary alcohols ketone -> Secondary alcohols NOTE By reduction of Corboxylic acid and ester. RCOOH (i) H20 RCH20H. (expansive) R COOH ROH RCOOR H2 RCH201+ + R'OH. e Grignand reagent From C = 0 + (R + Mg - X - Mg - X)> C - 0 Mg+-X Adduct <u> С-он + Мд (он) Х.</u> H20 DELTA®Notebook www.notesdrive

Date Page No. H C=0 + RMgX -> RCH2 OMgX Methonal. 0 H20 (OH)X. RCH2OH + Mg 1° al Cohal. - CH.-OMg X 0 20 H20. OH + Mg (OH)x R ¢ MgX R H20 OM > primary alcohol. > Secondary alcohol > tertiary alcohol. Methanal - aldehyde Ketone .notesdrive

Preparation of phenol OH -90m halogrenes ONat HU +NOOH Gask ; 300atm Sodium phenoxide 1 1 benzenesulphonic aud 7 1210m 3 So3H OF -Oleum, (1) NOOH 4 (ئٹ 1 Benzene Solphonic aud diazonium Salt D D N2 Q 0 3 NH2 0+ NaNOZ 1+20 +HU. Aniline Nitopus acid 1970m amene 413-4100 43 OH 02 Ht CH3 COC H, o gietone Cumene Umene Phend hydroperoxide amount ange

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Physical properties. # Boiling point. B.P. of alcohols and phenol. increase with. Increase in number of Corbon atoms. B.P. of alcohols decrease with increasing. in branching. As Vander Jurale Jorce decrease with decrease is Surface orea. Note: B.P. of alcohols and phenol higher in. Comparison to other class of compound. (Hydrocorbon). due to the presence of intermolecular hydrogen bonding. Solubility. -> Solubility. cop alcohol and phenol is in water is due to their ability to form hydragen. bond with water. -> Solubility decrease with increase in Size of alkyllaryl (hydrophobic) group.

# CHEMICAL REACTIONS · Alcohols are versatile compounds. They react as nucleophiles as well as electrophiles. NOTE: when alcohol react with as nucleophiles. bond bliv O-H is broken.  $R - O - H + C - \rightarrow R - O - C - + H^+$ (ii) when alcoh react as electrophiles.bond b/w C-O is broken.  $H - C - K - CH_2 - OH + H^+ \longrightarrow R - CH_2 - OH_2$  $\frac{12}{B8 + H - C - OH} \xrightarrow{\oplus} B8 - CH_2 + H_2O$  RReaction involving Cleavage of 0-H bond. 1 Acidity of alcohols and phenols. → Alcohol and phenol react with Metal Such as Sodium potassium and aluminium to yield alkoxide/phenoxide.

> 2R-O-Na + H. Sodium 2R-0-H+2Na- $(\cdot)$ alkoxide 413 6 CH3 - C-OH - 2 Al A1 +3H. 72  $(H_2 - C - O$ CH3 CH3 tert - Butyl alcohol. Alyminium tert - butoxide OH ONA +2Na H2 Sodium phenox de PTO ONA + NOOM H20 The above reaction Show that alcohol and phend are acidic in nature. www.notesdrive.co

Alcohol and phendl are Bronsted acid. i.e. they can donate a proton to a Strong. base. . B: + H-O-R → B-H + :O-R Base (onjugate Conjugate acid base Acidity of phenol & alcohol: It is due to the O-H bond. Presence of e donating group. (-CH3 - C2H5) increase e density on Oxygen. Vesult in decreasing the polarity of OH bond. Hence, decrease the acid Strength.  $R \rightarrow (H_2 OH) \qquad R \rightarrow (HOH) \qquad R \rightarrow (C-OH) \qquad R \rightarrow (H_2 OH) \qquad R \rightarrow (HOH) \qquad R \rightarrow (C-OH) \qquad R \rightarrow (HOH) \qquad (HOH) \qquad$ 2° 3° Alcohols are weaker acid than water  $R - \dot{0} + H - \dot{0} - H -$ > R-O-H + OH Conjugate Conjugate acid. base Alcohol act as Bronstead base as well due . to the presence of Unshaired paired e- on Oxygen which make them proton acceptor. v.notes Scanned by CamScanner

Heidity of phenols. Hydroxy group is clivetly attached to Sp<sup>2</sup>hybridises Carbon of benzene ring and act as eullet-> Due to charge distribution and its resonance Structure Cause Oxygen of OH group to be Dositive positive. ÷Ö The R<sup>n</sup> of phenol with a NaOH indicate that phenol are Strong acid than alcohol and water • Ionisation of an alkoh alcahol and phenol take place as Jallow  $R - O - H \implies R - O + H^+$ OH A Due to highen electronegativity of Sp<sup>2</sup> & hybridised Corbon of phenol to which - on is attached, electron density dect. On Oxygen and incr. The populty of 0-H bond and increase ionisation in phend that of DELTA Notebook www.notesdrive.co

Page No.\_\_\_\_ alcahal. → The pseisence of C withdrawing group Such as Nitro group increase the acidic Strength of phenol. This effect is more pronounced when Such a group is present at Ortho and para positions. (1,2) (1,4) Presence of c<sup>-</sup> donating group Such as cilkyl group. decrease the acidic Strength of phenol. # Esterification. Alcohal and phenol Teact with Carboxylic acid acid chloride and acid onhydrides to form ester AXR-OH + R'- COOH + H+ AX ROCOR + H2O Conc. H2 Soy  $CH_3OH + C_2H_5COOH \xrightarrow{H^+} CH_3OCOC_2H_5 + H_2O$ Ar R-OH + (R'CO)20 = ARROLOR' + R'COOM  $C_{H_{5}OH} + (CH_{3}C_{0})_{2}O \xrightarrow{H^{+}} C_{2}H_{5}OCOCH_{3} + CH_{3}COOH$ OR/Aron + R'Cod - Ryridine RIArdor + Ma DELTA® Notebook www.notesdrive.cor Scanned by CamScanner

Acetylation ob Salicylic acid. • Introduction of acetyl (CH3 (0) group in alcohal and phenol is known as acetylation.  $\bigcirc \rightarrow$ LOOH  $\frac{1}{1} + (CH_{3}C_{0}) - \frac{H^{+}}{2} + CH_{3}C_{0}OH$ Salicylic acid (Aspinin) Reaction involving Cleavage of C-0 bond in alcahols. i] Reaction with hydrogen halides:  $ROH + RX \longrightarrow R-X + H_2$ Reactivity of three class of alcohol with Hel distinguishes from Lucas test Lucas Reagent (Conc. Hill and Zollz 3 alcohol -> turbidity produce immediately 2° alcohol -> Take Some time. 1° alcohol -> do not produce turbidity.

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Dehydration Closs of water] (H+) Z Z = C + H  $\begin{array}{c} C - C - \\ I & I \\ H & OH \end{array}$ H2 Soy / 43 Po3  $OH \xrightarrow{H_2So_4} CH_2 = CH_2 + H_2O$ C2 H5  $\odot$ CH3-CH-CH3 85.1. H3P03 (H3-CH= 2 440 K  $\odot$ CH (. Tertiary > Secondary > Primary Mechanism Formation of protonated allahal OSTEP1 - H-C-C-0+- $\frac{H-c-c-\tilde{o}-H+H^+}{I} =$ Restonated alcohol (Ethyl Oxonnun

STEP 2: Formation of Carbocation: It is Slowest Step and hence the bate determining Step of reaction. 4 4 4 STEP3: Formation of ethere by elimination of m  $H = C = C + H^{+}$   $H = C = C + H^{+}$ 61 The acid used in Step 1 released & in Step 3. Oxidation: involve the formation of Carbon Orygen double bond with cleavage of an O-H and C-H bond. 1 S  $H_{+}C_{+}O-H \rightarrow C=0$ also known as dehydrogenation reaction as loos

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RCH, OH - Oxidation, R-C=O -> R-C=O acidic KMnoy RCH20H CrO3 RCHO 0 O CH3-CH=CH-CH2OH PCC CH3-CH-CHO Pyridinium chlosochromate  $\overline{\bullet}$  $\frac{R-CH-R'}{12^{\circ}} \xrightarrow{(-803)} \frac{R-C-R'}{11}$ NOTE: 3° Alcohal do not Undergo Oxidation Ower heated in at 573 k. then RCH,OH 573K RCHO  $\frac{R-CH-R'}{I} \xrightarrow{C_{4}} \frac{C_{4}}{573k} \xrightarrow{R-C-R'} \frac{R-C-R'}{1}$ DELTA®Notebook w.notesdrive

# Reactions of Phenols 1. Electrophilic aromatic Substitution. The or group attached to beizene my activates it toward electrophilic Substitution. Also it direct the incoming group to or the and para possition in ring as these position become electric rich due to resonance effect • Caused by -OH group Nitration OM -NO2 Dil. HNO: P-Nitrophenal. O. Nitrophenal -> O-Nitrophenal is Steam Valatile due to intramoleul--an hydrogen bonding 0=N-0--> p-nitrophenol is less volatile due to intermolecular hydrogen banding which cause the association of molecule www.notesdrive.

OH OH Conc. HNO3 No. NOZ NO2 2, 4, 6 - Trinitophenal (picone acid The yield of reaction product is poor. Nousdays, OH OH DH No2 SozH Conc. HNG Con. H2Soy SO3M Halogenations: Treating phenol with brom different product are formed under different Condition. OH Bog in Csz B-6 273K Solvent of Br low polouity. Mai monopromophenal • Halogenation of benzene take place in presence of Lewis acid Such as Fe Brz, which polarise halogen molecule In Case of phenal polarisation of bromine molecule take place in absence of lewis acid due to highly activating DELTA Notebook

OH OH BX - 3 Bro, 8 2 Kolbe's Seaction OH OH ONa LOOM Naoh (i) (02 (ii) H Ht TI 17 No. YTT 2 - Hydroxy benzoic aud 10 Salicylic and a la T Convert phenol into Aspinir 1 LOOM OH 20 (001/2 0 0 NaOH 5 ona DH LOOM (1) (02 11 4+ 1 0 0 C 1

Reimen - Tiemann Reaction ONO DH ONA CHO CH(l2 Vapt CHCB+ benzal chlonde Salicylaldeby de 4 Reaction of phenol with Zinc dust. OH Zn + Zm0 Oxidation. 5. Na260207 benzo guinone

# COMMERCIALLY IMPORTANT ALCOHOLS 1. Methand. → Josmula - CH30H → produce by destructive distillation of wood Today, Methanal is produce by Catalytic hydrogenation of CO at high pressure and temprature in presence Zno-Cr203 (atalyst (0 + 2H2 200-(8,03> (H30H. 200-300 atm 573-673K → It is a Colourless liquid and boil at 337K → poisnous in nature → Used as Solvent in paints, Varnishes and for making Josmaldehyde. 2. Ethanol. [C2H50H] ~ Commercially produce by Fermentation of Sugar. C12 H22 O11 + H20 invertase > C6H12O6 + C6H12O6 JZymase 2C2H50M+CO2 -> It is a colouriers and boil at 351 K. Used as Solvent in point industury. Commercially alcohol made Unfit for drively by adding Cysoy and pyridine. It DELTA® Notebook www.notesdrive.c

Date Page No.\_ ETHERS 11 Preparation of ether. by dehydration of alcahol. Alcohale Undergo dehydration in presence of pratic acid [H2Son H3Poy]. reaction product depend on reaction Condition. 3  $\frac{H_2Soy}{443} \leftarrow (H_2 = CH_2)$  (ethene)CH3CH, OH H2 Sou C2H5OC2H5 413 K Lethoxy estethene Formation of ether is (SN2) reaction involving the attack of alcohol on a protonated alcohol.  $( \cdot )$  $(H_3 - CH_2 - 0 + H + H^+ - + CH_3 - CH_2 - 0 - H)$  $CH_3 CH_2 - 0; + CH_3 - CH_3 CH_2 - 0 - CH_3 CH_2 - 0 - CH_2 CH_3 + h_2$ [iii] CH3CH2-0-CH2CH5 - CH3CH2-0-CH2CH2 + H+ etter ether www.notesdrive Scanned by CamScanner

The method is Suitable you preparation of ethers having primary alkyl groups only. The reaction follow SN1 pathway when the alcohol 2° or 3°. O dehydration of Secondary and tertiary alcahols
to give ethers is unsuccesful. and alkenes
are easily Josmed. Williamson Synthesis O In this method an alkyl hallde is allowed to react with Sodium alkoxide.  $R - X + R - O'Na \longrightarrow R - O - R' + NaX$ Ethers containing Substituted alkyl group (3 or 2°) also & prepared by this method. (•) Better result are obtained if alkyl halide is primary In case offer 2° or 3° alkyl halide elimination competers Over Substitution

 $H_3 - C - B_X + NaO - CH_3 \longrightarrow CH_3 - C = CH_2 + NaBx + CH_3OH$ → It is because alkoxide are also strong base as well. They react with alkyl halide leading to elimination R<sup>n</sup>. Phenol are also converted into ether. iOH iOH iOH  $+N_{0}OH$   $+N_{0}O$ Physical properties B.P. of ethers are Comparable of alkene having Comparable molecular mass but less than that to of alcahol. 0) The miscibility of ether with water sesembless those of alcohol of Same molecular mass, due to the presence of Oxygen in ether- which (an also Joom hydrogen bonding with water,

# CHEMICAL REACTION. 1. Cleavage of C-0 bond in ethers. Reaction of dialkyl etter etter give two molecules alkyl halide when react with Excess of hydrogen halide.  $R \rightarrow -R \rightarrow R \times + R \rightarrow R \times + R \rightarrow OH$ R-OH + MX -> R-X+H20 5 + H-x  $\rightarrow$  () + R-x  $R - o - R' + H \times \longrightarrow R - \chi + R' - OH$ orden of reactivity of hydrogen halide HISHBY SHOL Cleanage of ether take place with Conc. HIOS HBS at high tempsature. Mechanism 1.  $(H_3 - 0 - (H_1, CH_3 + H - 1) = (H_3 - 0^{+} - (H_1, CH_3 + 1))$ 2.  $T + CH_3 - O' - CH_2(H_3 \rightarrow T - CH_3 - O - CH_2(H_3 \rightarrow CH_3 - T)$ + CH2CH-OH

3.  $(H_3(H_2 - 0 - H + H - I) \longrightarrow (H_3(H_2 - 0 + + I))$   $I + (H_2 - 0 + 2) \longrightarrow (H_3(H_2 I + H_2 0))$  $\bigcirc \begin{array}{c} (H_2 & H_3 \\ (H_3 - C - \rho - H_3 + HI \longrightarrow (H_3 OH + CH_3 - C - I \\ H_3 & H_3 \\ (H_3 - C - \rho - H_3 + HI \longrightarrow (H_3 OH + CH_3 - C - I \\ H_3 & H_3 \\ (H_3 - C - \rho - H_3 + HI \longrightarrow (H_3 OH + CH_3 - C - I \\ H_3 & H_3 \\ (H_3 - C - \rho - H_3 + HI \longrightarrow (H_3 OH + CH_3 - C - I \\ H_3 & H_3 \\ (H_3 - C - \rho - H_3 + HI \longrightarrow (H_3 OH + CH_3 - C - I \\ H_3 & H_3 \\ (H_3 - C - \rho - H_3 + HI \longrightarrow (H_3 OH + CH_3 - C - I \\ H_3 & H_3 \\ (H_3 - C - \rho - H_3 + HI \longrightarrow (H_3 OH + CH_3 - C - I \\ H_3 & H_3 \\ (H_3 - C - \rho - H_3 + HI \longrightarrow (H_3 OH + CH_3 - C - I \\ H_3 & H_3 \\ (H_3 - C - \rho - H_3 + HI \longrightarrow (H_3 OH + CH_3 - C - I \\ H_3 & H_3 \\ (H_3 - C - \rho - H_3 + HI \longrightarrow (H_3 OH + CH_3 - C - I \\ H_3 & H_3 \\ (H_3 - C - P - H_3 + HI \longrightarrow (H_3 OH + CH_3 - C - I \\ H_3 & H_3 \\ (H_3 - C - P - H_3 + HI \longrightarrow (H_3 - C - I \\ H_3 & H_3 \\ (H_3 - C - P - H_3 + HI \longrightarrow (H_3 - C - I \\ H_3 & H_3 \\ (H_3 - C - I \\ H_3 & H_3 \\ (H_3 - C - I \\ H_3 & H_3 \\ (H_3 - C - I \\ H_3 & H_3 \\ (H_3 - C - I \\ H_3 & H_3 \\ (H_3 - C - I \\ H_3 & H_3 \\ (H_3 - C - I \\ H_3 & H_3 \\ (H_3 - C - I \\ (H_3 - C - I \\ H_3 & H_3 \\ (H_3 - C - I \\ (H_3 - C - I \\ H_3 & H_3 \\ (H_3 - C - I \\ (H_3 - I \\ (H_3$ Mechanism  $(H_3 - C - O - (H_3 - C + C + C + 3 O H_3 - C + C + C + 3 O H_3 - C + C + C + 3 O H_3 O H_3 - C + C + C + 3 O H_3 O H_$  $\begin{array}{c} (\mathcal{H}_{3} \\ \mathcal{H}_{3}-\dot{c}^{+} + \overline{L} \\ 1 \end{array} \xrightarrow{(\mathcal{H}_{3}} \mathcal{H}_{3} - \dot{c}^{-} \overline{L} \\ 1 \end{array}$ +0-413 + ]= + HI  $\longrightarrow$ 0 + CH2T -> The bond blue O-CH3 is weaken the the bond blue O-C, H5 because Carbon of phenyl group is Sp<sup>2</sup> hybridised and thre is a partial double bond 1 Character

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Electrophilic Substitution. The alkoxy group (-OR) is Ortho and para. directing. (•) Halugenation : phenylalkyl ethers undergo halogenation in benzene ning. OCH3 OC • BX Brz in 9 Anisole 90% 0% 1- Bromoanisole Friedal Craft Treaction O Anisole Undergoes friedal - Craft reaction i.e alkyland acyl group are introduced at Ortho and para possition. With alkyl halide and acyl halide. Out 3 9(4)2 QCH3 at3 Anhyd. Aldz + CH3C 2-Methoxy toluene CH 4 - methoxy tolyene. www.notesdrive.

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)	pcH3	OCH3	1
)		- 60	(413
)	[] + CH3 cocl	Anhyd. Allz,	+
}	511		CocH3
)	E thanoyf Chloride	7-Mattoxy	4 - methoxy
}	Chloride	2-Methoxy acetophenone	4 - methoxy O acetophenome
3		queiophenore	
3			
Y	NPL / J		
Jul	Nitration: OCH3	0413	0413
3		No,	
3	H2SO4	F 1002 +	
3	HNO3		
3			Noz
		2-Nitroanisole	1002
2		KIVI BOANSOLC	4-nitsoanisole
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