ABC-3 (Alkyl halide, Alcohol & Ether)

(A) **ALKYL HALIDE** Preparation of alkyl halides (5-Methods)

1.	From alcohol	
	(i) from (SOCl ₂) in presence of pyridine	$CH_3-CH_2-OH \xrightarrow{SOCl_2} CH_3-CH_2-CI + SO_2 + HCI$
	$\xrightarrow{\text{SOCI}_2}$	Ethanol Pyridine Chloroethane By products
	R–OH heat, pyridine R–CI + SO ₂ + HCI	are gases
	It is known as Darzon method.	
	(ii) from PCI₅	$CH_3-CH-OH+PCI_5 \longrightarrow CH_3-CH-CI+HCI+POCI_3$
	$R-OH + PCI_5 \longrightarrow R-CI + HCI + POCI_3$	ĊH ₃ ĊH ₃
		Propan-2-ol 2-Chloropropane
	(iii) from PX ₃	
	$2P \cap H : PX_{3} \xrightarrow{(PX_{3} = PCI_{3}, PBr_{3}, PI_{3})} 2P$	$3CH_3-CH_2-OH+PCI_3 \rightarrow 3CH_3-CH_2-CI+H_3PO_3$
	$3R - OH + F \wedge 3$ $3R - OH + F \wedge 3$	Ethanol Chloroethane
	(iv) Lucas test : from HX(X= Cl. Br.I)	
	$P O H + H X ZnCl_2 > P X + H O$	$ + HCl \xrightarrow{ZnCl_2} + H_2O $
	$R = O \Pi + \Pi A \xrightarrow{} R = A + \Pi_2 O$ (rate : 30 POH > 20 POH > 10 POH)	
2	Halogenation of alkane	
۷.	Halogenation take place either at high	$CH_4 + CI_2 \longrightarrow CH_3CI + HCI$ Methane Chloromethane
	temperature (573-773 K) or in the presence	ÇI
	of diffuse sunlight or ultraviolet light.	
	Rate of reaction of alkanes with halogens :	$+ Cl_2 \longrightarrow$ + HCl
	$F_2 > CI_2 > Br_2 > I_2$	
3	Addition of hydrogen balides	$CH_2 = CH_2 + HBr \longrightarrow CH_2CH_2Br$
5.	Hydrogen balides add up to alkenes to form	Ethene Bromoethane
	alkyl halides. The order of reactivity of	ÇI
	hydrogen halides is HI > HBr > HCl.	$CH_3-C=CH_2 + HCI \longrightarrow CH_3-C-CH_3$
	, <u>-</u>	
		2-Methylprop-1-ene 2-Chloro-2-methylpropane
4.	Finkelstein reaction	Ĥ Ĥ
	Alkyl iodides often prepared by the reaction	
	of alkyl chloride / bromide with Nal in dry	$C\Pi_3 = C = C\Pi_3 + NaCI $
	acetone. This reaction is known as	ĊI
	Finkelstein reaction.	2-Chloropropane 2-Iodopropane
		Br I Not dry acetone
		1-Bromocyclohexane 1-lodocyclohexane
5.	Swart reaction	CH_3 CI + AaF $\xrightarrow{\Delta}$ CH $_3$ F + AaCl
	The synthesis of alkyl fluoride is best	Chloromethane Fluoromethane
	accomplised by heating an alkyl chloride/	ÇI
	bromide in the presence of a metallic fluoride	CH_{2} $-CH_{2}$ $-CH_{2}$ $+$ AgF \rightarrow
	such as AgF, Hg ₂ F ₂ , CoF ₂ or SbF ₃ .	2-Chlorobutane
	The reaction is termed as Swart reaction.	
		F ^{2-Fluorobutane}

Chemical reactions of alkyl halide (4-Reactions)

1.	Reaction of alkyl halide with (a) KCN KCN is predominantly ionic and provides cyanide ions in solution. Although both carbon and nitrogen atoms are in a position to donate electron pairs, the attack takes place mainly through carbon atom and not through nitrogen atom since C–C bond is more stable than C–N bond.	$\begin{array}{c} H\\ CH_{3}-CH-CH_{3}+KCN \longrightarrow CH_{3}-C-CH_{3}+KCI\\ \downarrow\\ CI\\ 2^{-Chloropropane}\\ & 2^{-Methylpropanenitrile}\\ \hline\\ & & & & & \\ \end{array}$		
	AgCN is mainly covalent in nature and nitrogen is free to donate electron pair forming isocyanide as the main product.	Methylchloride Methylisocyanide CH_3 — CH — CH_3 + $AgCN$ \rightarrow CH_3 — C — CH_3 + $AgCI$ CI 2-Chloropropane V		
	(c) KNO ₂ Alkyl halides (R–X) react with KNO ₂ to give R–O–N=O (Alkylnitrite).	$\begin{array}{c} H \\ CH_{3}-CH-CH_{3}+KNO_{2} \longrightarrow CH_{3}-C-CH_{3}+KCI \\ CI \\ Iso-propylchloride \\ \hline \\ Fr \\ Cyclohexylbromide \\ \hline \\ Cyclohexylbromide \\ \hline \\ Cyclohexylnitrite \\ \hline \\ Cyclohexylnitrite \\ \hline \\ \hline \\ Cyclohexylnitrite \\ \hline \\ \hline \\ Cyclohexylnitrite \\ \hline \\ \hline \\ \hline \\ Cyclohexylnitrite \\ \hline \\ $		
	(d) AgNO ₂ Alkyl halides (R–X) react with AgNO ₂ to give R–NO ₂ (Nitroalkane)	$CH_{3} - CI + AgNO_{2} \rightarrow CH_{3}NO_{2} + AgCI$ $Chloromethane \qquad Nitromethane$ $CH_{3} - CH_{2} - CH_{2} - CI + AgNO_{2}$ $1 - Clorobutane$ $\rightarrow CH_{3} - CH_{2} - CH_{2} - CH_{2} - NO_{2} + AgCI$ $1 - Nitrobutane$		
	(e) Aqueous KOH Alkyl halides (R–X) when reacts with aq. KOH gives alcohol	$CH_{3}-CH_{2}-CI + aq. KOH \longrightarrow CH_{3}-CH_{2}-OH + KCI$ $Chloro ethane Ethanol H I I$ $CH_{3}-C-CH_{3} + KOH(aq.) \longrightarrow CH_{3}-C-CH_{3} + KCI$ $I OH$ $2-Chloropropane Propan-2-ol$		
2.	Wurtz reaction Alkyl halide on treatment with sodium metal in dry ether solution give higher alkanes. The reaction is known as Wurtz reaction. It is used for the preparation of higher alkanes containing even number of carbon atoms.	$\begin{array}{c} CH_{3}-Br+2Na+Br-CH_{3} \xrightarrow{ary \ etner}} CH_{3}-CH_{3}+2NaBr\\ Bromomethane & Ethane \\ CH_{3} & CH_{3} \\ CH_{3}-C-Br+2Na+Br-C-CH_{3} \\ H & H \\ 2-Bromopropane \\ CH_{3} & CH_{3} \\ dry \ ether \\ CH_{3}-C -C-CH_{3}+2NaBr \\ H & H \\ 2,2-Dimethyl \ butane \end{array}$		

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3.	Wurtz-Fittig reaction A mixture of an alkyl halide and aryl halide give an alkyl arene when treated with sodium in dry ether.	$Br \\ + 2Na + Br \\ -CH_3 \\ + 2NaBr \\ Methylbenzene \\ Methylbenzene \\ Br \\ + 2Na + \\ Br \\ - \\ Cyclohexylbenzene \\ Cyclohexylbenzene \\ - \\ Cycloh$
4.	Williamson ether synthesis	$\begin{array}{c} CH_{3}CI + CH_{3}O^{-}K^{+} \longrightarrow CH_{3} - O - CH_{3} + KCI \\ Methyl Potassium Dimethyl \\ chloride methoxide ether \end{array}$



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	It is anti addition. Both OH groups add on the opposite side of pi-bond. Peroxyacid may be any one of these: a. m-CPBA (Metachloro perbenzoic acid) b. PAA (Peracetic acid) c. PBA (Per benzoic acid)	
	d. TFPAA (Trifluoro peracetic acid).	
4.	Acid catalyzed hydration of alkene Reagents: dil. H ₂ SO ₄ or H ₂ O/H ⁺ or H ₃ O ⁺	$CH_{3}-CH=CH_{2}+H_{2}O \xrightarrow{H^{\oplus}} CH_{3}-CH-CH_{3}$
	$C = C \qquad \underbrace{H_2O/H^{\oplus}}_{H = 0H} H = OH$	(a) CH_3 -CH=CH-CH ₃ $\xrightarrow{H_2O/H^{\oplus}}$ CH ₃ -CH-CH-CH ₃ (b) H OH
	Remarks: Markovnikov's addition	(b)

Preparation of ethers (2-Methods)

1.	Williamson synthesis It is an important laboratory method for the preparation of symmetrical and unsymmetrical ethers. In this method, an alkyl halide is allowed to react with sodium alkoxide. $RX + R'O - Na \longrightarrow R' - O - R + NaX$	(a) $CH_3-X + CH_3-CH_2-CH_2O-Na \longrightarrow CH_3-O-CH_2CH_2CH_3$ (b) $CH_3CH_2-X + PhO-Na \longrightarrow Ph-O-CH_2-CH_3$ (c) $Ph-CH_2-X + Ph-CH_2-O-Na \longrightarrow PhCH_2-O-CH_2-Ph$
2.	From alcohol Alcohols undergo dehydration in the presence of protic acids (H ₂ SO ₄ , H ₃ PO ₄) at 413 K temperature (140°C). $\xrightarrow{H_2SO_4}$ R-OH $\xrightarrow{413 \text{ K}}$ R-O-R Remark : Alcohols undergo dehydration by heating with conc. H ₂ SO ₄ at 443K and give alkene.	$\begin{array}{c} CH_{3}-CH_{2}-OH \xrightarrow{H_{2}SO_{4}} C_{2}H_{5}-O-C_{2}H_{5} \\ (a) \\ CH_{3}-OH + CH_{3}OH \xrightarrow{H_{2}SO_{4}} CH_{3}-O-CH_{3} \\ (b) \\ (c) \\ CH_{3}-OH + CH_{3}-CH_{2}-OH \xrightarrow{H_{2}SO_{4}} CH_{3}-O-CH_{3} \\ + CH_{3}-CH_{2}-O-CH_{2}-CH_{3} + CH_{3}-O-CH_{2}-CH_{3} \end{array}$

Chemical reactions of alcohols (5-Reactions)

1.	Reaction with HX: $R-OH + HX \longrightarrow R-X + H_2O$ The reactions of primary and secondary alcohols with HCI require a catalyst (ZnCl ₂). With tertiary alcohols, the reaction conduct by simply shaking with concentrated HCI at room temperature.	(a) $CH_3-CH_2-OH \xrightarrow{HBr} CH_3-CH_2-Br$ $CH_3-CH-OH \xrightarrow{HCl}{ZnCl_2} CH_3-CH-Cl$ (b) $CH_3 \xrightarrow{CH-OH} CH_3$
2.	Reaction with phosphorus trihalides: 3R–OH + PX ₃ → 3R–X + H ₃ PO ₃ PX ₃ = PCl ₃ , PBr ₃ , Pl ₃	(a) $CH_3-CH_2-CH_2-OH \xrightarrow{PBr_3} CH_3-CH_2-CH_2-Br$ $CH_3 \qquad \qquad$
3.	Reaction with PCI₅	
	$R-OH + PCI_5 \longrightarrow R-CI + HCI + POCI_3$	(a) ^{PhCH} 2 [−] OH ⁺ OH ⁺ OF PhCH ₂ Cl + POCl ₃

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* 2° and 3° alcohols generally give alkene at little less temperature than required for 1° alcohols.

Test of alcohols (3-Test)

S.No	Test / Reagent	Observation				
1	Cerric ammonium nitrate test	Red colour compound is formed				
	Reagent : [(NH ₄) ₂ Ce(NO ₃) ₆]					
2	Lucas reagent Reagent : [Conc. HCI + anhyd. ZnCl ₂] Remarks : It gives white turbidity or cloudiness with alcohols (OH groups attached with sp ₃ hybridised carbon).	 (a) 1° alcohol does not give appreciable reaction. White turbidity is obtained on heating in 30 minutes. (b) 2° alcohol gives white turbidity in 5 minutes. (c) 3° alcohol gives white turbidity immediately. 				
3	Victor Mayer test Reagent : (i) P + I ₂ (ii) AgNO ₂ (iii) HNO ₂ (iv) Base	 (a) 1° alcohol – Blood red colour. (b) 2° alcohol – Blue colour. (c) 3° alcohol – No colour. 				

Exercise

ONLY ONE OPTION CORRECT TYPE

PART-A (Alkyl halides)











36.	Predict the reagent for the following reaction:					
	Ph–CH	$_2-OH \longrightarrow Ph-CH_2-O-$	-CH2–Ph			
	(A) dil. H ₂ SO ₄	(B) KMnO4	(C) LiAlH ₄	(D) conc. H ₂ SO ₄ / 140°C		
37.	Which alcohol gives ins	tant turbidity with Lucas	reagent?			
		CH ₃ –CH–CH ₃	CH ₃ –Ċ–CH ₃			
	(A) CH ₃ –CH ₂ –OH	(В) ОН	(C) OH	(D) CH ₃ CH ₂ CH ₂ OH		
38.	Which alcohol give whit	e turbidity in 5 minutes w	vith Lucas reagent?			
			Ph I			
			Ph–Ċ–CH₃			
	(A) CH3–CH2–OH		(B) OH			
			ÇH₃			
	CH ₃ –CH–CH ₂ –CH ₃		CH₃–Ċ–CH₃			
	(C) OH		(D) OH			
39.	Which test is used to di	stinguish 1°, 2°, and 3° a	llcohols?			
	(A) Victor Mayer test		(B) lodoform test			
			(D) Bayer's test			
40.	Which test is not given	by alcohols?	(B) Neutral FeCla Test			
	(C) Victor major test		(D) Cerric ammonium n	itrate test		

	Answ								
1.	(A)	2.	(A)	3.	(B)	4.	(A)	5.	(B)
6.	(B)	7.	(D)	8.	(A)	9.	(C)	10.	(C)
11.	(B)	12.	(A)	13.	(B)	14.	(D)	15.	(C)
16.	(A)	17.	(B)	18.	(C)	19.	(A)	20.	(A)
21.	(C)	22.	(B)	23.	(C)	24.	(A)	25.	(A)
26.	(B)	27.	(C)	28.	(D)	29.	(B)	30.	(B)
31.	(B)	32.	(A)	33.	(B)	34.	(C)	35.	(C)
36.	(D)	37.	(C)	38.	(C)	39.	(A)	40.	(B)