CHEMISTRY XII (Headway Batch)

Practice Aid

Important Reactions & Reagents in Organic Chemistry

REAGENTS:

I - Oxidising Agents

(1) $KMnO_4$ or $K_2Cr_2O_7$

1° Alcohol	\longrightarrow	Acid
1° Alcohol	\longrightarrow	Acid

 2° Alcohol — Ketone

Alkene :
$$\underset{R}{\overset{R}{\triangleright}} C = C \underset{R'}{\overset{H}{\longleftarrow}} R_2 C = O + R'COOH$$

Alkyne: $R-C\equiv C-R' \longrightarrow RCOOH + R'COOH$

Oxidation of aromatic side chain:

$$(CH_2)_n$$
- CH_3 $COOH$ \longrightarrow \bigcirc

(2) CrO₃/H⁺/Pyridine (PCC)

(Pyridinium chloro chromate)

1° ROH — → Aldehyde

2° ROH — → Ketone

3° ROH ----- No reaction

(3) HIO₄ (Periodic Acid)

Condition : Vicinal diol, α - Hydroxy ketone, α -diketone & α -hydoxyacid can oxidise by HIO₄

$$-C$$
—OH \longrightarrow 2 $-C$ =O

$$-C=0$$
 $-C=0$ \longrightarrow 2 -COOH

(4) Cu/573 K

3° Alcohol → Alkene

(5) Al[OCMe₃]₃/in Acetone

(Oppeneur oxidation)

2° Alcohol ------- Ketone

(6) Baeyer's reagent or OsO₄ + NaHSO₃

stereospecific syn addition

$$-C \equiv C - \longrightarrow - \stackrel{O}{\longleftarrow} \stackrel{O}{\longleftarrow} \stackrel{O}{\longleftarrow}$$

(7) Baeyer-Villiger oxidation

(MCPBA or CH₃CO₃H)

Priority of shift (O accepting aptitude)

 $R' = H > Ph > 3^{\circ} > 2^{\circ} > 1^{\circ} > Me$

(8) Prilezhaev reaction

$$-\overset{1}{C} = \overset{1}{C} - \xrightarrow{\text{MCPBA}} -\overset{1}{C} -\overset{1}{C} -\overset{1}{C}$$

II - Reducing Agents

(1) LiAIH,

$$R-C-OR' \longrightarrow RCH_2OH + R'OH$$

$$\bigcirc \longrightarrow \bigcirc_{\mathsf{O}^{\mathsf{H}}}$$

$$\begin{array}{c} \mathsf{R}\text{-}\mathsf{C}\text{-}\mathsf{C}\mathsf{I} \\ \mathsf{II} \\ \mathsf{O} \end{array} \longrightarrow \mathsf{R}\text{-}\mathsf{C}\mathsf{H}_{\scriptscriptstyle{2}}\mathsf{O}\mathsf{H}$$

 $C = C / C \equiv C \longrightarrow No reaction$

Exception

Ph-CH=CH-COOH -----> Ph-CH,-CH,-CH,OH

(2) NaBH, EtOH

Aldehyde ______ 1° Alcohol

Ketone _____ 2 °Alcohol

Acid halide ______ 1° Alcohol

(3) Na/EtOH

Aldehyde → 1° Alcohol

Ketone ---- 2º Alcohol

Acid halide → 1° Alcohol

RCN ----- RCH₂NH₂

(4) Na-Hg/HCI or AI[OCHMe₂]₃ (MPV Reduction)

(5) Birch reduction (Li/Na/K + Liquid NH₃)

$$R-C=C-R \longrightarrow R C=C \stackrel{H}{\longrightarrow} C=C \stackrel{H}{\searrow} (trans alkene)$$

$$\bigcup \longrightarrow \bigcup$$

Terminal alkynes not reduced

(6) Rossenmund's Reduction

$$\begin{array}{c} R-C-CI & \xrightarrow{H_2/Pd/BaSO_4} & R-CH=O \\ \parallel & & \\ O & & \end{array}$$

(7) Stephen's Reduction

$$R-C \equiv N \xrightarrow{(1) SnCl_2/HCl} R-CH = O$$

DIBAL-H used for same function

(8) Clemmensen Reduction

$$C = O$$
(Keto)
 CH_2
(alkane)

Avoid if acid sensitive groups are present in molecule. e.g. C=C,C=C,OH, OR, CN

(9) Wolff-Kishner Reduction

$$C = O \xrightarrow{NH_2-NH_2/KOH/\Delta} CH_2$$
((Keto) (alkane)

Avoid if base sensitive groups are present in molecule. e.g.COOR,COX,CONH₂, -CO-O-CO-,CN,X

(10) Lindlar Catalyst

$$R-C = C-R \xrightarrow{H_2/Pd/CaCO_3/} \xrightarrow{R} C = C \xrightarrow{R}$$

Syn addition (Cis alkene)

(11) Red Phosphorus and HI

All functional group contaning compounds converts into corresponding alkane by red P + HI.

- R-CH₂OH → R CH₃
- R-CHO → R CH,
- R₂CO → R₂CH₂ (Alkane)

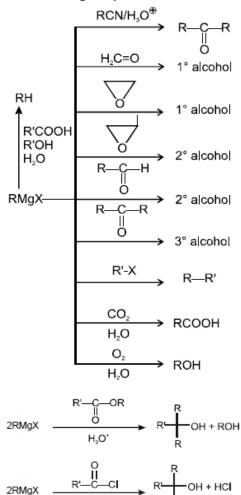
III-HYDROLYSIS

Functional	Reactant	Products	Reagent /	Remark
Groups			Catalyst	
Organometallic	R—Mg—Br	R—H	H ₂ O	
Compound	5			
	R——Li			
Acid Halides	R	R OH + HCI	Basic	
Acid Anhydrides	$R \longrightarrow 0$ R^1	R OH HO R'	Acidic or basic	
Acetals	>c	C=O + ROH		
Nitriles/Cyanides	R—— c = N	RC + NH ₃	Acidic	
Esters	R^1 O R	R^{1} O H H O R	Acidic or basic	
Isonitriles/isocyanides	R—N ≠ C	R—NH ₂ + HO	Acidic	
Amides Amides and N- substituted	R ¹ NH R	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Strong Acidic	
Alkyl Halides	R——CI	R	Basic	
Ethers	R R	R + H R R	Strong acidic HI	

IV - General Reagents

(1) Grignard's Reagent: RMgX (alkyl magnesium halide)

*Active – H Containing compounds \xrightarrow{RMgX} R – H



(2) Decarboxylation reagents :

(I) Soda lime d-carboxylation (NaOH / CaO / Δ) decarboxylates all types of carboxylic acids

(II) β-keto acid and 1, 1-dicarboxylic acids decarboxylate only on heating

(3) P₂O₅: (Phosphorous pentaoxide) or Al₂O₃ (Alumina) : Dehydrating Agent

- 2CH₃COOH <u>dehydration</u> (CH₃CO)₂O
- CH₃CONH₂ dehydration CH₃CN
- $\bullet \operatorname{C_2H_5OH} \xrightarrow{\quad \text{dehydration} \quad} \operatorname{CH_2=CH_2}$

(4) Diazonium salt
$$\begin{bmatrix} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & &$$

(5) PCI₅: (Phosphorous pentachloride) :

•R-OH
$$\longrightarrow$$
 R-CI; •R-COOH \longrightarrow R-COCI; •R-CONH₂ \longrightarrow R-C \equiv N
• R-CONH₂ \longrightarrow R-C \equiv N

- (6) Silver (Ag) metal:
 - $2CHI_3 + 6Ag \longrightarrow HC \equiv CH + 6AgI$

•
$$CH_2 = CH_2 + \frac{1}{2} O_2 \xrightarrow{Ag} CH_2 CH_2$$

(7) Zinc (Zn) metal:

$$\bullet \operatorname{C_6H_5OH} \xrightarrow{\operatorname{Zn},\Delta} \operatorname{C_6H_6} + \operatorname{ZnO} \quad ; \qquad \bullet \operatorname{2RX} \xrightarrow{\operatorname{Zn}} \operatorname{R} - \operatorname{R} \left(\operatorname{alkane} \right) + \operatorname{ZnX}_2$$

(8) Sodium (Na) metal:

• 2RX
$$\xrightarrow{\text{Na/dryether}}$$
 R - R (alkane) + 2NaX ; • ROH $\xrightarrow{\text{Na}}$ RONa + $\frac{1}{2}$ H₂ \uparrow

• R-C = CH
$$\xrightarrow{\text{Na}}$$
 R - C = $\overset{\Theta}{\text{CNa}}$ + $\frac{1}{2}$ H₂ \uparrow ; • PhOH $\xrightarrow{\text{Na}}$ PhONa + $\frac{1}{2}$ H₂ \uparrow

•RCOOH
$$\xrightarrow{\text{Na}}$$
 RCOONa + $\frac{1}{2}$ H₂ \uparrow $\xrightarrow{\text{Na}}$ + $\frac{1}{2}$ H₂ \uparrow

(9) Alc. KOH or NaNH₂: (Sodium amide or sodamide)

$$\begin{array}{c|c}
\cdot & C - C \\
 & I \\
 & I \\
 & H \\$$

• R - CH - CH - R
$$\xrightarrow{\text{2 alc. KOH or 2NaNH}_2}$$
 R - C = C - R Br Br

(Vicinal dihalide)

•
$$CH_3-C \equiv C-CH_3 \xrightarrow{NaNH_2} CH_3-CH_2-C \equiv CH_3$$

•
$$CH_3-CH_2-C \equiv CH \xrightarrow{\text{alc. KOH}} CH_3-C \equiv C-CH_3$$

•
$$C_6H_5CI + NaNH_2 \xrightarrow{liq. NH_3} C_6H_5NH_2 + NaCI$$

(10)N-Bromo succinimide (NBS):

•
$$CH_3 - CH = CH_2$$
 Allylic bromination CH_2 - $CH = CH_3$

• CH_3 CH_2 Br

• CH_3 CH_2 Br

• R – CH₂OH
$$\xrightarrow{\text{Oxidation}}$$
 R – CHO (aldehyde); • R₂CHOH $\xrightarrow{\text{Oxidation}}$ R₂CO (ketone)

(11)KCN/AgCN:

•
$$R-X \xrightarrow{\overline{KCN}} R-C \equiv N \text{ (Alkyl cyanide)}$$
 ; • $R-X \xrightarrow{AgCN} R-N \Longrightarrow C \text{ (Alkyl isocyanide)}$

(12)KNO,/AgNO,:

• R-X
$$\xrightarrow{\text{KNO}_2}$$
 R - O - N = O (Alkyl nitrite); • R-X $\xrightarrow{\text{AgNO}_2}$ R - N (Nitro alkane)

(13) Hydrating agents:

$$\begin{array}{c} \text{CH}_{3}\text{CH}_{3} \\ \text{CH}_{3} - \text{C} - \text{CH} - \text{CH}_{3} \\ \text{CH}_{3} - \text{C} - \text{CH} - \text{CH}_{3} \\ \text{CH}_{3} - \text{C} - \text{CH} - \text{CH}_{3} \\ \text{CH}_{3} \\ \text{CH}_{3} - \text{C} - \text{CH} - \text{CH}_{3} \\ \text{CH}_{3} \\ \text{CH}_{3} \\ \text{CH}_{3} \\ \text{CH}_{3} \\ \text{CH}_{2}\text{OH} \\ \end{array}$$

Ziegler-Natta catalyst: (C2H5)3 AI + TiCl4

$$n(CH_3 - CH = CH_2) \xrightarrow{\text{Polymerization}} (Propylene) \xrightarrow{\text{CH}_3} (CH_3 - CH_2 - CH_2)_{\pi}$$

$$(Propylene) \qquad (Polypropylene)$$

CH₂N₂ (Addition/insertion of carbene):

• Formation of carbene
$$\longrightarrow$$
 $CH_2N_2 \xrightarrow{\Delta} : CH_2 + N_2 \uparrow$
• Formation of carbene \longrightarrow $CH_2=C=O \xrightarrow{\Delta} CH_2 + CO$
 \longrightarrow $CH_2I_2/Zn \xrightarrow{\Delta} : CH_2 + ZnI_2$

$$-C \equiv C - \frac{\text{CH}_2}{\text{CH}_2} - C \xrightarrow{\text{CH}_2} C - \text{(Bicyclo alkane)} ; \qquad \text{CH}_2 = \text{CH}_2 \xrightarrow{\text{CH}_2 \text{N}_2} C \xrightarrow{\text{CH}_2 \text{N}_2} C \xrightarrow{\text{CH}_2} C \xrightarrow{\text$$

$$R = C \xrightarrow{O} \xrightarrow{CH_2N_2} R - CH_2 - C \xrightarrow{O}$$
; $RO-H \xrightarrow{CH_2N_2} R-O-CH_3$

$$\mathsf{R}-\mathsf{NH}-\mathsf{H} \xrightarrow{\ :\mathsf{CH}_2\ } \mathsf{R}-\mathsf{NH}-\mathsf{CH}_3\ (\mathsf{N}-\mathsf{methyl}\ \mathsf{amine})$$

SOCI,: (16)

$$\text{R-OH} \xrightarrow{\text{SOCl}_2, \text{Pyridine}} \text{R-CI (Inversion, S}_{\text{N}} \text{2 reaction)}$$

$$R-OH \xrightarrow{SOCl_2} R-CI \text{ (Retention)} \quad ; \qquad \qquad R-C \xrightarrow{O} \xrightarrow{SOCl_2, Pyridine} R-C \xrightarrow{O} CI$$

V - Name Reactions :

(1)Aldol condensation :

Reagents: dilute base (i) NaOH / KOH / \(\Delta \) (ii) Ca(OH), / Ba(OH),

Conditions: a - H must be present w.r.t. carbonyl group

$$\begin{array}{c} \text{(i) } \text{CH}_3-\text{C}-\text{H} \longrightarrow \text{CH}_3-\text{CH=CH-CHO} \ ; \\ \text{(iii) } \text{H}-\text{C}-\text{(CH}_2)_4-\text{C}-\text{CH}_3 \longrightarrow \\ \text{O} \end{array} \\ \begin{array}{c} \text{C} \\ \text{H}_3\text{C} \end{array} \\ \begin{array}{c} \text{C} \\ \text{C} \\ \text{C} \end{array} \\ \begin{array}{c} \text{C} \\ \text{C} \\ \text{C} \end{array} \\ \begin{array}{c} \text{C} \\ \text{C$$

(2) Arndt-Eistert reaction:
$$RCOCI + CH_2N_2 \xrightarrow{-HCI} RCOCHN_2 \xrightarrow{(i)Ag_2O/\Delta} R-CH_2-COOH$$

(3) Cannizzaro's Reaction (Redox or disproportion):

Reagents: Conc. NaOH or KOH / Δ

Hydride (H-ion) transfer is RDS

(i)
$$HCHO \longrightarrow HCOO^- + CH_3OH$$
 (ii) $Ph - C = O \longrightarrow Ph - CH - OH + CH = O$ $H - C = O$ COO^-

(iii) CHDO
$$\xrightarrow{\text{NaOH}}$$
 DCOO- + CH₂DOH (iv) HCHO + PhCHO \longrightarrow HCOO- + PhCH₂OH

Note: (i) α - H absent is primary condition. (ii) If α - H present then ald ol condensation occures.

(4) Curtius reaction:
$$RCOCI + NaN_3 \xrightarrow{\Delta : H_3O^{\oplus}} R - NH_2$$

(5) Cope reaction:
$$R-CH_2-CH_2-N-CH_3 \xrightarrow{\Delta} R-CH=CH_2+(CH_3)_2NOH$$

(7) Friedal-Craft's reaction:
$$\bigcirc$$
 + R - CI $\xrightarrow{\text{AlCl}_3}$ + HCI

(8) Fittig reaction:
$$2 \bigcirc -CI + 2Na \xrightarrow{\text{ether}} \bigcirc -CI + 2NaCI + 2NaCI$$

(9) Finkelstein reaction:
$$R - CI/R_O$$
 Br + NaI $\xrightarrow{acetone} R - I$ + NaCl/NaBr

(13) Gabriel pthalimide reaction : (Preparation of 1° aliphatic amine) :

$$\begin{array}{c}
COOH \\
COOH
\end{array}$$

$$\begin{array}{c}
COOTNH_{4} \\
COOTNH_{4}
\end{array}$$

$$\begin{array}{c}
COOTNH_{4} \\
COOTNH_{4}
\end{array}$$

$$\begin{array}{c}
COOTNH_{2} \\
COOTNH_{2}
\end{array}$$

$$\begin{array}{c}
COOTNH_{2} \\
COOTNH_$$

(14) HVZ Reaction (α-halogenation of carboxylic acid):

(15) Hydroboration Rxn. (No Rearrangement, Anti markownikoff's addition of H₂O)

$$R-CH=CH_{2} \xrightarrow{B_{2}H_{6}/THF} (R-CH-CH_{2})_{3}B \xrightarrow{H_{3}O_{2}/OH} R-CH-CH_{2}$$

$$H OH$$

$$CH_{3}COOH$$

$$R-CH-CH_{2}$$

$$H OH$$

$$CH_{3}COOH$$

$$R-CH-CH_{3}$$

$$H OH$$

(16) Haloform Reaction

(17) Hunsdiecker reaction: RCOOAg + Br₂
$$\xrightarrow{\text{CCl}_4}$$
 R - Br + CO₂ \uparrow + AgBr

(18) Oxymercuration – Demercuration (No Rearrangement, Markownikoff's Addition of H₂O)

Reagent: (i)
$$(CH_3COO)_2Hg / H_2O$$
 (ii) $NaBH_4$

$$R-CH = CH_2 \xrightarrow{(i)(CH_3COO)_2Hg} \xrightarrow{(ii)NaBH_4} R-CH-CH_2$$

$$H_2O \xrightarrow{H_2O} H_2O$$

(19) Perkin Reaction:

(22) Schmidt reaction:
$$RCOOH + N_3H \xrightarrow{H_2SO_4} R-NH_2 + CO_2 \uparrow + N_2 \uparrow$$

(23) Swart reaction:
$$R - CI + AgF/Hg_2F_2 \longrightarrow R - F + AgCI/HgCI_2$$

(25) Tischenko reaction :
$$2HCHO \xrightarrow{Al(EtO)_3} HCOOCH_3$$
 $2CH_3CHO \xrightarrow{Al(EtO)_3} CH_3COOC_2H_5$

(26) Wurtz reaction (Reagent : Na - ether)

$$R-X+2Na \xrightarrow{\text{ether}} R-R$$
; $R-X+R'-X+2Na \xrightarrow{\text{ether}} R-R'+R-R+R'-R'$
 $R-X+2Na \xrightarrow{\text{ether}} R-R'+R-R+R'-R'$

(27) Wurtz-Fittig reaction :
$$\bigcirc$$
 CI + 2Na+ CI-R $\xrightarrow{\text{ether}}$ \bigcirc R + 2NaCI

(28) Wittig reaction:
$$C = O + Ph_3P = CH_2 \longrightarrow C = CH_2 + Ph_3P = O$$

(29) Wacker process:
$$CH_2 = CH_2 + H_2O + PdCI_2 \xrightarrow{Cu_2CI_2} CH_3CHO + Pd + 2HCI$$

$$CH_3-CH=CH_2 + H_2O + PdCI_2 \xrightarrow{Cu_2CI_2} CH_3COCH_3 + Pd + 2HCI$$

VI- Rearrangement Reactions

(1) Beckmann rearrangement:

Reagents: Conc. H+ or H2SO4 or PCI3 or PCI5 or SOCI2

$$(i) \xrightarrow{R} C = N \xrightarrow{OH} \qquad \xrightarrow{H^{\oplus}} \begin{array}{c} R - C - NH - R' \\ \parallel \\ O \end{array}$$

group opposite to - OH migrates from carbon to nitrogen atom

(ii)
$$N - OH \xrightarrow{H^{\oplus}} C = O \xrightarrow{OH^{-}/H_{2}O} \xrightarrow{Polymerisation} Nylon-6$$
Caprolactum

(2) Benzil - Benzilic Acid Rearrangement

$$\begin{array}{c|c} & & \text{OH} \\ \text{Ph-C-C-Ph} & \underline{\quad conc. \, NaOH \quad } \\ \parallel & \parallel & \\ \text{O O } & & \parallel & \parallel \\ \text{Ph O } \end{array}$$

(3) Benzidine Rearrangement

(4) Claisen Rearrangement (intramolecular) / Cross products are not formed)

$$O - CH_2 - CH = \mathring{C}H_2$$

$$300^{\circ}C$$

$$OH$$

$$\mathring{C}H_2 - CH = CH_2 \quad Only \text{ Product}$$

$$H_3C$$
 CH_3 CH_3 CH_3 CH_3 CH_4 CH_5 CH_5 CH_5 CH_5 CH_5 CH_6 CH_7 CH_8 CH_8

(5) Cumene hydroperoxide Reaction:

$$\begin{array}{c|c} CH_3 & CH_3 \\ \hline \\ H_3C-CH_2-CH_2-CI \\ \hline \\ AlCl_3 \end{array} \begin{array}{c} CH_3 \\ \hline \\ H_3C-C-O-O-H \\ \hline \\ Cumene \\ Cumene \\ \hline \\ Cumene \\ C$$

(6) Fries Rearrangement (Intermolecular Rearrangement / Cross products are also formed)

$$\begin{array}{c|c}
O & O & O \\
 & & & O \\
O - C - R & A | C |_3 / \Delta
\end{array}$$

$$\begin{array}{c}
O + P \\
O - C - R
\end{array}$$

(Phenyl ester)

(7) Hofmann Bromamide Reaction

$$R-C-NH_2 \xrightarrow{2Br_2+4KOH} R-NH_2+K_2CO_3+4KBr+2H_2O$$
or KOBr
or O'Br

(8) Pinacol-Pinacolone Rearrangement

VII - Lab Tests

(1) 2, 4-Dinitro phenyl hydrazine (DNP) DNP test for carbonyl compounds (Brady's Reagent)

$$NO_2$$
 NO_2
 NO_2
 NO_2
 NO_2
 NO_2
 NO_2
 NO_2
 NO_2
 $(Yellow orange crystal)$

(2) Bromine water (Br₂ + H₂O):

$$\begin{array}{c}
OH \\
+ Br_2 \\
(Red)
\end{array}$$
Br
$$OH \\
Br$$
(White ppt)

(3) Biuret Test :

 $\begin{tabular}{l} O \\ \hline \bullet \mbox{Compounds containing} - \mbox{C} - \mbox{NH}^- \mbox{group gives this test.} \\ \end{tabular}$

$$\begin{array}{c|c} H_2N-C-NH_2+H-NH-C-NH_2\\ \hline O~(2~moles~of~urea)~O~132°C-NH_3\\ \hline H_2N-C-NH-C-NH_2~(Biuret)\\ \hline O~CuSO_4NaOH\\ \hline Violet~colour \end{array}$$

(4) Hinsberg's Reagent:

$$\begin{split} &C_6H_5SO_2CI \, (\text{Benzene sulphonyl chloride}) \\ &\text{It is used to distinguish between 19/29/39 amines} \\ &^*R-NH_2 \xrightarrow{\quad (i) \ C_6H_5SO_2CI (ii)KOH \quad} \text{Soluble salt} \\ &^*R_2NH \xrightarrow{\quad (i) \ C_6H_5SO_2CI (ii)KOH \quad} \text{Insoluble} \\ &^*R_3N \xrightarrow{\quad (i) \ C_6H_5SO_2CI (ii)KOH \quad} \text{No reaction} \end{split}$$

(5) HNO₂ (NaNO₂ + HCI): It is used to distinguish between 1º/2º/3º amines.

• R-NH $_2$ $\xrightarrow{\text{HNO}_2}$ R - OH + N $_2$ \uparrow - H $_2$ O

• $R_2NH \xrightarrow{HNO_2} R_2NNO + H_2O$

(N-nitroso compound yellow oily liquid)

$$\bullet R_3 N \xrightarrow{HNO_2} R_3 N_7 HNO_2 (salt)$$

• $C_6H_5NH_2 \xrightarrow{HNO_2} C_6H_5N_2CI$ (Benzene diazonium chloride)

•
$$CH_3$$
- $CONH_2$ $\xrightarrow{HNO_2}$ CH_3COOH + N_2 \uparrow + H_2O

(6) Schiff's Reagent:

It is a pink coloured organic dye (p-rosaniline hydrochloride) which has been decolourised by passing SO₂ gas through it.

*R-CHO ____decolourised shiff reagent ____ Pink colour (restored)

* R – C – R
$$\longrightarrow$$
 No Pink colour