CARBOXYLIC ACID AND ITS DERIVATIVES

PROBLEM 1130 How could you use an acid base extraction technique to separate a mixture of carboxylic acid and phenol into its pure components?

PROBLEM 1131 A carboxylic acid (A) of unknown structure was found to contain only C,H and O. 150 mg of A required 11.9 mL of 0.22 N NaOH to reach the equivalent point. Gentle heating of A evolves CO_2 and a new carboxylic acid (B) was formed whose equivalent weight was found to be 74.Identify A and B.

PROBLEM 1132 Propose mechanism:

(a)
$$OH \longrightarrow Br_2/CCl_4$$
 $OH \longrightarrow Br$

PROBLEM 1133 Predict major product in the following reaction:

(a)
$$COOH$$
 $COOH$ OOH O

PROBLEM 1134 Bring about the following transformations:

PROBLEM 1135 Complete the following reactions:

(e)
$$H_3C$$
 CN
 CN

PROBLEM 1136 Convert:

PROBLEM 1137 Bring about the following conversions:

(a)
$$PhCH_2OH \longrightarrow PhCH_2CN$$
 (b) $PhCOOH \longrightarrow PhC(CH_3)_2OH$ (c) $EtOOC \longrightarrow COOEt$

PROBLEM 1138 Show how would you accomplish the following synthesis in good yield?

PROBLEM 1139 Show how would you accomplish the following multisteps synthesis?

(a) 6-hepten-1-ol \longrightarrow caprolactum

PROBLEM 1140 Synthesize the following compounds from indicated starting materials:

PROBLEM 1141 Show how would you accomplish the following synthesis:

- (a) Isobutyl amine —— N-isobutyl formamide
- (b) Ethylacetate \longrightarrow 3-methyl-3-pentanol.
- (c) Cyclohexyl amine ------ N-cyclohexylacetamide
- (d) Bromocyclohexane ---- dicyclohexylmethanol

PROBLEM 1142 A neutral organic compound A has molecular formula $C_5H_8O_2$ and does not decolourise Bayer's reagent. A on acidic hydrolysis produced $B(C_5H_{10}O_3)$ which is resolvable. B on heating with concentrated H_2SO_4 undergo dehydration to produce C, an isomer of A. C decolourises Bayer's reagent and show stereoisomerism. Also B changes colour of acidic dichromate solution from orange to blue-green converting itself into $D(C_5H_8O_3)$ which is non-resolvable and forms an yellow precipitate on treatment with NaOI solution. Deduce structures of A to D.

PROBLEM 1143 A neutral organic compound $A(C_5H_8O_2)$ does not decolourise Bayer's reagent and on hydrolysis with dilute H_2SO_4 produces $B(C_5H_{10}O_3)$ which is diastereomeric. B on heating with concentrated H_2SO_4 undergoes dehydration producing $C(C_5H_8O_2)$ which shows geometrical isomerism. Also B on treatment with acidic dichromate solution produced $D(C_5H_8O_3)$ which is enantiomeric and gives an yellow precipitate with NaOI. D on gentle heating produces $E(C_4H_8O)$ which is nonresolvable. Deduce structures of A to E.

PROBLEM 1144 An organic acid $A(C_5H_{10}O_2)$ reacts with Br₂ in presence of phosphorus to produce a resolvable B. B on dehydrobromination yields C. C does not show geometrical isomerism and on decarboxylation gives an alkene D. D on ozonolysis gives E and F. Compound E gives positive Schiff's test but F does not. Give structures of A to F.

PROBLEM 1145 A monobasic acid A has neutralization equivalent 116 and does not decolourise Bayer's reagent. Also A is enantiomeric. A on treatment with Br₂/red phosphorus produces B which is still resolvable. B on dehydrobromination produced C which show stereo isomerism. C on decarboxylation produced D which does not show stereoisomerism. Deduce structures of A to D.

PROBLEM 1146 An organic lactum A on acid hydrolysis produced B, an amino acid. B on treatment with nitrous acid gives C. C on heating with concentrated H_2SO_4 produces a lactone D. A can also be synthesized by the reaction of cyclopentanone with hydroxylamine followed by treatment of product with concentrated H_2SO_4 . Deduce structures of A to D.

PROBLEM 1147 A neutral organic compound A has formula $C_9H_{16}O_3$ and rotates plane polarized light. A on acid hydrolysis produces B and $C(C_3H_8O)$. C on partial oxidation with PCC gives $D(C_3H_6O)$ which

does not gives iodoform test. D on treatment with dilute solution of NaOH gives $E(C_6H_{12}O_2)$ which is diastereomeric. E on treatment with acidic solution of KMnO₄ produces B. Deduce structures of A to E.

PROBLEM 1148 An organic compound $A(C_9H_6O_3)$ does not reacts with aqueous solution of NaHCO₃ and does not change the colour of litmus paper. A on acid hydrolysis gives $B(C_9H_8O_4)$ whereas A on treatment with methanol in acid medium gives $C(C_{10}H_{14}O_4)$ as the major alcoholysis product. B on heating with excess of soda-lime produces toluene. Deduce structures of A to C.

PROBLEM 1149 Diethyl malonate on treatment with one mole of C_2H_5ONa followed by reaction with one mole of 5-bromoethyl pentanoate produces $A(C_{14}H_{24}O_6)$. A on heating with dilute H_2SO_4 yields $B(C_7H_{12}O_4)$. B on treatment with excess of C_2H_5OH in presence of catalytic amount of H_2SO_4 yields $C(C_{11}H_{20}O_4)$. C on treatment with one mole of EtONa followed by work-up with dilute HCl yields $D(C_9H_{14}O_3)$. D on further treatment with one mole EtONa followed by reaction with CH_3I yields $E(C_{10}H_{16}O_3)$. E on heating with HCl yields 2-methylcyclohexanone. Deduce structures of A to E.

PROBLEM 1150 An organic compound contain C,H and oxygen and its aqueous solution is neutral. 1.44 g of A on refluxing with dilute H_2SO_4 produces two organic compound B and C of which only B is resolvable and gives effervescence with NaHCO₃. Also neutralization of entire B require 0.4 g of NaOH. B on reduction with HI/red phosphorus produces a hydrocarbon D which is non-resolvable. Also D on monochlorination yields three alkyl halide in which only one is resolvable. Deduce structures of A to D.

PROBLEM 1151 Identify the labelled product and explain their formations:

PROBLEM 1152 Give structural formula of all possible products in the following reactions:

(a)
$$MeO \longrightarrow NH_2 \xrightarrow{(CH_3CO)_2O} \longrightarrow$$

(b) $COOEt \xrightarrow{NH_2OH} \longrightarrow$

(c) $CH_2COOH \xrightarrow{(CH_3CO)_2O} \longrightarrow$

(d) $CHO \xrightarrow{Ag_2O/H_2O} \longrightarrow X \xrightarrow{H^+} Y$

(e) $CHO \xrightarrow{Ag_2O/H_2O} \longrightarrow X \xrightarrow{(CH_3CO)_2O} \longrightarrow Y$

PROBLEM 1153 Complete the following reactions:

(a) OMe NaBH₄
$$A$$
 SOCl₂ B

(b) CF_3 C $CH_3)_2SO_4$ D H^+ heat E

PROBLEM 1154 Complete the following sequence of reaction:

$$HOCH_{2} \longrightarrow \begin{array}{c} TsOH \\ \hline \\ O \\ \hline \\ E \\ \hline \\ \end{array} \longrightarrow \begin{array}{c} B \\ \hline \\ BrCH_{2}CH_{2}CI \\ \hline \\ NaCN \\ \hline \\ OH_{2} \\ D \\ \end{array}$$

PROBLEM 1155 Complete the following sequence of reaction explaining the formations of products in the second step:

$$\xrightarrow{\text{mcpba}} A \xrightarrow{\text{CH}_3\text{COCl/LiCl}} \text{H}_3\text{C} \xrightarrow{\text{O}} \text{O}$$

PROBLEM 1156 Bring about the following transformations:

(a)
$$H_3C$$
 H CH_2CI H CH_2CH_2Br

(b) H_3C H CHO

(c) H_3C H CHO

(e) HO
$$COOC_2H_5$$
 $COOC_2H_5$
 $COOC_2H_5$

PROBLEM 1157 Bring about the following transformations:

$$\begin{array}{c} \text{COOH} \\ \text{O} \\ \text{CD}_3 \\ \text{CD}_2 \text{OCOPh} \\ \text{CD}_3 \\ \text{CD}_3 \\ \end{array}$$

PROBLEM 1158 An organic compound exist in three isomeric forms A, B and C with their molecular formula $C_{10}H_{12}O_2$ and all are resolvable. Decarboxylation of either B or C gives the same $D(C_9H_{12})$ whereas decarboxylation of A gives E an isomer of D. Both D and E are non-resolvable. Treatment of either D or E with KMnO₄ in acidic medium produces benzoic acid as one product. Monobromination of E in presence of sunlight yields only two isomeric products whereas D on monobromination yields three isomers. Also E is more reactive than E towards decarboxylation reaction. Deduce structures of E to E.

PROBLEM 1159 An organic compound $A(C_6H_{10})$ decolourises Bayer's reagent and it is nonresolvable. A on treatment with acidic permanganate solution gave $B(C_6H_{10}O_4)$ which is still nonresolvable. B on treatment with excess of ethanol in presence of acid catalyst gave $C(C_{10}H_{18}O_4)$ which is a neutral sweet smelling liquid. C on refluxing with ethanolic solution of C_2H_5ONa gave $D(C_8H_{12}O_3)$ which is resolvable. D on treatment with acidic solution of ethylene glycol yields $E(C_{10}H_{16}O_3)$. E on treatment with one equivalent of Grignard reagent followed by reduction of product with Zn(Hg)—HCl and finally hydrolyzing product yields 2-ethylcyclopentanoate. Deduce structures of A to E.

PROBLEM 1160 Provide products:

PROBLEM 1161 Predict products and write mechanism of their formations:

(a)
$$H_2SO_4$$
 (b) H_2N $COOH$ KOH O

PROBLEM 1162 Provide organic products in the following reactions:

PROBLEM 1163 Indicate how each of the following compounds can be synthesized from the given starting material?

PROBLEM 1164 Bring about the following transformations:

PROBLEM 1165 Propose mechanism:

(a)
$$H$$
OH
OH
COOEt
HCI

PROBLEM 1166 Provide mechanism:

PROBLEM 1167 Starting from ethyl propanoate synthesize:

$$(a) \qquad (b) \qquad (c) \qquad Ph$$

$$(d) \qquad (e) \qquad N \qquad N \qquad O$$

PROBLEM 1168 Bring about the following conversions:

PROBLEM 1169 Propose mechanism of formation of products in the following reactions:

(a) MeOOC COOMe + OOOEt
$$O$$
 COOMe + OOOEt O CH₃ONa heat O COOEt O COOEt

PROBLEM 1170 Propose mechanism of the following transformations:

$$OH \xrightarrow{K_2Cr_2O_7} COOCH_3$$

PROBLEM 1171 Devise synthesis of the compounds shown below from the indicated starting materials:

(b)
$$OH$$
 OH OH

PROBLEM 1172 Propose an efficient synthesis of the compound shown below from indicated starting material and methanol.

$$O$$
 HO O OH

PPROBLEM 1173 Propose mechanism of the following reactions:

(a)
$$OH CH_3Li$$
 Excess CH_3

(b)
$$R$$
—CN $\xrightarrow{\text{H}_2\text{O}}$ R COOH $\xrightarrow{\text{SOCl}_2}$ R —COCl

(c)
$$R - C - N_3 \xrightarrow{\text{H}_2O} R - NH_2 + CO_2 + N_2$$

PROBLEM 1174 Provide a mechanism for the following reaction:

$$CH_3O$$
 CH_3O
 CH_3O
 CH_3O
 CH_3O
 CH_3O
 CH_3O

PROBLEM 1175 Bring about the following transformations:

(a)
$$CH_3O$$
 OCH_2CH_3 OCH_2CH_3 (b) $COOH$

PROBLEM 1176 Arrange the followings in increasing order of reactivity towards nucleophile:

(a)
$$H_3C - C - NH_2(I)$$
, $CH_3 - C - CI(II)$, $CH_3 - C - OAc(III)$, $H_3C - C - OCH_3(IV)$
(b) $CH_3 - C - CI(I)$, $CH_3CH_2 - C - CI(II)$, $(CH_3)_2CH - C - CI(III)$, $(CH_3)_3C - C - CI(IV)$
(c) $CH_3 - C - OCH_3(I)$, $CH_3 - C - OCH_2CH_3(II)$, $H_3C - C - OCH(CF_3)_2(III)$

PROBLEM 1177 Convert

(a) $CH_3CH_2CH_2COOH \longrightarrow CH_3CH_2CH_2CH_2COOCH_3$

PROBLEM 1178 Consider the following acid derivative:

$$\begin{array}{c|c}
H & C \\
N & CH_3
\end{array}$$

(a) Which of the groups in square will hydrolyze first in base catalyzed medium?

- (b) How the rate of hydrolysis be affected if a nitrogroup is substituted at C-4?
- (c) How the rate of hydrolysis be affected if an amino group is substituted at C-4?
- (d) How the rate of hydrolysis be affected if a methoxy group is substituted at C-3?

PROBLEM 1179 Propose mechanism of the following reaction and calculate enthalpy of reaction from the given bond-energies data:

BE: C—C = 85 kcal/mol; C—O = 91 kcal/mol; O—H = 102 kcal/mol; C—H = 99 kcal/mol.

PROBLEM 1180 Predict major product in the following giving mechanistic reasoning:

PROBLEM 1181 An optically active organic compound A has molecular formula $(C_7H_{12}O_3)$ and found to produce an yellow precipitate with alkaline solution of Iodine. Also A neither decolourised brown colour of bromine water nor evolved any gas with aqueous solution of NaHCO3 but evolved a gas on heating with sodium metal. On hydrolysing in acidic medium, A produced antoher optically active compound $B(C_7H_{14}O_4)$ which also produced yellow ppt with NaOH/I2. Also B evolved a colourless, acidic gas on treatment with aqueous NaHCO3 solution. A on treating with $CC_3/HCI/P$ yridine in CH_2CI_2 produced another optically active compound $C(C_7H_{10}O_4)$. C on refluxing with aqueous $CC_3/HCI/P$ on simple heating. However, heating D with sodalime gave $CC_5/H_{10}O_5$. In a separate analysis, 3-oxo ethylbutanoate was heated with excess of sodium metal and then with $CC_3/H_{10}O_5$. X on hydrolysis followed by simple heating of product yielded E. Identify A to E and X.

PROBLEM 1182 An oily liquid A is insoluble in water but on heating with aqueous NaOH for half an hour it dissolves. From the reaction mixture a liquid B can be distilled, which gave an yellow precipitate with iodine and NaOH. On careful oxidation, B gives an aldehyde, C, which also gives an yellow precipitate with iodine and NaOH solution. If sulphuric acid is added to the solution obtained from heating A with NaOH solution, a white precipitate D is obtained. D liberates a gas on treatment with aqueous NaHCO₃. Heating D with sodalime produced benzene. Identify A–D.

PROBLEM 1183 An organic compound A has molecular formula $C_9H_8O_2$ and if exist in stereoisomeric forms. A effervesces with NaHCO₃. A decolourises brown colour of bromine water forming $B(C_9H_8O_2Br_2)$ which is distereomeric. B on hydrolysing with aqueous NaOH followed by refluxing of product with acid gave $C(C_9H_{10}O_4)$. C on oxidising with acidified dichromate solution gave $D(C_9H_6O_4)$ which gives orange precipitate with 2,4-dinitrophenylhydrazine but did not react with ammonical AgNO₃ solution. D on reacting with PCl₅ yielded a steamy fumes of $E(C_9H_5O_3Cl)$. E on treatment with aqueous ammonia yielded $F(C_9H_7O_3N)$. Both A and F are oxidized by hot aqueous KMnO₄ solution to yield a white crystalline substance which on heating with sodalime yielded benzene. Identify A to F.

PROBLEM 1184 Propose mechanism of the following reactions:

(a)
$$\frac{\text{(i) NaOH/H}_2O}{\text{(ii) H}_3O}$$
COOH
$$\frac{\text{(ii) TsCl}}{\text{(ii) NaOH}}$$
NC
$$\frac{\text{(iii) H}_3O^+}{\text{(iii) H}_3O^+}$$
COOH
$$\frac{\text{(iii) H}_3O^+}{\text{(iii) H}_3O^+}$$

PROBLEM 1185 Propose mechanism of the following reactions:

(a)
$$\frac{K_2CO_3}{BrCH_2CH_2Br}$$
 OEt $\frac{Na/excess}{EtOOC}$

PROBLEM 1186 Propose mechanism:

PROBLEM 1187 (a) Indicate a mechanism of the following reaction:

(b) Devise a sequence by which product of the reaction in part "a" converted into the following comopunds:

(i)
$$(ii)$$
 (iii) (iii) Ph (iv) $(iv$

PROBLEM 1188 Bring about the following transformations:

PROBLEM 1189 Bring about the following transformations:

(a)
$$\longrightarrow$$
 Br COOH

(b) CH_3CH — CH_2CN \longrightarrow CH_3CHCH_2 CH_2OH
 C_6H_5 C_6H_5

PROBLEM 1190 Propose mechanism:

$$\begin{array}{c|c} O & & & O \\ \hline O & & & \\ \hline O & & \\ \hline COOH & & \\ \end{array}$$

PROBLEM 1191 Propose mechanism of the following reactions:

PROBLEM 1192 Provide missing reagents/products in the following reactions:

(a)
$$\frac{Br_2/NaOH}{H_2O}$$

(b) $\frac{NH_2}{NH_2}$ $\frac{P}{H_2O}$

(c) $\frac{P}{OCH_3}$ $\frac{P}{HO}$ $\frac{OCH_3}{OCH_3}$

PROBLEM 1193 Bring about the following transformations:

$$PhBr \longrightarrow PhCH_2-N = \sqrt{}$$

PROBLEM 1194 A neutral organic compound $A(C_4H_6)$ reacts with Br_2/CCl_4 solution to form a compound $B(C_4H_6Br_2)$. A on treatment with acidified permanganate solution yields $C(C_4H_6O_3)$. C gives an orange precipitate with 2,4-dinitrophenylhydrazine. C on refluxing with NaHCO₃ evolves a

gas. Treating C with NaBH₄ gave a new compound $D(C_4H_8O_3)$ which also produces a gas with NaHCO₃ solution. Deduce a structure of A—D.

PROBLEM 1195 2.81 g of an optically active diester A, containing only C, H and oxygen was saponified using 30 mL 1.0 M NaOH solution. Following saponification, the solution required 6 mL 1.0 M HCl solution to titrate unreacted base. The saponification products were an optically inactive diacid B, methanol and an optically active alcohol C. Alcohol C reacted with alkaline solution producing an yellow precipitate and C_6H_5COONa . Also, the diacid B reacted with Br_2 in CCl_4 to give a single, optically inactive product D. Ozonolysis of B gave only one product. Also, the diester A reacts with Br_2/CCl_4 to give a mixture of E and F, both optically active. Identify A to F.

PROBLEM 1196 The following three reactions occurs by a common mechanism. Write detailed mechanism for the reaction A. Then indicate, which reaction will be the fastest and which reaction will be the slowest and explain briefly, why?

Br
$$CH_3CN$$

$$H_3CO$$

$$H_3CO$$

$$R$$

$$CH_3CN$$

$$H_2O/\Delta$$

$$O_2N$$

$$O_2N$$

$$R$$

$$CH_3CN$$

$$H_2O/\Delta$$

$$O_2N$$

$$NH-C-CH_3$$

$$NH-C-CH_3$$

$$NH-C-CH_3$$

$$NH-C-CH_3$$

$$NH-C-CH_3$$

PROBLEM 1197 Propose mechanism of the reaction:

PROBLEM 1198 Complete the following reactions:

(a) COOCH₃ (i) NaOH
$$\Delta$$
 (ii) NaOH Δ (ii) NaOH Δ (ii) H₃O⁺ (ii) H₂O (c) (d) $\frac{I_2/H_2O}{(ii) SOCl_2}$ (f) $\frac{(i) Me_2NH}{(ii) LiAlH_4}$ (i) NaOH Δ (ii) NaOH Δ (ii) NaOH Δ (ii) NaOH

PROBLEM 1199 Propose mechanism of the reaction:

PROBLEM 1200 Provide products of the following reactions:

(a)
$$CH_3$$
 CH_2SNa H_3O^+ H_2O

(b) $COOEt$ CCI_4 $COOEt$ $OOET$ $OOET$

PROBLEM 1201 Provide selective reagents that will bring about the following transformations:

$$(d) \quad MeO \longrightarrow MeO \longrightarrow OH$$

PROBLEM 1202 Propose mechanism of the following reactions:

(a) OEt
$$CH_3MgI$$
 H_3O^+ O O

(b) CN CH_3Li Et_2O H_3O^+

PROBLEM 1203 Synthesize the following compound starting from diethylmalonate and other necessary reagents:

PROBLEM 1204 Write product of the following reactions:

(d)
$$\xrightarrow{\text{EtO}^-} \xrightarrow{\text{H}_3\text{O}^+}$$

PROBLEM 1205 An organic compound A reacts with I_2 in basic medium to give a yellow precipitate. A on treatment with Br_2 in acetic acid medium gives B which readily undergoes reaction with cyanide ion to give C. C on reduction with NaBH₄ forms D—an optically active substance. Acid hydrolysis of D followed by treatment with acidic ethanol gives E. Gentle oxidation of E with pyridinium chlorochromate gives F, which on treatment with potassium ethoxide in ethanol followed by reaction with ethyl iodide and then heating the final product yields 1-phenyl-1-butanone. Identify A to F.

Solutions

CARBOXYLIC ACID AND ITS DERIVATIVES

1130. Extraction of a solution of carboxylic acid and phenol in CCl₄ with aqueous solution of NaHCO₃ will bring carboxylic acid in aqueous phase as RCOONa leaving phenol in organic phase.

1131. A: 2-methylmalonic acid, B: Propanoic acid.

(d) $CH_3CH_2CH(COOEt)_2$

(e) (i)
$$H_3C$$
—COOH (ii) H_3C —CH₂NH₂ (iii) H_3C —Ph

1136. (a) HOOC+CH₂
$$\xrightarrow{}_{4}$$
COOH $\xrightarrow{C_{2}H_{5}OH}$ $\xrightarrow{C_{2}H_{5}O}$ \xrightarrow{O} \xrightarrow{O}

(b)
$$CH_3COOH \xrightarrow{P_4} ICH_2COOH \xrightarrow{aqueous} \xrightarrow{H_3O^+} HOOC \longrightarrow CH_2 \longrightarrow COOH$$

$$C_2H_5OH/H^+/Heat$$

$$tEOOC \longrightarrow COOEt$$

1137. (a) $PhCH_2OH \xrightarrow{SOCl_2} PhCH_2Cl \xrightarrow{NaCN} PhCH_2CN$

COOEt

(b) PhCOOH
$$\xrightarrow{\text{SOCl}_2}$$
 PhCOCl $\xrightarrow{\text{CH}_3\text{MgCl}}$ $\xrightarrow{\text{H}_3\text{O}^+}$ Ph $\xrightarrow{\text{C}}$ CH₃ OH

(c) EtOOC COOEt
$$COOEt$$
 $COOEt$ $COOEt$ $COOH$ $COOH$ $COOH$

(b) $PhCH_2Br \xrightarrow{NaCN} \xrightarrow{NaBH_4} PhCH_2CH_2NH_2$

(c)
$$PhCHO + CH_3MgBr \xrightarrow{H_3O^+} PhCHCH_3 \xrightarrow{H_2SO_4} PhCH = CH_2 \xrightarrow{Peroxide} \xrightarrow{NaCN} OH$$

 $PhCH_2CH_2CN$

1140. (a)
$$P_4/I_2$$
 COOH P_4/I_2 COOH P_2O_5 Heat P_2O_5

(b)
$$C_2H_5O-C-(CH_2)_4COOC_2H_5$$
 Et ONa Et ON H₃O+ He a t

1141. (a)
$$HCOOH$$
 $HCOOH$ HC

(b)
$$CH_3COOEt$$
 C_2H_5MgBr H_3O^+ OH

(c)
$$\begin{array}{c|c} NH_2 & \\ \hline \\ Heat \end{array} \begin{array}{c} NHCOCH_3 \\ \hline \end{array}$$

$$(d) \qquad \begin{array}{c} Br \\ \hline \\ \underline{Mg} \\ \hline \\ Et_2O \end{array} \qquad \begin{array}{c} HCOCl \\ \hline \end{array} \qquad \begin{array}{c} H_3O^+ \\ \hline \end{array} \qquad Product.$$

1142.
$$O$$

OH

COOH

CO

1146.
$$\bigcirc$$
 NH HOOC NH₂ HOOC OH \bigcirc OH \bigcirc O

$$\begin{array}{cccc} & & \text{OH} & \\ | & | \\ \text{CH}_3\text{CH}_2\text{CHO} & \text{CH}_3\text{CH}_2\text{CH} \text{--CH} \text{--CH}_3 \\ D & | & | \\ \text{CHO} & E \end{array}$$

1148.
$$COOH$$
 $COOH$ $COOH$ $COOH$ $COOH$

1149.
$$C_2H_5OOC-CH-COOC_2H_5$$
 HOOC COOH

1150.
$$COOC_2H_5$$
 $COOH$ C_2H_5OH $COOH$ $COOH$

1151.
$$OH$$
 B

1152. (a) MeO—NHCOCH₃ (b) Ph—C—NHOH (c)
$$\begin{array}{c} CH_2COOH \\ COOH \\ COOH$$

1158. Ph—CH—CH2COOH Ph—CH—CH2CH3 PhCH2CH—COOH PhCH2CH2CH3 COOH
$$B$$

 $\Pr_E(\operatorname{CH}_3)_2$

1159.
$$\bigcirc$$
 COOH COOEt \bigcirc COOEt \bigcirc COOEt \bigcirc COOEt \bigcirc COOEt \bigcirc COOEt

1161. (a) HOOC— $CH_2CH_2CH_2$ —OH (b) H_2N — CH_2COO^- (c) HOOC— $CH_2CH_2CH_2CONH_2$

1162. (a)
$$COOCH_3$$
 $COONa$ $COONA$

(b)
$$CH_3 - CH_2 - COOH$$

(e)
$$Ph-C-CH_2CH_3$$
 $\xrightarrow{Cl_2}$ $Ph-C-CHCH_3$ $\xrightarrow{C_2H_3ONa}$ $\xrightarrow{C_2H_3ONa}$ $\xrightarrow{C_2H_2OH}$

$$Ph-C-CH=CH_2 \xrightarrow{HBr} Ph-C-CH_2CH_2Br \xrightarrow{H^+} \xrightarrow{CH_2-CH_2} \xrightarrow{OH} OH$$

$$Product \xrightarrow{Ag_3O} Ph-C-CH_2CH_2CH_2CH_2OH \xrightarrow{H_3O^-} \xrightarrow{Mg} ether Ph-C-CH_2CH_2Br$$

(d) $\xrightarrow{CH_3O} \xrightarrow{CH_3O} \xrightarrow{CH_3O} \xrightarrow{COOEt} \xrightarrow{LDA} \xrightarrow{CH_3O} \xrightarrow{COOEt} \xrightarrow{LDA} \xrightarrow{CH_3CH_2Br}$

(e) C_2H_3O $\xrightarrow{COOEt} \xrightarrow{COOEt} \xrightarrow{CH_3CH_2CH_2CH_2OH} \xrightarrow{COOEt} \xrightarrow{COOEt} \xrightarrow{CH_3CH_3CH_2Br}$

1164. (a) $PhCOOH \xrightarrow{SOCl_2} Ph-C-Cl \xrightarrow{PhC=CNa} Ph-C-C=C-Ph \xrightarrow{N_2H_4} \xrightarrow{OH^-/Heat} \xrightarrow{Ph-C-OMe} \xrightarrow{H_3O^-} \xrightarrow{Ph-C-OMe} \xrightarrow{H_3O^-} \xrightarrow{H_3O_0} \xrightarrow{LIAIH_4} \xrightarrow{H_3O_0} \xrightarrow{H_3O_$

1165. (a)
$$\stackrel{O}{\longrightarrow}$$
 $\stackrel{H}{\longrightarrow}$ $\stackrel{H^+}{\longrightarrow}$ $\stackrel{O}{\longrightarrow}$ $\stackrel{O}{\longrightarrow}$ $\stackrel{H}{\longrightarrow}$ Product

$$\begin{array}{c|c} & & & \\ & & & \\ \hline \\ O & O \\ \end{array} \begin{array}{c} & & \\ Heat \\ \hline \\ O & O \\ \end{array} \begin{array}{c} & \\ COOEt \\ \hline \\ \end{array} \begin{array}{c} & \\ CH_3CHCOOEt \\ \hline \end{array}$$

(b) OEt
$$CH_3MgBr$$
 OEt OEt OET

(b)
$$NaNO_2$$
 $HCI/0°C$ $NaNO_2$ $HCI/0°C$ $N_2^+CI^ CHO$ $CUCN$ HCN CN CHO CHO

1172.
$$CH_3OH \xrightarrow{PBr_3} CH_3Br \xrightarrow{Mg} CH_3MgBr$$

1174. CH₃O Cl CH₃O Cl CH₃O OH NaH CH₃O OH SOCl₂ Mg ether
$$\frac{H_3O^+}{H_2O}$$
 OH $\frac{H_3O^+}{H_2O}$ OH $\frac{H_3O^+}{H_2O}$ OH $\frac{H_3O^+}{H_3O}$ OH $\frac{H$

- 1178. (a) A will hydrolyse first,
- (b) Rate will increase,
- (c) Rate will decrease,

(d) Rate will decrease.

Ph OCH₃

$$\begin{array}{c} O \\ Ph \\ \hline OCH_3 \end{array}$$

$$\begin{array}{c} O \\ OCH_3 \end{array}$$

$$\Delta H = (BE)_{Reactants} - (BE)_{Products} = 91 + 99 - (85 + 102) = 3 \text{ kcal}$$

Necleophile attack at more electrophilic. C

E D **1182.** $A: C_6H_5COOCH_2CH_3; B: CH_3CH_2OH; C: CH_3CHO; D: C_6H_5COOH.$ 1183. C₆H₅CH=CH—COOH C₆H₅CHBrCHBrCOOH C₆H₅CH(OH)CH(OH)COOH ${\rm C_6H_5COCOCOOH} \atop D$ $C_6H_5COCOCOC1$ ${\rm C_6H_5COCOCONH_2}_F$ COOH **1184.** (a) $H\bar{O}$ H_2O COOH НО€ ĎН TsCl (b) Product <u>:</u> H Ė H HO-TsO <

(c)
$$BuLi$$
 $N-OTs$

$$BuLi$$

$$N = C$$

$$O$$

$$H_2O$$

$$Product$$

$$H$$

$$OEt$$

$$H$$

$$OEt$$

$$CO_3^{2-}$$

$$OET$$

(iii) COOEt
$$\frac{H_2SO_4}{H_2O}$$
 Heat $\frac{KMnO_4}{H^7/heat}$ COOH $\frac{K_1SO_4}{H^7/heat}$ COOH $\frac{H_2SO_4}{H_2O}$ COOH $\frac{RNHNH_2}{H^1}$ COOEt $\frac{RNHNH_2}{H^2}$ $\frac{R}{H_2O}$ $\frac{$

(b)
$$S \stackrel{\text{i.i.}}{N} H_2$$
 $S \stackrel{\text{NH}_2}{N} H_2$ $S \stackrel{\text{NH}_2}{N} H_2$ $S \stackrel{\text{NH}_2}{N} H_2$

1192. (a) NH_2

(b) CH₃I (excess); Ag₂O/heat,

НО

(c) CH₃ONa; CH₃CH₂CH₂Br; NaOH/H₂O; heat,

(d) Mg/Et₂O; CO₂/H₃O⁺; CH₃OH/H⁺.

1196. All the three reaction involves SN-1 reaction of tertiary halide as:

$$CH_{3}O \longrightarrow CH_{3}O \longrightarrow CH_{3}O \longrightarrow CH_{3}O \longrightarrow CH_{3}O \longrightarrow CH_{3}CH$$

The above mechanism reveal that electron donating group will increase the reactivity and electron withdrawing group will decrease the reactivity. Therefore, reaction A will be the fastest and reaction B will be the slowest.

1200. (a)
$$OEt$$
 OEt OEt OEt OEt OOH OEt OOH OOH

1201. (a) Ag_2O/H_2O , (b) $\{(CH_3)_3CO\}_3AI$, (c) CH_3MgCI ; PCC, (d) $NaBH_4$.

1202. (a)

OEt
$$CH_3MgI$$

OEt CH_3MgI

OET CH_3

1-Phenyl-1-butanone