

14.2 Derivatives of Carboxylic acids

Learning outcomes

After the lesson, learners should be able to:

- Show the preparation of acid derivatives from carboxylic acid.
- Explain the comparative physical properties of acid derivatives.
- Explain the comparative chemical properties of acid derivatives (hydrolysis, ammonolysis, amines- RNH_2), alcoholysis, and reduction only. Claisen condensation and Hofmann bromamide reaction.
- Describe amphoteric nature of amide and relative reactivity of acid derivatives.

1. Acid Halides or Acyl Halides (R-COX)

These are the derivatives of carboxylic acids in which $-\text{OH}$ part of carboxyl group is replaced by halo ($-\text{Cl}$, $-\text{Br}$ or $-\text{I}$) group. The most reactive, most common and least expensive compounds among the acid halides are acid chlorides.

Nomenclature

The names of acid halides are derived from IUPAC or common names of the corresponding acids by replacing the suffix $-\text{ic}$ acid with $-\text{yl}$ halide. Or secondary suffix for the acid chloride group is **$-\text{oyl chloride}$** . E.g.

Formula	IUPAC names	Common names
HCOCl	Methanoyl chloride	Formyl chloride
CH_3COCl	Ethanoyl chloride	Acetyl chloride
$\text{CH}_3\text{CH}_2\text{COCl}$	Propanoyl chloride	Propionyl chloride

2. Acid Amide or amide ($-\text{CONH}_2$)

Acid amides can be regarded as the derivatives of carboxylic acids in which $-\text{OH}$ part of the carboxylic group are replaced by the $-\text{NH}_2$ group.

1) Write the functional group of amide.

1

Nomenclature

Acid amides are named by replacing the suffix –ic acid of the common name or –oic acid of the IUPAC name of the corresponding acid with the suffix ‘amide’. Or secondary suffix for the functional group amide is **–amide**. e.g.

Formula	IUPAC names	Common names
HCONH_2	Methanamide	Formamide
CH_3CONH_2	Ethanamide	Acetamide
$\text{CH}_3\text{CH}_2\text{CONH}_2$	Propanamide	Propionamide

3. Ester (-COOR)

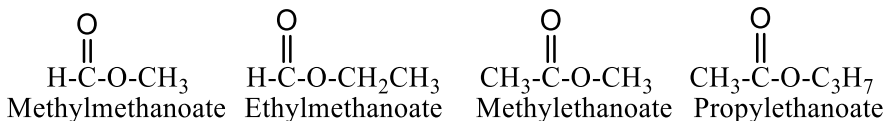
Ester is considered the derivative of carboxylic acid whose –OH group is replaced by alkoxy group (-OR).

2) *Write the functional group of ester.*

1

Nomenclature

While writing the IUPAC name of an ester secondary suffix **–oate** is used and the alkyl group is written as a prefix.

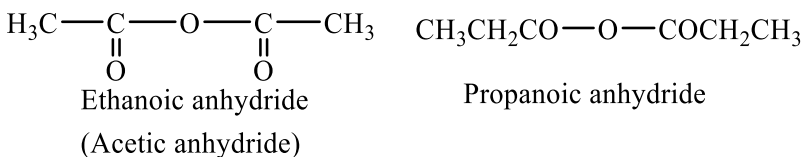


4. Acid Anhydride (-CO-O-CO-)

Acid anhydrides are considered to be derived from carboxylic acids formed by the removal of water from the two molecules of the acid.

Nomenclature

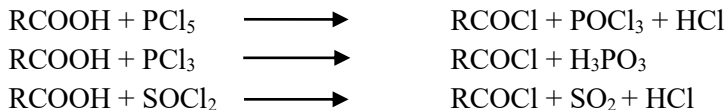
The acid anhydrides are named by replacing the suffix ‘acid’ of the IUPAC or common name of the carboxylic acids with ‘anhydride’. Some examples are



Preparations of the derivatives from carboxylic acids

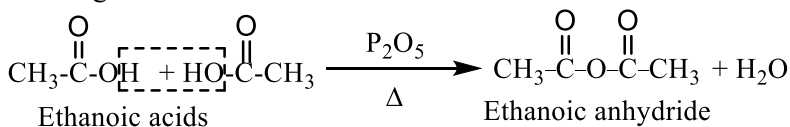
1. Preparation of acid chloride (studied in carboxylic acids already)

Acyl chlorides can be prepared by the reaction of carboxylic acids with phosphorus pentachloride, phosphorus trichloride or thionyl chloride in the presence of pyridine.

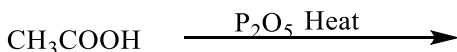


2. Preparation of acid anhydride (studied in carboxylic acids already)

Acid anhydrides can be prepared by heating carboxylic acids in presence of P_2O_5 . e.g.



3) Predict the major product of the following reaction.



1

4) What happens when Ethanoic acid is heated with P_2O_5 ?

1

5) How would you convert Ethanoic acid into Ethanoic anhydride?

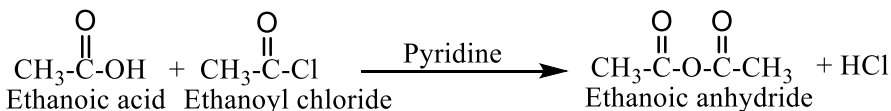
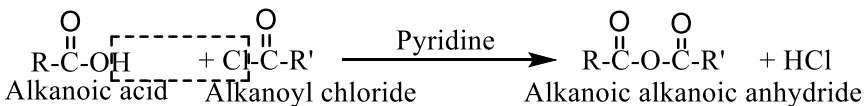
1

6) Identify the product A and B and give their IUPAC name.



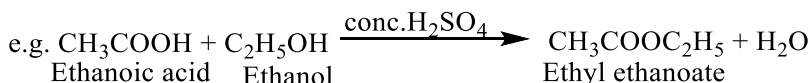
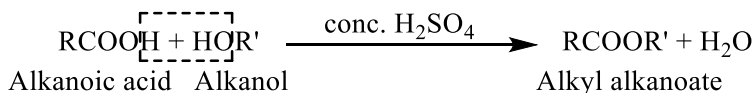
2

3. By treatment of carboxylic acids with acid chlorides



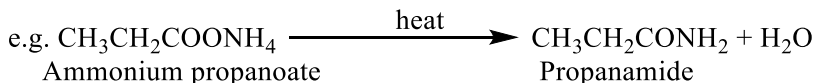
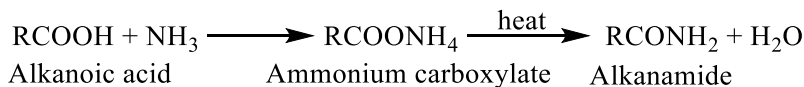
4. Preparation of ester (studied in alcohols chapter already)

Esters can be prepared by the reaction of carboxylic acids with alcohols in the presence of concentrated sulphuric acid. This is called the Esterification reaction.



- 7) How would you convert Ethanoic acid into Methyl ethanoate? 1
8) How does Methanoic acid act upon methanol/H⁺? 1

5. Preparation of acid amide



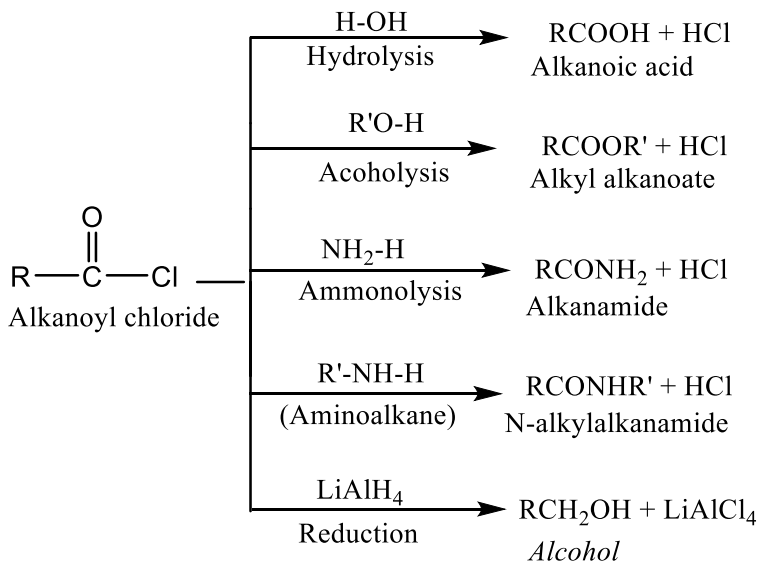
Comparative physical properties of acid derivatives

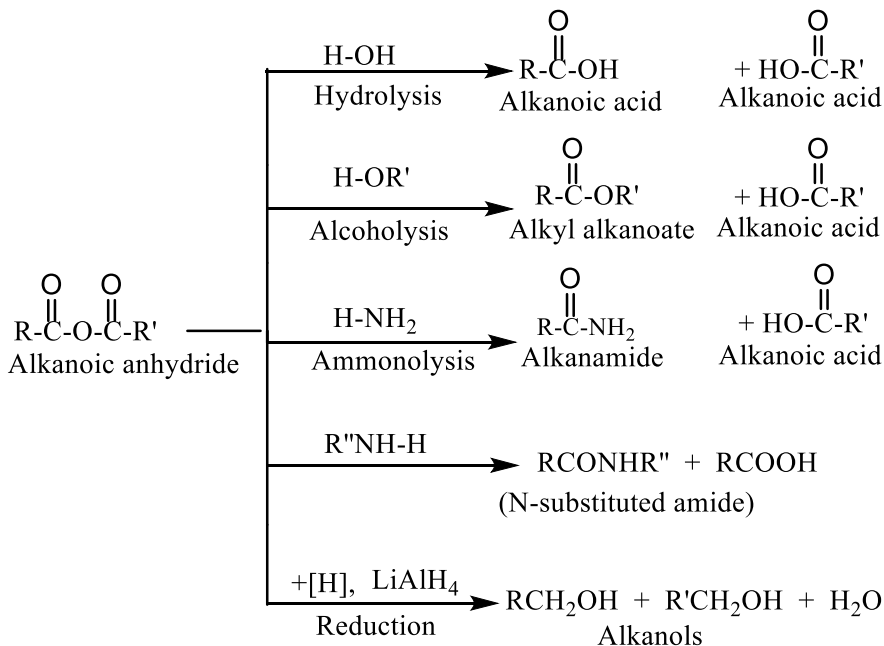
	State	Boiling Point	Solubility
Acid chlorides	Lower members - colourless liquids with pungent smell Higher members - colourless solids	Less than that of parent acids due to absence of hydrogen bonding	Soluble in organic solvents. Can't be used in water as they undergo hydrolysis.
Acid anhydrides	Lower members - colourless liquids with pungent smell Higher members - colourless solids	Higher than that of parent acid due to larger relative molecular mass.	Soluble in organic solvents. Can't be used in water as they undergo hydrolysis.
Esters	Lower members - colourless liquids with	Lower than that of acid with	Soluble in organic

	pleasant fruity smell Higher members - colourless odorless solids	comparable molecular wt. due to lack of H- bonding.	solvents. Soluble in water as well.
Amides	First member- Methanamide- liquid All other colourless odourless crystalline solids.	Higher than corresponding acid due to availability of 2 H atoms for H- bonding.	Soluble in organic solvents. Lower members soluble in water due to H- bond formation.

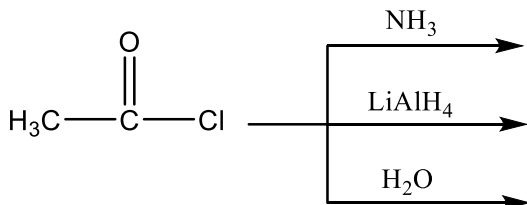
Comparative chemical properties of acid derivatives

Acid chlorides are most reactive derivatives of carboxylic acids. These mainly give following reactions.

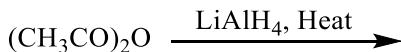




9) Write the products of the following reactions with IUPAC name. 3



10) Predict the major product of the following reaction.

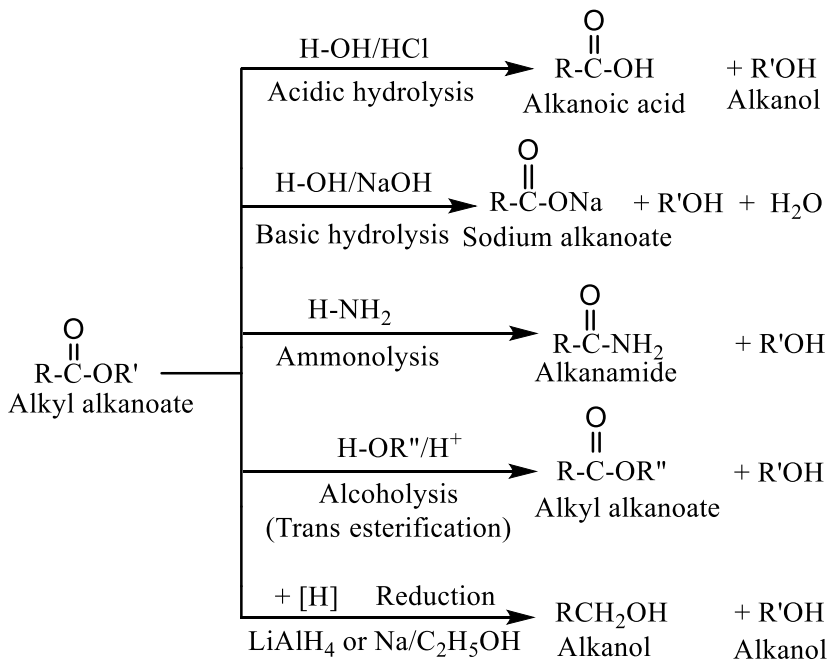


1.

11) Predict the major product of the following reactions;

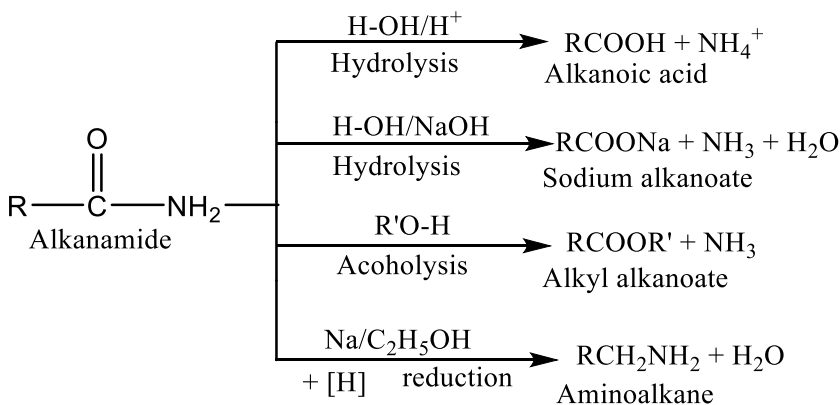


1



11) Write chemical reaction when an ester is hydrolyzed?

2



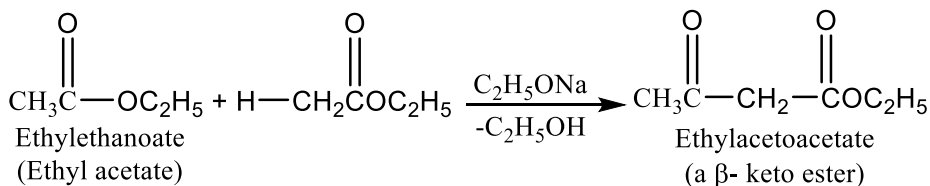
Alcoholysis

12) Write chemical reaction when an amide is hydrolysed.

2

14.2.4 Claisen condensation

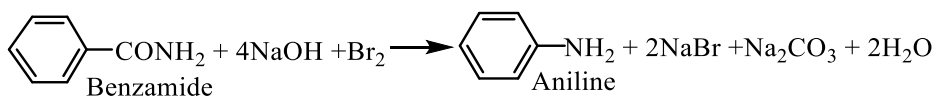
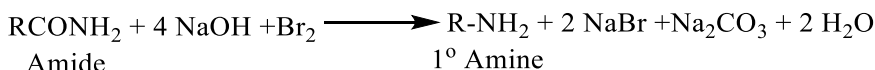
Esters containing α -hydrogen undergo self-condensation in presence of strong base such as sodium ethoxide to form β -keto esters; such reaction is called claisen condensation.



13) write a chemical reaction for Claisen condensation reaction. [1]

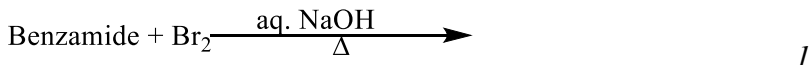
14.2.5 Hofmann Bromamide degradation reaction

Amides react with bromine in the presence of alkali to form a primary amine carrying one carbon less than the parent amide. This is also called degradation reaction.



13) What happens when Benzamide is heated with bromine and aq. KOH? 2

14) Give the major product of the following reaction



15) What happens when the product obtained by action of Ethanoyl chloride and ammonia is heated with Br_2 and aqueous KOH? 2

16) Define and give an example of Hofmann's hypobromite reaction. 1

17) What happens when Benzamide allowed to react with bromine in presence of KOH solution? 1

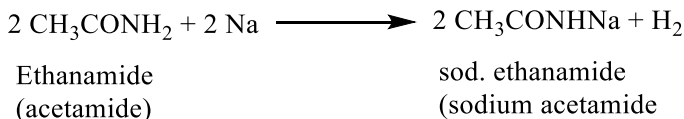
18) Give an example of decarbonylation reaction. 1

Amphoteric nature of amide

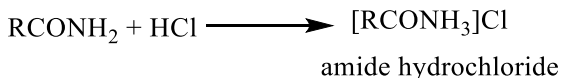
Amides behave both as weak acid and weak bases i.e., they are amphoteric in nature.

Amides react with reactive metals like Na, K etc. to release hydrogen.

Similarly, it also reacts with mercuric oxide producing salt and water. These reactions show acidic nature.



Amides are Lewis bases as they have a lone pair of electrons in N atom. But these are weaker bases than amines, as the electrons are delocalized due to resonance. These react with strong acids to form salts.

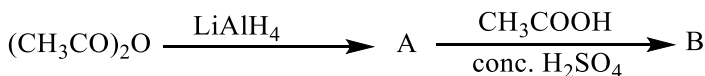
**Relative reactivity of acid derivatives**

The relative reactivity of acid derivative is in the following order.

Acid chlorides > acid anhydrides > esters > amides

Conversions:

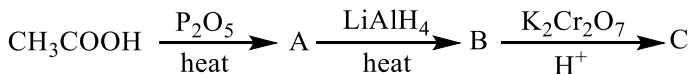
20) Identify A and B in the following sequence of reaction and give their IUPAC name.



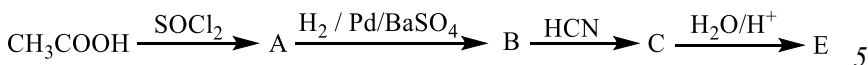
1

21) Identify the product A, B and C and give their IUPAC name.

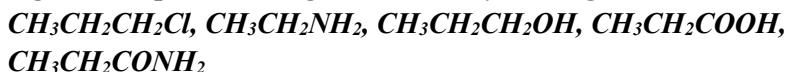
2



22) Identify each lettered compound in the following reaction sequence:



23) Represent a regular sequence of reaction of the following sets of organic compounds using suitable catalysts, reagents or conditions.



24) An aliphatic compound A reacts with SOCl_2 to give B. The compound B is heated with ammonia to produce C. The compound C is further heated with Br_2/KOH to yield D. The compound D gives E when treated with NaNO_2/HCl at low temperature. The compound E is primary alcohol which gives iodoform test. Identify A, B, C, D and E. Write reactions involved. 5

25) $\text{A} \xrightarrow{\text{NH}_3} \text{B} \xrightarrow{\text{Br}_2/\text{KOH}} \text{C} \xrightarrow{\text{HNO}_2} \text{D} \xrightarrow{\text{I}_2 / \text{NaOH}} \text{E}$
 Compound E produces Ethyne when heated with silver powder. Identify A, B, C, D and E. 5

26) An organic compound (A) of molecular formula $\text{C}_4\text{H}_8\text{O}_3$ undergoes acidic hydrolysis to give a carboxylic acid(B). When A is reduced with LiAlH_4 an alcohol (C) is produced. The alcohol (C) if oxidised with KMnO_4/H^+ , gives back (B)

i. Draw molecular structure of (A), (B) and (C) with reactions involved.

ii. What happens when (B) is heated with P_2O_5 ? [4+1]

27) An organic compound (A) of molecular formula $\text{C}_4\text{H}_8\text{O}_2$ undergoes acidic hydrolysis to give a carboxylic acid(B) and alcohol (C). When (B) is reduced with LiAlH_4 an alcohol (C) is produced. The alcohol (C) if oxidised with KMnO_4/H^+ , gives back (B)

i. Draw molecular structure of (A), (B) and (C) with reactions involved.

ii. What products would you expect when (A) is reduced with LiAlH_4 ? [4+1]

28) How would you convert Propanone to Ethanal? 2

29) How would you convert Ethanol into Methanol? 3

MCQs

- Which of the following acid derivative is most reactive?
 - Acid chloride
 - Amide
 - Ester
 - Acid anhydride
- Alcoholysis of acid derivatives give
 - Amide
 - Ester
 - Acid anhydride
 - Acid chloride
- An ester is obtained by the reaction between
 - An alkyl halide and a sodium alkoxide
 - An acid and a base
 - An alkyl halide and an alcohol
 - An alcohol and a carboxylic acid
- Ethanamide is obtained from Ethanoic acid by the reaction of
 - conc. H_2SO_4
 - P_2O_5
 - NH_3
 - anhy. AlCl_3
- Which of the following acid derivative is amphoteric?
 - Acid chloride
 - Acid anhydride
 - Ester
 - Amide
- Amide is
 - Ambident group
 - Acidic
 - Basic
 - Amphoteric
- The colourless liquid (A) reacts with sodium metal at room temperature to produce sodium salt of carboxylic acid and ammonia. Identify liquid compound(A).**
 - Propanamide
 - Formamide
 - propanoic acid
 - methyl ethanoate
- The process of conversion of an ester into a β keto ester is
 - Perkin condensation
 - Claisen condensation
 - Aldol condensation
 - Benzoin condensation

9. Claisen condensation results
- A β -keto ether
 - A β -hydroxy aldehyde
 - A β -keto ester
 - A β -hydroxy ketone
10. Acetic anhydride is obtained from acetyl chloride by the reaction of
- Conc. H_2SO_4
 - P_2O_5
 - CH_3COONa
 - CH_3COOH
11. Ester is obtained from acid anhydride by the reaction with
- Alcohol
 - water
 - amine
 - acid
12. Which among the following cannot undergo Claisen condensation?
- Methyl ethanoate
 - Ethyl methanoate
 - Ethyl ethanoate
 - Propyl ethanoate
13. An organic compound X reacts with NaOH and Br_2 to yield aminoethane. The probable organic compound X is;
- Ethanamide
 - Ethanenitrile
 - Propanenitrile
 - Propanamide
14. An organic compound A reacts with ethanol to produce ethyl ethanoate. The product ethyl ethanoate is further treated with ammonia to yield two products X and Y. The organic compounds A, X and Y are respectively;
- Ethanamide, ethanol and ethanoic acid
 - Ethanoic acid, ethanamine and ethanol
 - Ethanoic acid, ethanamide and ethanol
 - Ethanoic acid, ethanamide and ethanal
15. An organic compound A reacts with ammonia to give B. The compound B further reacts with Br_2 and KOH to yield methanamine. The organic compounds A and B are respectively;
- Ethanal and ethanamide

- b. Ethanoic acid and ethanamine
 - c. Ethanol and ethanamide
 - d. Ethanoic acid and ethanamide
16. But-2-ene undergoes ozonolysis to give A. The compound A reacts with acidified potassium dichromate to produce B. The compound B further reacts with P_2O_5 to yield C. The organic compounds A, B and C are respectively;
- a. Butanal, butanoic acid and butanoic anhydride
 - b. Ethanal, ethanoic acid and ethanoic anhydride
 - c. Ethanal, ethanoic acid and ethyl ethanoate
 - d. Butanal, butanoic acid and butyl butanoate
17. Ethanoic anhydride on treatment with methanol produces;
- a. ethanoic acid and ethyl methanoate
 - b. Ethanoic acid and ethyl ethanoate
 - c. ethanoic acid and methyl methanoate
 - d. Ethanoic acid and methyl ethanoate
18. An acid derivative reacts with Na to produce hydrogen as well reacts with HgO to yield respective salt and water. The probable acid derivative is;
- a. Ethanoic anhydride
 - b. Ethyl ethanoate
 - c. Ethanamide
 - d. Ethanoyl chloride
19. Acidic hydrolysis of ethanoic anhydride produces;
- a. Ethanoic acid and ethanol
 - b. Ethanol
 - c. Ethanol and ethyl acetate
 - d. Ethanoic acid
20. Ethanamide reacts with Br_2 and KOH to produce a compound X as major product. The compound X further reacts with HNO_2 to yield Y as the major product. The respective organic compounds X and Y are;
- a. Ethanamine and nitroethane
 - b. Methanamine and methanol

- c. Methanamine and nitromethane
 - d. Ethanamine and ethanol
21. An organic compound A reacts with SOCl_2 to produce B. The compound B further reacts with methanol to yield methyl ethanoate. The organic compounds A and B are respectively;
- a. Methanoic acid and methanoyl chloride
 - b. Ethanol and chloroethane
 - c. Methanol and chloromethane
 - d. Ethanoic acid and ethanoyl chloride
22. The products of the following reaction are:
- $$\text{C}_6\text{H}_5\text{COOCH}_3 + \text{LiAlH}_4 \rightarrow$$
- a. $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ and CH_3OH
 - b. $\text{C}_6\text{H}_5\text{-OH}$ and CH_3OH
 - c. $\text{C}_6\text{H}_5\text{CH}_3$ and CH_3OH
 - d. $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ and CH_4

Amides can be converted into amines by

- a. Perkin reaction b. Claisen reaction
- b. Hoffmann reaction d. kekule reaction

***** This is not a complete note. It is just to guide you. It is recommended to study prescribed textbooks along with this material. *****