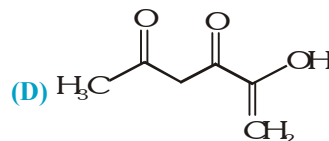
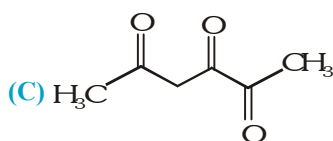
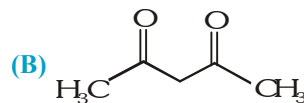
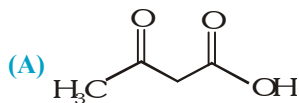


**SOLVED EXAMPLES**

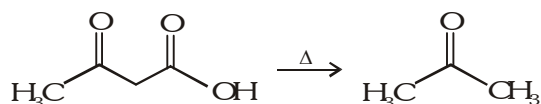
**Ex. 1** Which of the following does not undergo Hell-volhard Zelinsky reaction ?  
**(A)** HCOOH                      **(B)** CCl<sub>3</sub>COOH                      **(C)** C<sub>6</sub>H<sub>5</sub>COOH                      **(D)** All

**Sol.** **(D)** None of these contain alpha H-atom.

**Ex. 2** Which of the following compound would be expected to decarboxylate when heated :

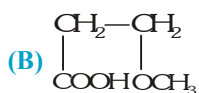
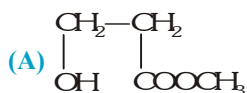


**Sol.** **(A)**



In case of β-keto acid, the decarboxylation occurs readily due to 6-membered low energy transition state formation.

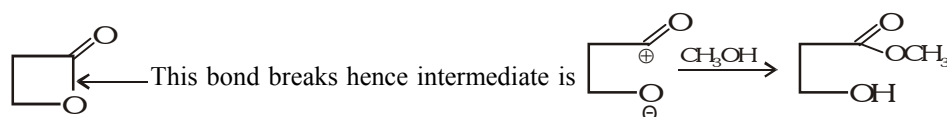
**Ex. 3** A ; A is ?



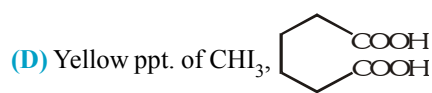
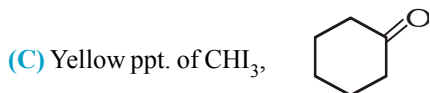
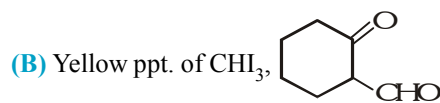
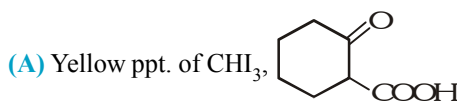
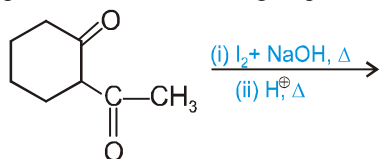
**(C)** both are correct

**(D)** None is correct

**Sol.** **(A)**



**Ex. 4** End product of the following sequence of reaction is :

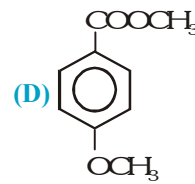
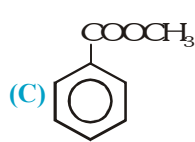
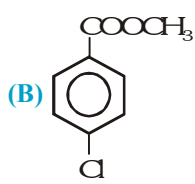
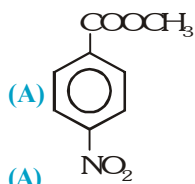


**Sol.** **(C)**

Intermediate is ; which loses CO<sub>2</sub> on heating (β-keto acid)

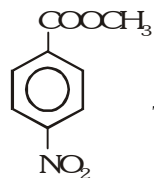


Ex. 10 The ease of alkaline hydrolysis is more for :



Sol.

(A)

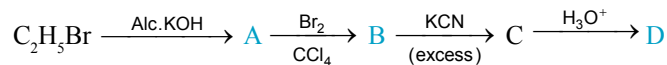


There is more electron deficiency on carbonyl carbon.

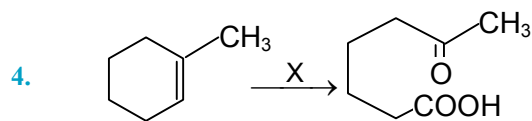
## Exercise # 1

[Single Correct Choice Type Questions]

1. The acid D obtained through the following sequence of reactions is

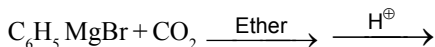


- (A) Succinic acid      (B) Malonic acid      (C) Maleic acid      (D) Oxalic acid
2. Pure acetic acid is known as glacial acetic acid because :
- (A) It is white liquid below 16.6°C      (B) It is solid as Ice below 16.6°C  
(C) It form ester with methanol      (D) None of the above
3. In which of the following reaction the final product is neither an acid nor an acid salt.

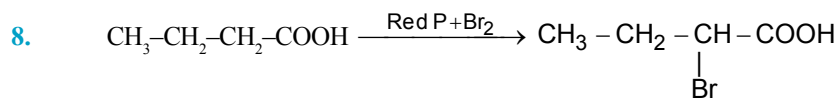


Reagent [X] is :

- (A) HCN      (B)  $\text{O}_3/\text{H}_2\text{O}$       (C) PCC      (D)  $\text{LiAlH}_4$
5. In the following reaction final product is :



- (A) Benzoic acid      (B) Benzaldehyde      (C) Benzamide      (D) Benzene
6. Which of the following does not give benzoic acid salt on oxidation with hot alkaline  $\text{KMnO}_4$ .
- (A)  $\text{Ph-CH}_3$       (B)  $\text{Ph-CH=CH-CH}_3$       (C)  $\text{Ph-C}\equiv\text{C-CH}_3$       (D)  $\text{Ph-C}(\text{CH}_3)_3$
7. Which of the following will not undergo Hell-Volhard Zelinsky (HVZ) reaction ?
- (A) HCOOH      (B)  $\text{CH}_3\text{COOH}$       (C)  $\text{CH}_3\text{CH}_2\text{COOH}$       (D)  $\text{CH}_3\text{CHBrCOOH}$ .



This reaction is called

- (A) Cannizzaro reaction      (B) Schmidt reaction  
(C) Hell Volhard Zelinsky reaction      (D) Reimer tiemann reaction
9. What product is formed when acetic acid heated with  $\text{P}_2\text{O}_5$ .
- (A) Acetyl chloride      (B) Acetate ester  
(C) Acetic anhydride      (D) Acetaldehyde
10. Formic acid can be distinguish from acetic acid because formic acid :
- (A) release  $\text{H}_2$  with sodium      (B) gives ester with alcohol  
(C) reduces  $\text{AgNO}_3$       (D) turns red litmus to blue

## CHEMISTRY FOR JEE MAIN & ADVANCED

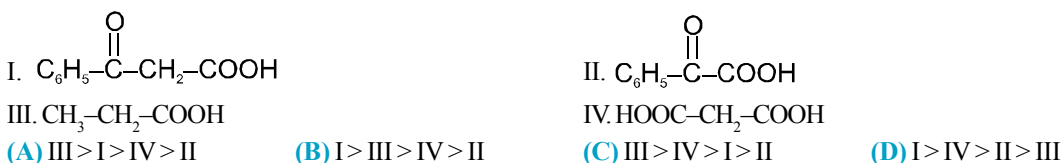
11. Sodium bicarbonate reacts with salicylic acid to form:



12. Which of the following methods is not used for the conversion of carboxylic acids into acid halides ?



13. For the following acids the rate of decarboxylation on heating would be :



14. Which of the following will not yield a cyclic compound on heating :



15. Which optically active compound on reduction with  $LiAlH_4$  will give optically inactive compound?



16.  $RCOOH \longrightarrow RCH_2COOH$ . This conversion is known as reaction :



17. The reaction :  $RCOOAg + Br_2 \xrightarrow{CCl_4, \text{Reflux}} R-Br + AgBr + CO_2$

is called



18. Benzoyl chloride on treatment with ammonia gives

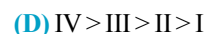
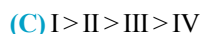
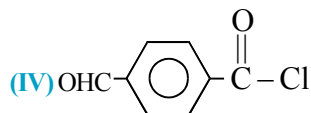
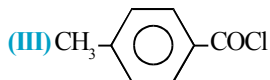
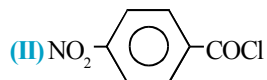
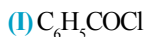


19. The product formed by the reaction of acetamide with  $Br_2$  in presence of  $NaOH$  is :

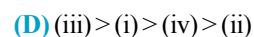
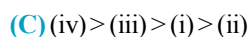
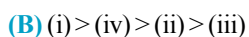
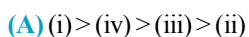
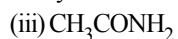


## CARBOXYLIC ACID AND THEIR DERIVATIVES

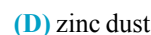
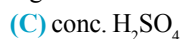
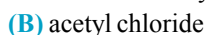
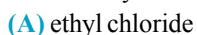
20. Arrange following compounds in decreasing order of reactivity for hydrolysis reaction :



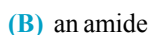
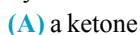
21. The decreasing order of reactivity towards nucleophilic acyl substitution is



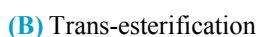
22. Acetic anhydride is prepared in the laboratory by heating sodium acetate with



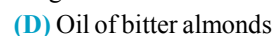
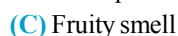
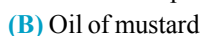
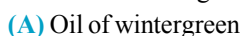
23. Synthesis of an ester involves the reaction of alcohols with



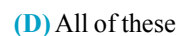
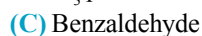
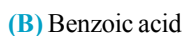
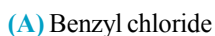
24. The reaction,  $RCOOR' + R''OH \xrightarrow{H^+ \text{ or } OH^-} RCOOR'' + R'OH$  is called.



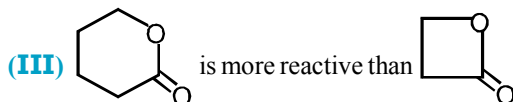
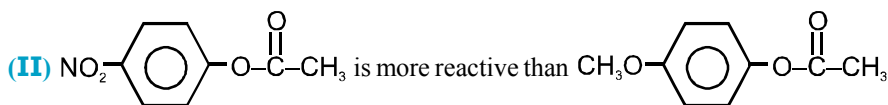
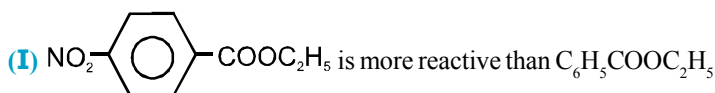
25. Ethanol on heating with acetic acid in the presence of a few drops of sulphuric acid gives the smell of



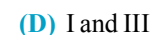
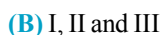
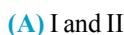
26. The reduction of benzoyl chloride with Pd and  $BaSO_4/CaCO_3$  produces:



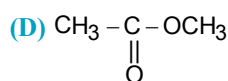
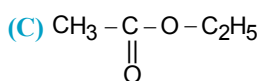
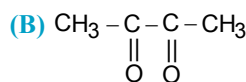
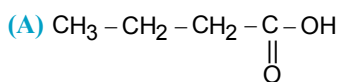
27. Consider the following statements for hydrolysis reaction :



Of these the correct statements are

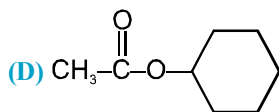
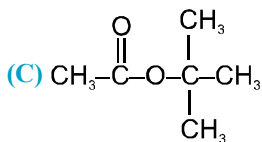
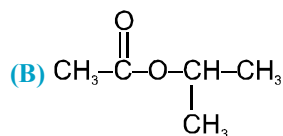
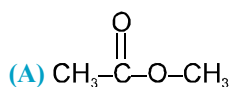


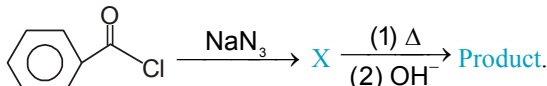
28. An organic compound X ( $C_4H_8O_2$ ) gives positive test with NaOH and phenolphthalein. Structure of X will be :



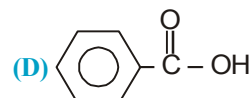
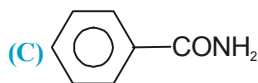
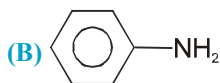
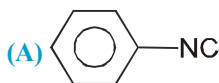
## CHEMISTRY FOR JEE MAIN & ADVANCED

29. Which one of the following esters is the most reactive for saponification ?

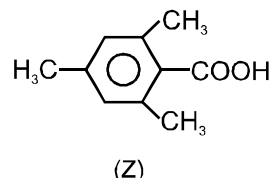
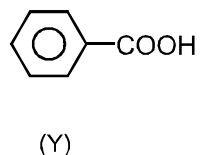
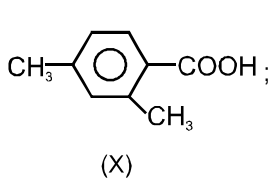


30.   $\text{C}_6\text{H}_5\text{COCl} \xrightarrow{\text{NaN}_3} \text{X} \xrightarrow[\text{(2) OH}^-]{\text{(1) } \Delta} \text{Product.}$

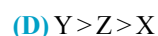
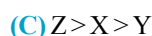
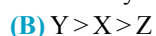
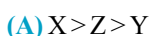
Product is/are



31. Given three acids

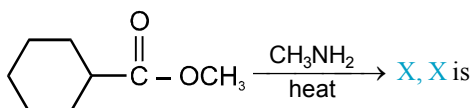


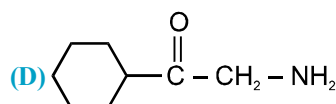
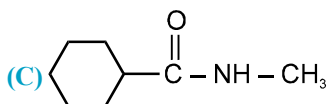
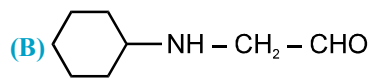
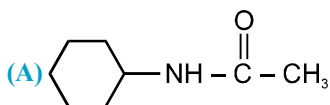
The correct order of ease of acid catalysed esterification is :



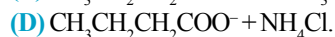
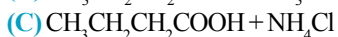
32. A compound with molecular formula  $\text{C}_4\text{H}_{10}\text{O}_4$  on acylation with acetic anhydride gives a compound with molecular formula  $\text{C}_{12}\text{H}_{18}\text{O}_8$ . How many hydroxyl groups are present in the compound ?



33.   $\text{C}_6\text{H}_{11}\text{COOCH}_3 \xrightarrow[\text{heat}]{\text{CH}_3\text{NH}_2} \text{X, X is}$



34.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CONH}_2$  is boiled with aqueous  $\text{NaOH}$ , then the reaction mixture is acidified with  $\text{HCl}$ . The products obtained are







## CHEMISTRY FOR JEE MAIN & ADVANCED

45. Among the following, which is the strongest acid?  
 (A)  $\text{CHF}_2-\text{CH}_2-\text{CH}_2-\text{COOH}$  (B)  $\text{CH}_3-\text{CH}_2-\text{CF}_2-\text{COOH}$   
 (C)  $\text{CH}_2\text{F}-\text{CHF}-\text{CH}_2-\text{COOH}$  (D)  $\text{CH}_3-\text{CF}_2-\text{CH}_2-\text{COOH}$
46. In the Rosenmund reduction, the catalyst used is:  
 (A) Pd/BaSO<sub>4</sub> (B) Raney Ni (C) Sn/HCl (D) Zn/HCl
47. In a set of the given reactions, acetic acid yielded a product C.  

$$\text{CH}_3\text{COOH} + \text{PCl}_5 \longrightarrow \text{A} \xrightarrow[\text{AlCl}_3]{\text{C}_6\text{H}_6} \text{B} \xrightarrow[\text{(ii) H}_3\text{O}^+]{\text{(i) C}_2\text{H}_5\text{MgBr/ether}} \text{C}$$
; product C would be:-  
 (A)  $\text{CH}_3\text{CH}(\text{OH})\text{C}_2\text{H}_5$  (B)  $\text{CH}_3\text{COC}_6\text{H}_5$  (C)  $\text{CH}_3\text{CH}(\text{OH})\text{C}_6\text{H}_5$  (D)  $\text{CH}_3-\overset{\text{C}_2\text{H}_5}{\underset{\text{OH}}{\text{C}}}\text{C}_6\text{H}_5$
48. The correct reactivity order with the nucleophile is :  
 (A)  $\text{CH}_3\text{COCl} > \text{CH}_3\text{CONH}_2 > \text{CH}_3\text{COOCH}_3$   
 (B)  $\text{CH}_3\text{COCl} > \text{CH}_3\text{COOCH}_3 > \text{CH}_3\text{CONH}_2$   
 (C)  $\text{CH}_3\text{CONH}_2 > \text{CH}_3\text{COOCH}_3 > \text{CH}_3\text{COCl}$   
 (D)  $\text{CH}_3\text{COOCH}_3 > \text{CH}_3\text{COCl} > \text{CH}_3\text{CONH}_2$
49. 
$$\text{CH}_3-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2 \xrightarrow{\text{A}} \text{CH}_3-\text{CH}_2-\text{NH}_2 \xrightarrow{\text{B}} \text{CH}_3-\text{CH}_2-\text{OH}$$
  
 In the above sequence A & B respectively are -  
 (A) Br<sub>2</sub>/KOH, NaOH (B) Br<sub>2</sub>/KOH, HNO<sub>2</sub> (C) KMnO<sub>4</sub>, KOH (D) HNO<sub>2</sub>, Br<sub>2</sub>/KOH
50. Which of the following carboxylic acids undergoes decarboxylation easily?  
 (A)  $\text{C}_6\text{H}_5\text{COCH}_2\text{COOH}$  (B)  $\text{C}_6\text{H}_5\text{COCOCH}_3$  (C)  $\text{C}_6\text{H}_5\underset{\text{OH}}{\text{CH}}-\text{COOH}$  (D)  $\text{C}_6\text{H}_5\underset{\text{NH}_2}{\text{CH}}\text{COOH}$
51. The reactivities of acid halides (I), anhydrides (II), esters (III) and amides (IV) with nucleophilic reagents follow the order  
 (A) I > II > III > IV (B) IV > III > II > I (C) I > III > II > IV (D) III > II > I > IV
52. In the following sequence of reactions  

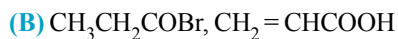
$$\text{C}_6\text{H}_6 + \text{CH}_3\text{CH}_2\text{COCl} \xrightarrow{\text{AlCl}_3} \text{A} \xrightarrow[\text{conc. HCl, Heat}]{\text{Zn (Hg)}} \text{B}$$
  
 the product (B) is:  
 (A)  $\text{PhCOCH}_2\text{CH}_3$  (B)  $\text{PhCHOHCH}_2\text{CH}_3$  (C)  $\text{PhCH}_2\text{CH}_2\text{CH}_3$  (D)  $\text{PhCH}=\text{CHCH}_3$
53. Kolbe electrolysis of potassium succinate gives CO<sub>2</sub> and ..... :  
 (A) C<sub>2</sub>H<sub>6</sub> and KOH (B) C<sub>2</sub>H<sub>2</sub> and KOH  
 (C) C<sub>2</sub>H<sub>4</sub>, KOH and H<sub>2</sub> (D) CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub>
54. In the following reaction identify compounds A, B, C and D :  

$$\text{PCl}_5 + \text{SO}_2 \longrightarrow \text{A} + \text{B};$$
  

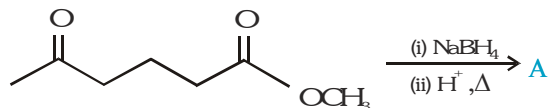
$$\text{A} + \text{CH}_3\text{COOH} \longrightarrow \text{C} + \text{SO}_2 + \text{HCl}$$
  

$$2\text{C} + (\text{CH}_3)_2\text{Cd} \longrightarrow \text{D} + \text{CdCl}_2$$
  
 (A) SOCl<sub>2</sub>, POCl<sub>3</sub>, CH<sub>3</sub>COCl, CH<sub>3</sub>COCH<sub>3</sub> (B) SOCl<sub>2</sub>, HCl, CH<sub>3</sub>Cl, CH<sub>3</sub>CHO  
 (C) SO<sub>2</sub>, Cl<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>Cl, CH<sub>3</sub>COCH<sub>3</sub> (D) None of these

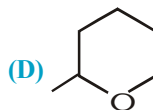
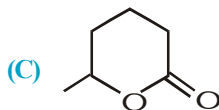
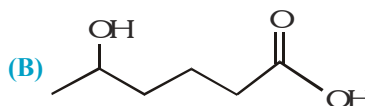
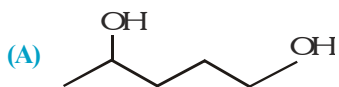
55. What are A and B in the following sequence of reactions :



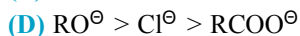
56. Consider the following reaction.



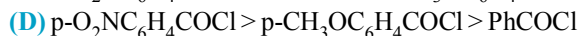
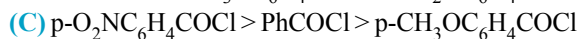
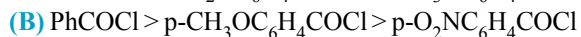
The product (A) is :



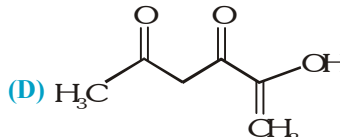
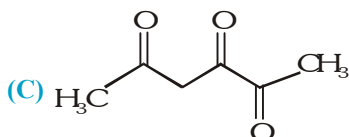
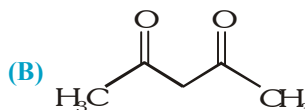
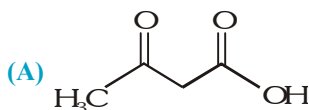
57. Which of the following orders regarding the base strength of a leaving group in a reaction of an acid derivative with a nucleophile is correct :

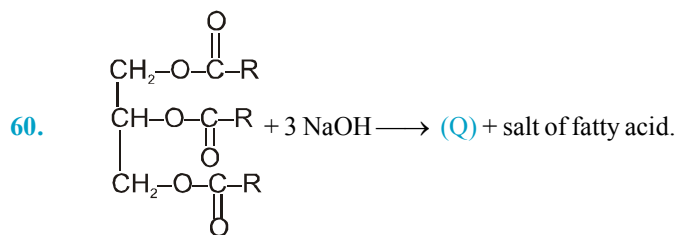


58. The correct sequence of decreasing order of reactivity of hydrolysis of acid chlorides is :



59. Which of the following compound would be expected to decarboxylates when heated :-

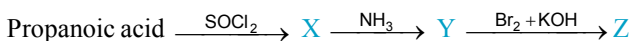




Product (Q) of the reaction is

- (A) Ethylene glycol (B) Glycerol  
(C) Glyceryl tri nitrate (explosive) (D) Cumene hydrogen peroxides

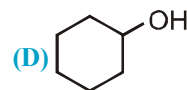
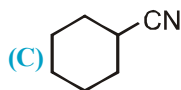
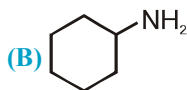
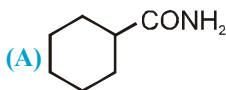
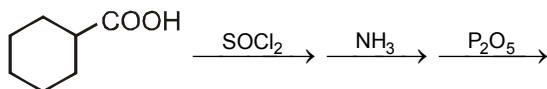
61. Starting from propanoic acid, the following reactions were carried out



What is the compound Z

- (A)  $\text{CH}_3\text{-CH}_2\text{-Br}$  (B)  $\text{CH}_3\text{-CH}_2\text{-NH}_2$   
(C)  $\text{CH}_3\text{-CH}_2\text{-C}(=\text{O})\text{Br}$  (D)  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-NH}_2$

62. Identify the final product in the following sequence of reaction.



63. Which of the following does not give benzoic acid on hydrolysis ?

- (A) Phenyl cyanide (B) Benzoyl chloride (C) Benzyl chloride (D) Methyl benzoate

64. When excess of chlorine is passed through acetic acid in presence of red phosphorus, it forms

- (A) Acetic anhydride (B) Chloral (C) Trichloroacetic acid (D) Methyl chloride.

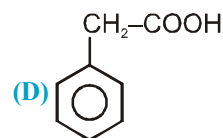
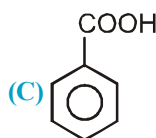
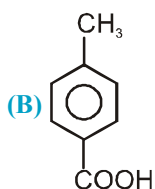
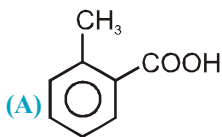
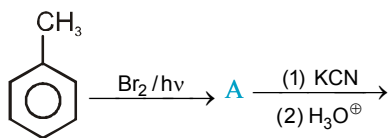
65. Acetamide and ethyl acetate can be distinguished by reacting with

- (A) Aqueous HCl and heat (B) Aqueous NaOH and heat  
(C) Acidified  $\text{KMnO}_4$  (D) Bromine water.

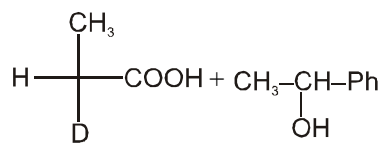
66. Which of the following acids remains unaffected on heating

- (A) Malonic acid (B) Malic acid (C) Fumaric acid (D) Succinic acid

67. Identify the final product in the following sequence of reaction.

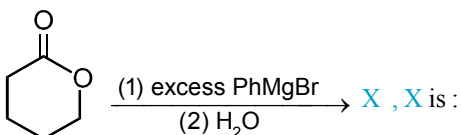


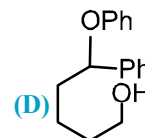
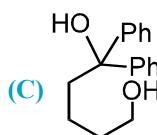
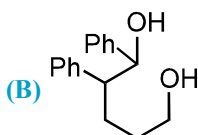
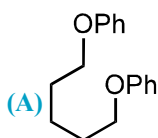
68. Esterification of the acid (P) with the alcohol (Q) will give



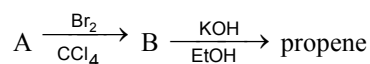
(R-configuration)      ( $\pm$ )

- (A) only one enantiomer      (B) a mixture of diastereomer  
(C) a mixture of enantiomer      (D) only one fraction on fractional distillation

69.  X, X is :

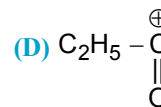
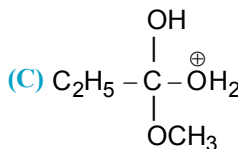
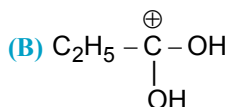
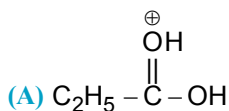


70. The compound (A) in the following sequence of reactions is a silver salt of

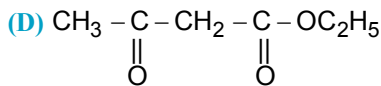
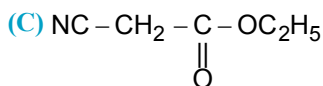
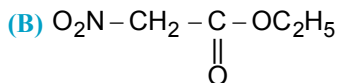


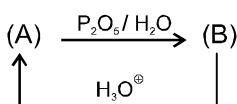
- (A) Propanoic acid      (B) Butyric acid      (C) isobutyric acid      (D) Both (B) and (C)

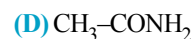
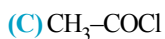
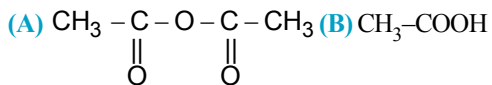
71. In the esterification of propanoic acid with methanol in the presence of a mineral acid, which is not the expected intermediate species ?



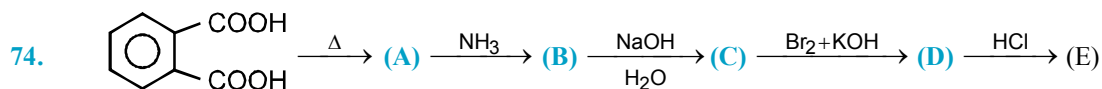
72. Which of the following ester have most acidic  $\alpha$ -hydrogen atom.



73.  (A) would be : (A)

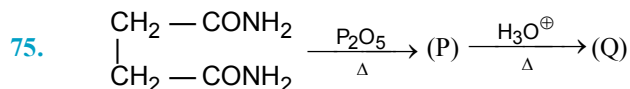


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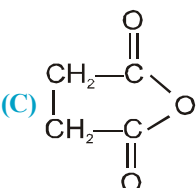


In this reaction the product (E) is :

- (A) o-nitrobenzoic acid    (B) Salicylic acid    (C) anthranilic acid    (D) Crotonic acid



The product (Q) is

- (A)  $\text{CH}_3 - \text{CH}_2 - \text{COOH}$     (B)  $\begin{array}{c} \text{CH}_2 - \text{COOH} \\ | \\ \text{CH}_2 - \text{COOH} \end{array}$     (C)     (D)  $\text{CH}_3 - \text{COOH}$

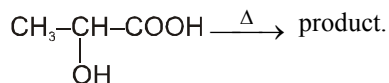
76. Which of the following is correct order of esterification of following acids with  $\text{CH}_3\text{OH}$  :

$\text{HCOOH}$  ,  $\text{CH}_3\text{COOH}$  ,  $\text{CH}_3 - \text{CH}_2 - \text{COOH}$  ,  $\begin{array}{c} \text{CH}_3 - \text{CH} - \text{COOH} \\ | \\ \text{CH}_3 \end{array}$

I                      II                      III                      IV

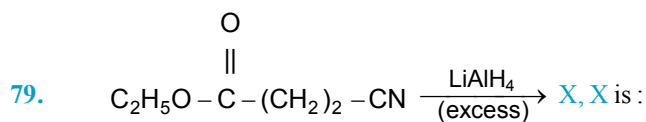
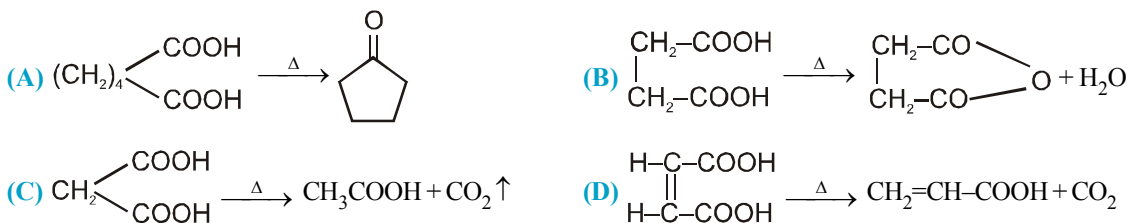
- (A)  $\text{I} = \text{II} = \text{III} = \text{IV}$     (B)  $\text{I} > \text{II} > \text{III} > \text{IV}$     (C)  $\text{I} < \text{II} < \text{III} < \text{IV}$     (D)  $\text{I} > \text{IV} > \text{III} > \text{II}$

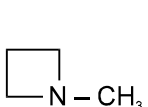
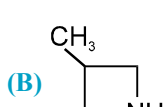
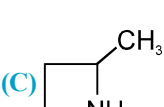
77. Identify final product in the following reaction

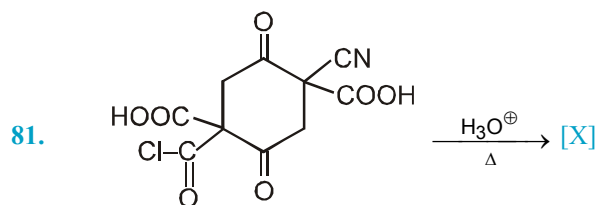
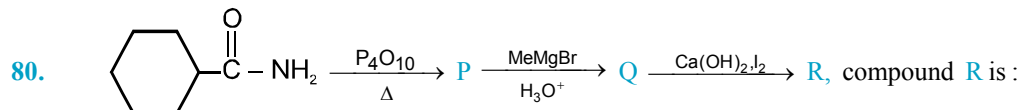


- (A)     (B)  $\text{CH}_2 = \text{CH} - \text{COOH}$     (C)  $\begin{array}{c} \text{CH}_3 - \text{C} - \text{COOH} \\ || \\ \text{O} \end{array}$     (D)  $\text{CH}_3 - \text{CH}_2 - \text{OH}$

78. Which of the following reaction represents **incorrect** product.



- (A)     (B)     (C)     (D) 



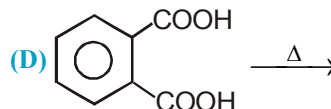
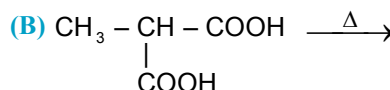
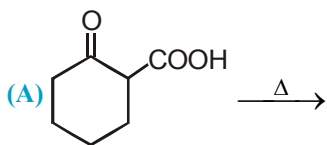
Select the correct **statement**.

- (A) X gives effervescence of  $\text{CO}_2$  with  $\text{NaHCO}_3$   
 (B) X will produce alkane when treated with  $\text{Zn-Hg/HCl}$   
 (C) X will produce symmetrical diketone when treated with soda lime  
 (D) All of these
82. In order to prepare acetone from  $\text{CH}_3\text{COCl}$  in one step, which of the reagent is best?  
 (A)  $\text{H}_2/\text{Pd-BaSO}_4$  (B)  $\text{HI}$  (C)  $\text{CH}_3\text{MgCl}$  (D)  $(\text{CH}_3)_2\text{Cd}$

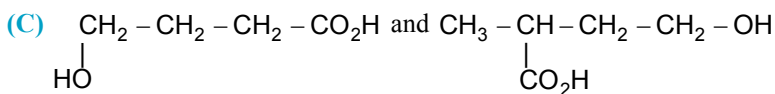
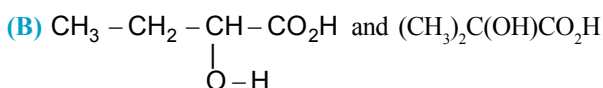
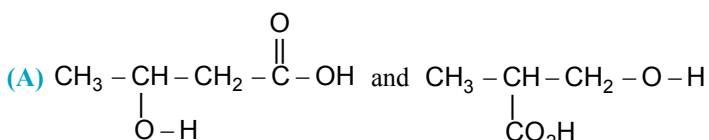
Exercise # 2

Part # I [Multiple Correct Choice Type Questions]

1. Which of them liberate a gas which turns lime water milky.

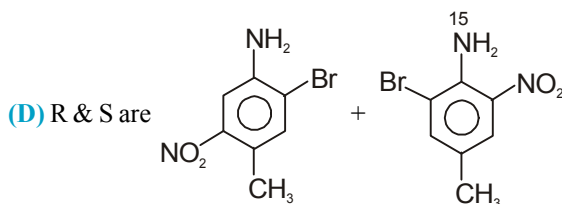
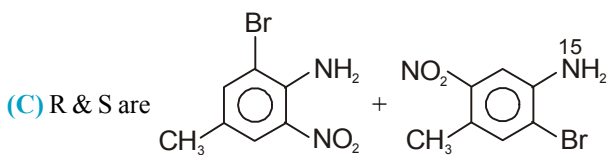
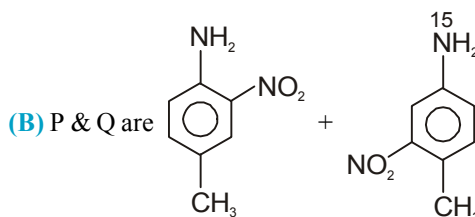
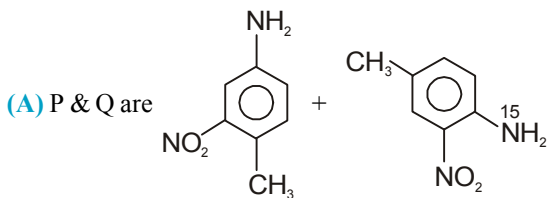
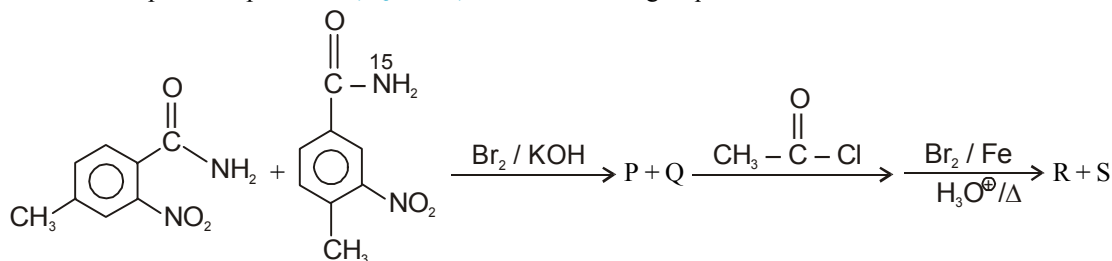


2. Which pair of compounds on heating give isomeric products



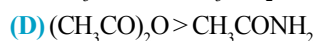
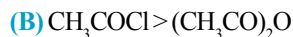
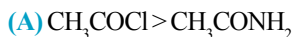
(D) None of these

3. The correct option for products P, Q and R, S in the following sequence of reaction is / are :

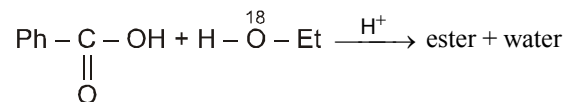


## CARBOXYLIC ACID AND THEIR DERIVATIVES

4. The correct order/s of decreasing reactivity of the given compound towards hydrolysis under identical condition is/ are :

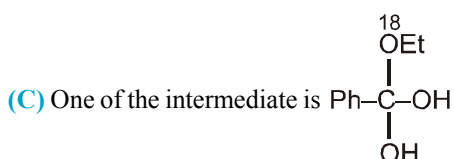


5. The correct statements about following reaction are :



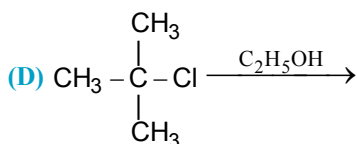
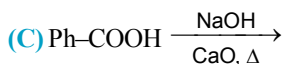
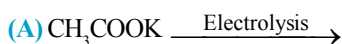
(A) It is an equilibrium reaction

(B)  $\text{O}^{18}$  is found in ester



(D)  $\text{EtOH}^{18}$  ionises to  $\text{Et}^{\oplus}$  in this reaction

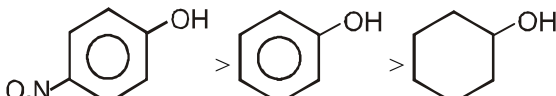
6. In which reaction product is hydrocarbon?



7. Which are correct against property mentioned ?

(A)  $\text{CH}_3\text{COCl} > (\text{CH}_3\text{CO})_2\text{O} > \text{CH}_3\text{COOEt} > \text{CH}_3\text{CONH}_2$  (Rate of hydrolysis)

(B)  $\text{CH}_3-\text{CH}_2-\text{COOH} > \text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{COOH} > \text{CH}_3-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{COOH}$  (Rate of esterification)

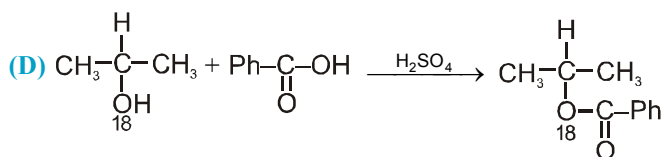
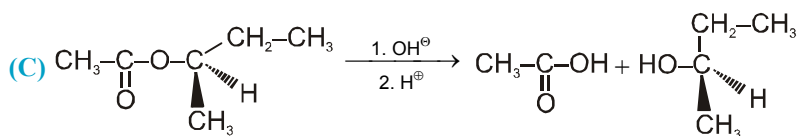
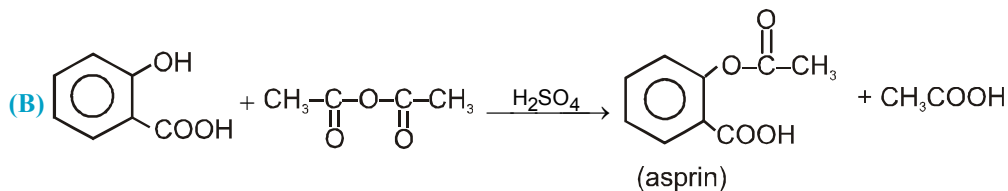
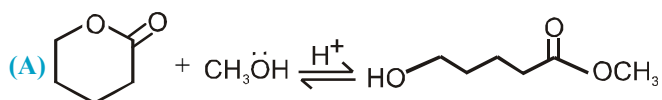
(C)  (Rate of esterification)

(D)  $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{COOH} > \text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{COOH} > \text{Ph}-\text{CH}_2-\text{COOH}$  (Rate of decarboxylation)

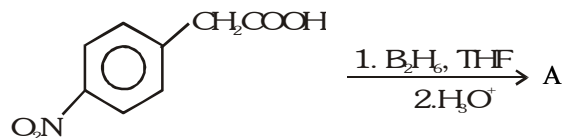


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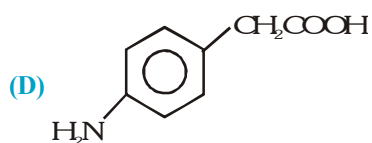
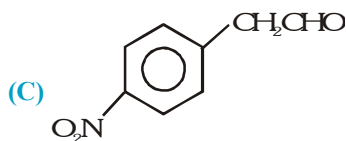
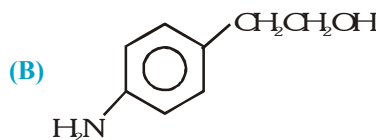
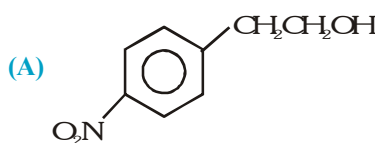
8. In which of the following reactions correct major product is mentioned ?



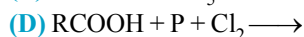
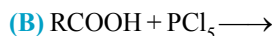
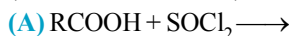
9. Consider the following reaction.



The product (A) is



10. Which of the following methods are used for the conversion of carboxylic acids into acid chlorides ( $\text{RCOOH} \rightarrow \text{RCOCl}$ )?



11. Which of the following statements are correct for benzoic acid ?

(A) Nitration gives o-and p-nitrobenzoic acid.

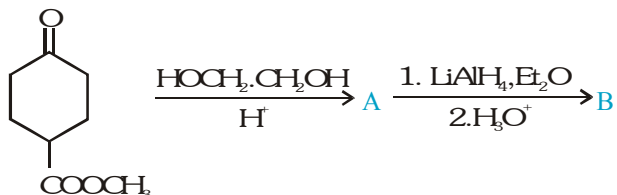
(B) Bromination ( $\text{Br}_2/\text{FeBr}_3$ ) gives m-bromobenzoic acid.

(C) The Friedel-Crafts reaction with  $\text{CH}_3\text{COCl}/\text{AlCl}_3$  gives m-carboxyacetophenone.

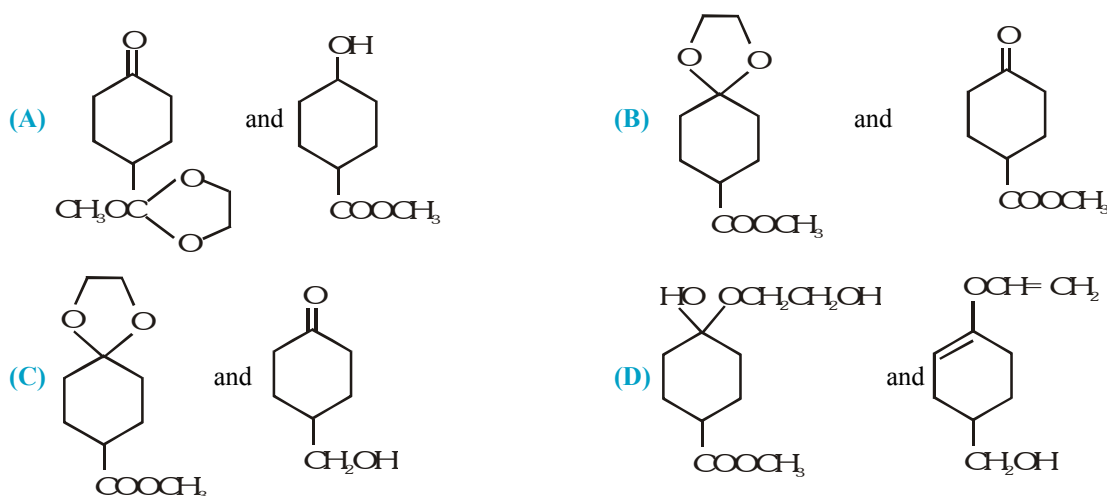
(D) The reaction with concentrated sulphuric acid gives 3-carboxybenzenesulphonic acid.

## CARBOXYLIC ACID AND THEIR DERIVATIVES

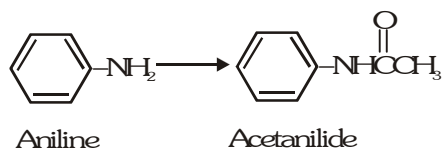
12. Which of the following reactions involve a decrease in the length of the carbon chain :-  
 (A) Schmidt reaction (C) Hofmann's bromamide reaction  
 (C) Hell-Volhard-Zelinski reaction (D) All of these
13. Dry distillation of a mixture of calcium formate and the calcium acetate gives –  
 (A) HCHO (B) CH<sub>3</sub>CHO (C) CH<sub>3</sub>COCH<sub>3</sub> (D) None
14. Consider the following sequence of reactions.



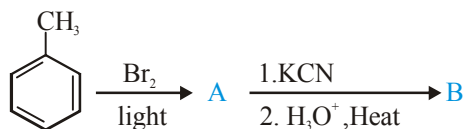
The products (A) and (B) are, respectively,



15. Which of the following compounds react with aniline to give acetanilide :  
 Which of the following compounds react with aniline to give acetanilide.

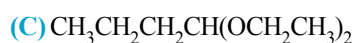


16. What is the final product (B) of this sequence :

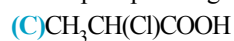
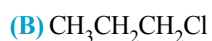


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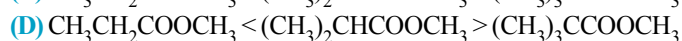
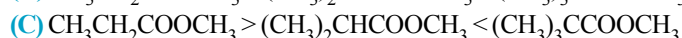
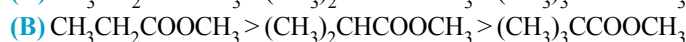
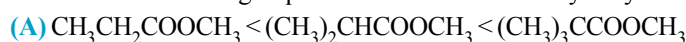
17. What is compound Z :



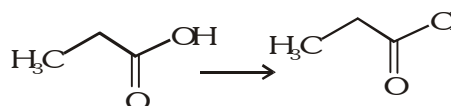
18. The treatment of  $\text{CH}_3\text{CH}_2\text{COOH}$  with chlorine in the presence of phosphorus gives :

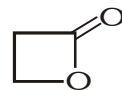


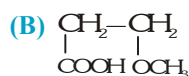
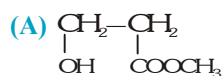
19. Which of the following sequences of rate of alkaline hydrolysis of esters is correct :



20. Which of the following is used to perform following transformation :



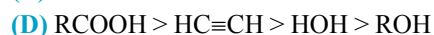
21.  A, A is :



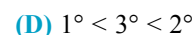
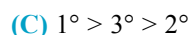
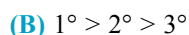
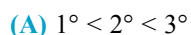
(C) Both are correct

(D) None is correct

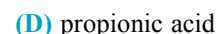
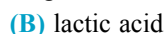
22. Which of the following orders of acid strength is correct :



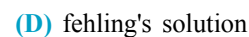
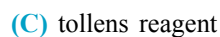
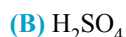
23. The relative order of esterification of alcohols is :-



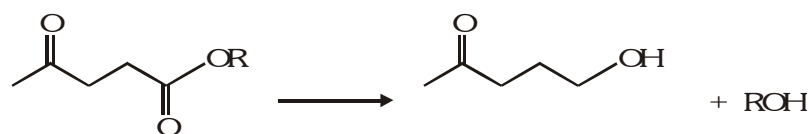
24. Which of the following does not give iodoform :

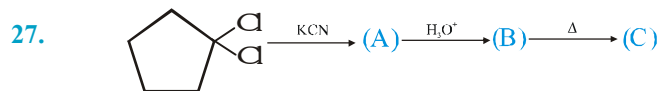


25. One can distinguish between  $\text{HCOOH}$  and  $\text{CH}_3\text{COOH}$  with :



26. Which of the following reagents are involved in the following transformation ?





Identify the correct statement(s) about the above sequence of reactions :

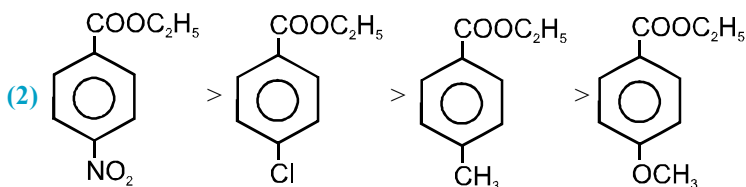
- (A) Compound (A) is formed through  $S_N$  reaction  
 (B) Compound (C) on reduction with  $LiAlH_4$  forms a product which on dehydration gives cyclohexene.  
 (C) compound (A) requires two moles of hydrogen for complete reduction.  
 (D) Compound (C) on Schmidt's reaction gives a product which reacts with  $HNO_2$  to give (D) as major product.  
 Compound (D) on dehydration gives cyclopentene
28. Which of the following on reduction with  $LiAlH_4$  will give ethyl alcohol ?  
 (A)  $(CH_3CO)_2O$       (B)  $CH_3COCl$       (C)  $CH_3CONH_2$       (D)  $CH_3COOC_2H_5$

## Part # II

## [Assertion &amp; Reason Type Questions]

These questions contains, Statement-I (assertion) and Statement-II (reason).

- (A) Statement-I is True, Statement-II is True ; Statement-II is a correct explanation for Statement-I  
 (B) Statement-I is True, Statement-II is True ; Statement-II is NOT a correct explanation for Statement-I  
 (C) Statement-I is True, Statement-II is False.  
 (D) Statement-I is False, Statement-II is True.
- Statement-I :** Benzoic acid on nitration will give m-Nitro benzoic acid.  
**Statement-II :**  $-COOH$  group will increase  $e^-$  density on meta position.
  - Statement-I :** Acyl halide are more reactive than acid substance amide towards nucleophilic substitution.  
**Statement-II :**  $X^-$  are better leaving group than  $NH_2^-$ .
  - Statement-I :** Unlike the  $>C=O$  group of aldehydes and ketones, the  $>C=O$  of  $R-\overset{O}{\parallel}{C}-OH$  does not undergo nucleophilic addition reactions.  
**Statement-II :** Carboxylic acids exist as dimers due to intermolecular hydrogen bonding in aprotic medium.
  - Statement-I :**  $CH_3COCH_2COOC_2H_5$  will give iodoform test.  
**Statement-II :** It contains  $CH_3-\overset{O}{\parallel}{C}-$  group linked to a carbon atom.
  - Statement-I :** Acetic acid does not undergo haloform reaction.  
**Statement-II :** Acetic acid has no  $\alpha$  hydrogen.
  - Statement-I :** Carboxylic acids have a carbonyl group but they do not give the test of carbonyl group.  
**Statement-II :** Due to resonance, the double bond character of carbonyl group is greatly reduced.
  - Statement-I :** The order of base catalysed hydrolysis of ester is  
 (1)  $CH_3-COOC_2H_5 > CH_3-COOC_2H_5 > CH_3-COOCH(CH_3)_2$ .



**Statement-II :**  $S_N2$  The reaction is sterically as well as electronically controlled reaction.

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8. **Statement-I:** Acid catalysed hydrolysis of ester is reversible while base catalysed hydrolysis is irreversible.  
**Statement-II:** In acid catalysed ester hydrolysis carboxylic acid is formed on which nucleophilic attack of alcohol is possible but in base catalysed ester hydrolysis carboxylate anion is formed on which nucleophilic attack is not possible.
9. **Statement-I:** 1° Amides react with Br<sub>2</sub> in presence of NaOH to form 1°-amine having one carbon atom less than amide.  
**Statement-II:** It is degradative reduction involving N-bromoalkanamide intermediate.
10. **Statement-I:** Acetic acid does not give haloform reaction.  
**Statement-II:** Acetic acid has no α-hydrogen.
11. **Statement-I:** Formic acid reduces mercuric chloride.  
**Statement-II:** Formic acid has reducing aldehydic group.
12. **Statement-I:** Acetate ion is more basic than the methoxide ion.  
**Statement-II:** The methoxide ion is resonance stabilized.
13. **Statement-I:** p-Hydroxybenzoic acid has a lower boiling point than o-hydroxybenzoic acid.  
**Statement-II:** o-Hydroxybenzoic acid has intermolecular hydrogen bonding.

## Exercise # 3

## Part # I

## [Matrix Match Type Questions]

1. Match the column I with column II.

**Column-I**

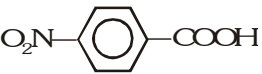
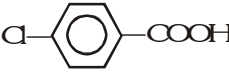
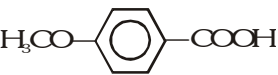
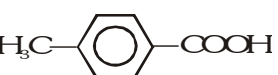
- (A) Schimidt reaction  
 (B) Curtius reaction  
 (C) Decarboxylation  
 (D) HVZ reaction

**Column-II**

- (p)  $\text{RCOOH} \xrightarrow[\Delta]{\text{NaOH/CaO}} \text{RH}$   
 (q)  $\text{R-CH}_2\text{COOH} \xrightarrow[\Delta]{\text{Red P/X}_2} \text{R}-\underset{\text{X}}{\text{CH}}-\text{COOH}$   
 (r)  $\text{RCOCl} \xrightarrow[\Delta]{\text{NaN}_3} \text{RNH}_2$   
 (s)  $\text{RCOOH} \xrightarrow[\Delta]{\text{N}_3\text{H}} \text{RNH}_2$

2. Match the column I with column II.

**Column-I (Acid)**

- (A) Benzoic acid  
 (B)   
 (C)   
 (D)   
 (E) 

**Column-II (K<sub>a</sub>)**

- (p)  $3.3 \times 10^{-5}$   
 (q)  $10.2 \times 10^{-5}$   
 (r)  $30.6 \times 10^{-5}$   
 (s)  $6.4 \times 10^{-5}$   
 (t)  $4.2 \times 10^{-5}$

3. Match the column I with column II.

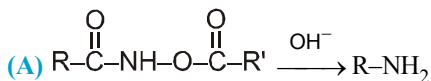
**Column-I (Reaction)**

- (A) Arndt Eistert synthesis  
 (B) Hunsdiecker reaction  
 (C) Claisen condensation  
 (D) Esterification reaction

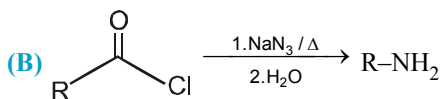
**Column-II (Possible products)**

- (p) Carbanion  
 (q) Carbocation  
 (r) Ketene  
 (s) Free radical

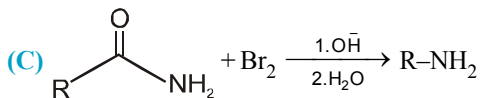
4. Select the correct name for the given reactions :



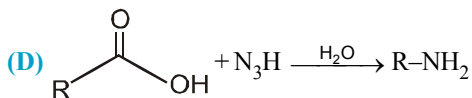
(p) Curtius reaction



(q) Hoffmann's reaction



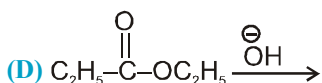
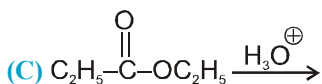
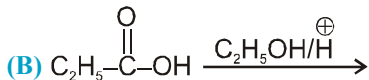
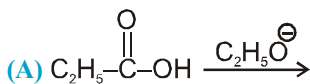
(r) Schmidt reaction



(s) Lossen rearrangement

5. Match the column

Column-I



Column-II

(p) Hydrolysis

(q) Esterification

(r) Saponification

(s) Acid base reaction

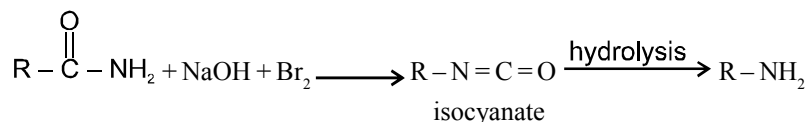
Part # II

[Comprehension Type Questions]

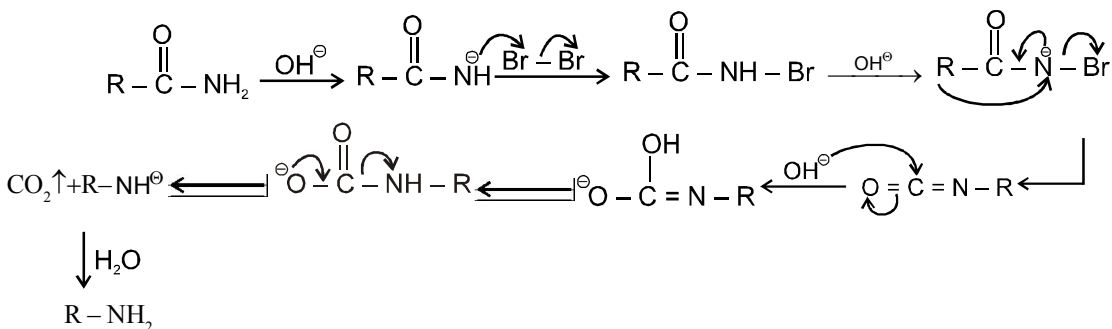
Comprehension # 1

In the Hofmann rearrangement an unsubstituted amide is treated with sodium hydroxide and bromine to give a primary amine that has one carbon lesser than starting amide.

General reaction :

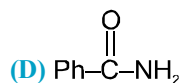
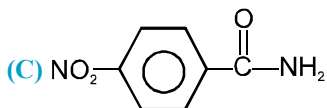
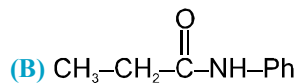
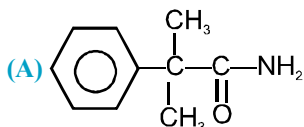


Mechanism :



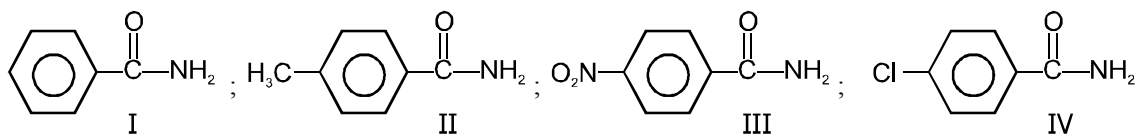
If the migrating group is chiral then its configuration is retained. Electron releasing effects in the migrating group increases reactivity of Hofmann rearrangement.

1. Which of the following compound(s) cannot give Hoffmann rearrangement :

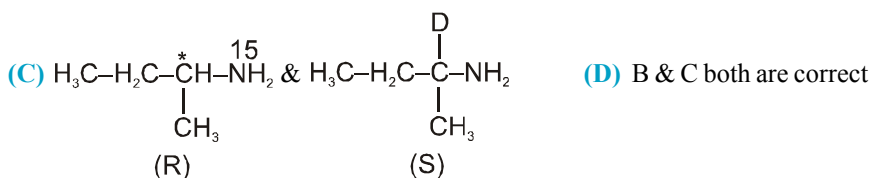
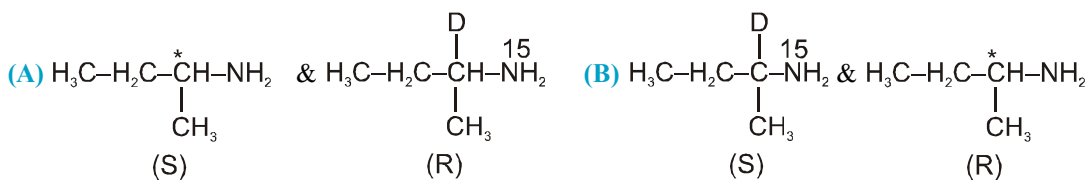
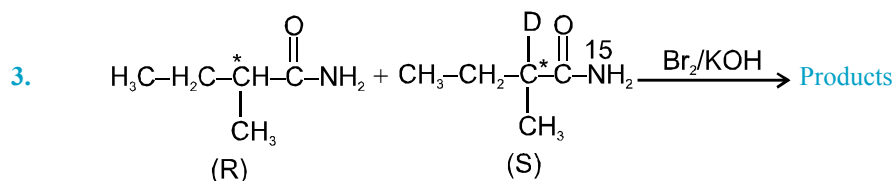


## CARBOXYLIC ACID AND THEIR DERIVATIVES

2. Arrange the following amides according to their relative reactivity when reacted with  $\text{Br}_2$  in excess of strong base

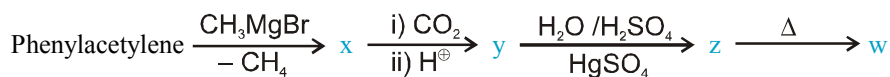


- (A)  $\text{IV} > \text{I} > \text{II} > \text{III}$       (B)  $\text{II} > \text{I} > \text{III} > \text{IV}$       (C)  $\text{II} > \text{IV} > \text{III} > \text{I}$       (D)  $\text{II} > \text{I} > \text{IV} > \text{III}$

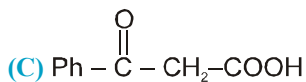
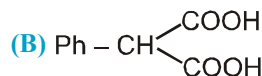
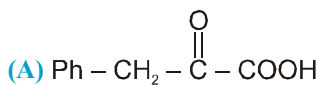


### Comprehension # 2

Observe the following sequence of reaction and answer the questions based on it



1. Compound  $\text{z}$  is :



2. Which of the following statement is not correct

- (A)  $\text{y}$  decolourises  $\text{Br}_2/\text{H}_2\text{O}$  solution  
 (B)  $\text{z}$  on heating liberates  $\text{CO}_2$  gas  
 (C)  $\text{w}$  on reaction with  $\text{NaOI}$  gives yellow ppt  
 (D)  $\text{x}$  liberates  $\text{H}_2$  gas with  $\text{Na}$  metal

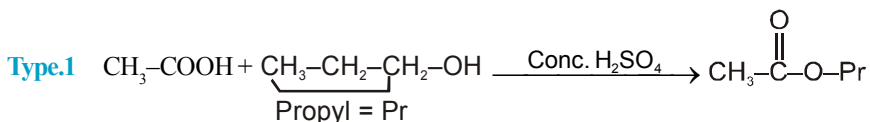
3. Which of the following compound give benzoic acid on  $\text{KMnO}_4$  oxidation

- (A)  $\text{w}$       (B)  $\text{y}$       (C)  $\text{z}$       (D) all

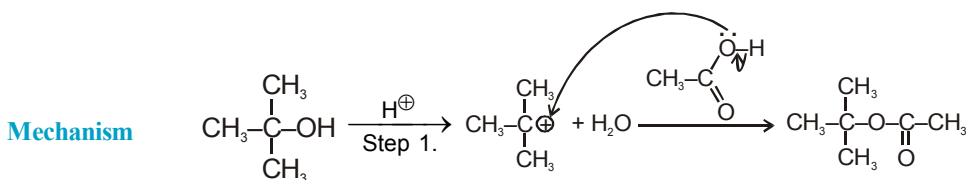
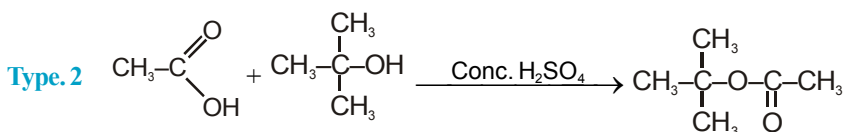
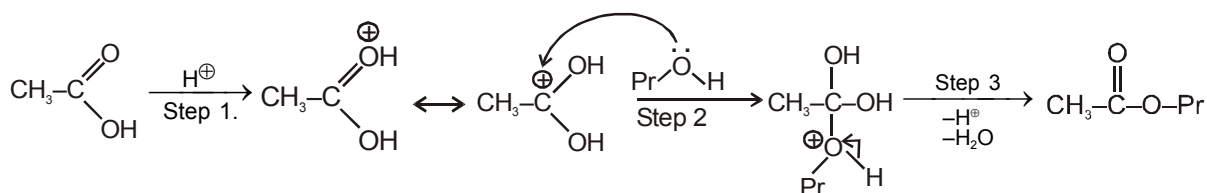


Comprehension # 3

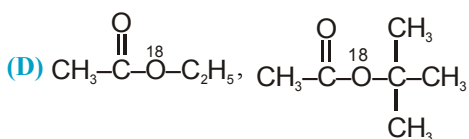
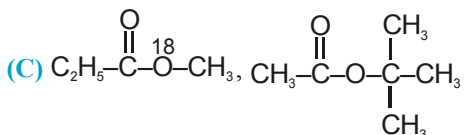
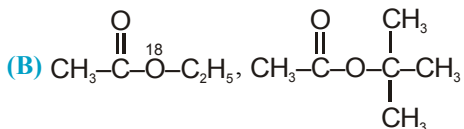
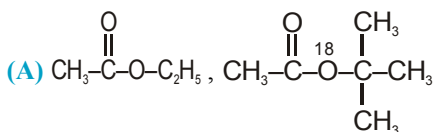
Observe the esterification mechanisms for primary and tertiary alcohols.

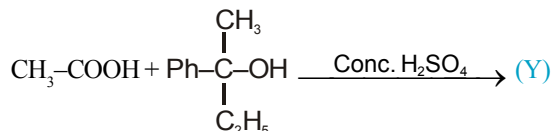
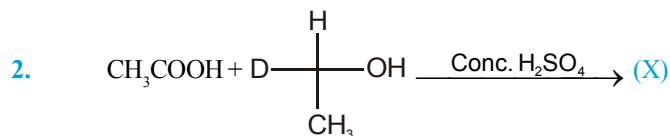


**Mechanism**



1.  $\text{CH}_3\text{-COOH} + \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{Conc. H}_2\text{SO}_4} \text{(P)}$   
 $\text{CH}_3\text{-COOH} + (\text{CH}_3)_3\text{C-OH} \xrightarrow{\text{Conc. H}_2\text{SO}_4} \text{(Q)}$   
 In the above reaction (P) and (Q) are respectively :

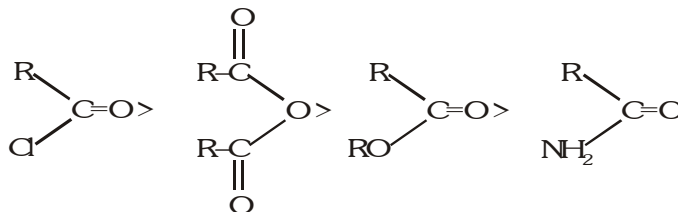




- (A) (X) is optically active while (Y) is optically inactive  
 (B) Both (X) and (Y) are optically active  
 (C) Both (X) and (Y) are optically inactive  
 (D) (X) is optically inactive while (Y) is optically active.
3. (+) Octan-2-ol esterifies with Acetic acid to give optically inactive racemised product. It must have gone by  
 (A) Type I mechanism (B) Type II mechanism  
 (C) Mix type I and type II mechanism (D) More by type I and less by type II mechanism

### Comprehension # 4

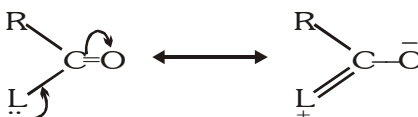
The reactivity of acid derivatives in general follows the order :



The above order of reactivity can be explained in terms of the :

(i) Basicity of leaving group (ii) Resonance effect (iii) Inductive effect

Weaker is the basic character of leaving group, more is the reactivity of acid derivative. In general, all the acid derivatives show resonance as follows:



More is the stabilization, lesser is the reactivity and *vice-versa*.

1. Which among the following anions is the most basic ?  
 (A)  $\bar{\text{N}}\text{H}_2$  (B)  $\bar{\text{O}}\text{R}$  (C)  $\text{R}-\text{CO}\bar{\text{O}}$  (D)  $\text{Cl}^-$
2. Which of the most reactive acid derivative?  
 (A)  $\text{R}-\text{COCl}$  (B)  $(\text{RCO})_2\text{O}$  (C)  $\text{RCOOR}$  (D)  $\text{RCONH}_2$
3. Which among the following ester is most reactive towards nucleophilic attack ?  
 (A)  $\text{CH}_3\text{COOCH}_3$  (B)  $\text{HCOOCH}_3$  (C)  $\text{CH}_3\text{CH}_2\text{COOC}_6\text{H}_5$  (D) All are equally reactive
4. Acid derivatives although contain  $\text{---C}(=\text{O})\text{---}$  group, yet do not undergo the usual properties of carbonyl group. It is due to:  
 (A) inductive effect (B) resonance (C) eletromeric effect (D) all of these

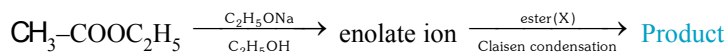
## CHEMISTRY FOR JEE MAIN & ADVANCED

5. Which of the following compounds will be most easily hydrolysed ?  
 (A) Acid halide                      (B) Acid amide                      (C) Ester                      (D) Acid anhydride

### Comprehension # 5

Ester gives nucleophilic addition reaction followed by elimination reaction with carbon nucleophile. When carbon nucleophile is of an ester then the reaction is known as Claisen condensation reaction. This reaction is also carried out between ester and a ketone. A successful Claisen condensation requires an ester with two  $\alpha$ -hydrogens and an equivalent amount of base rather than a catalytic amount of base.

1. Consider the given reaction



For the above reaction the most reactive ester is:

- (A)  $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$                       (B)  $\text{C}_2\text{H}_5\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OC}_2\text{H}_5$   
 (C)  $\text{HCOOC}_2\text{H}_5$                       (D)  $\text{C}_2\text{H}_5\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OC}_2\text{H}_5$

2. Intramolecular Claisen condensation given by diester is known as:  
 (A) Stobbe condensation                      (B) Dieckmann condensation  
 (C) Mannich reaction                      (D) Reformatsky reaction

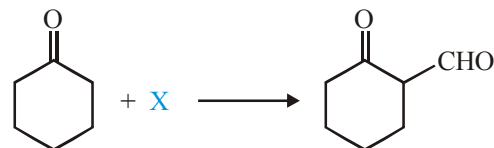
3. In the given reaction :



[X] is :

- (A)                       (B)   
 (C)                       (D) 

4. In the given reaction



[X] is :

- (A)  $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$                       (B)  $\text{HCl} + \text{CO}$                       (C)  $\text{HCOOC}_2\text{H}_5$                       (D)  $\begin{array}{c} \text{COOC}_2\text{H}_5 \\ | \\ \text{COOC}_2\text{H}_5 \end{array}$

Comprehension # 6

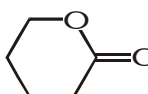
Amides undergo hydrolysis to yield carboxylic acid plus amine on heating in either aqueous acid or aqueous base. The conditions required for amide hydrolysis are more severe than those required for the hydrolysis of esters, anhydrides or acid chlorides, but the mechanism is similar (nucleophilic acyl substitution). Nucleophilic acyl substitutions involve a tetrahedral intermediate, hence these are quite different from alkyl substitution ( $\text{RCH}_2\text{Br} \xrightarrow{\text{NaCN}} \text{RCH}_2\text{CN}$ ) which involves a pentavalent intermediate or transition state.

One of the important reactions of esters is their reaction with two equivalent of Grignard reagent to give tertiary alcohols.

- The mechanism involved during the hydrolysis of acid derivatives is :  
 (A) elimination-addition (B) addition-elimination  
 (C) nucleophilic addition elimination (D) electrophilic addition elimination
- Which of the following constitutes the best substrate during the acidic hydrolysis of amides ?



- For which functional derivative of carboxylic acids, acidic hydrolysis is avoided?  
 (A) Acid chlorides (B) Acid amides (C) Acid anhydrides (D) Esters

- When  is treated with two equivalent of methyl magnesium iodide and the product acidified the final product will be

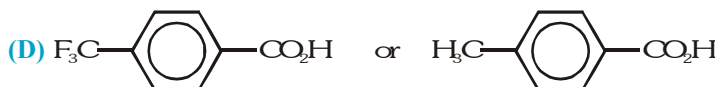


Exercise # 4

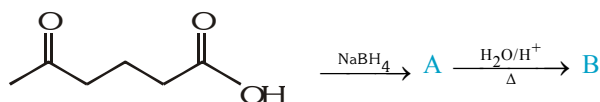
[Subjective Type Questions]

1. Which acid of each pair shown here would you expect to be stronger?

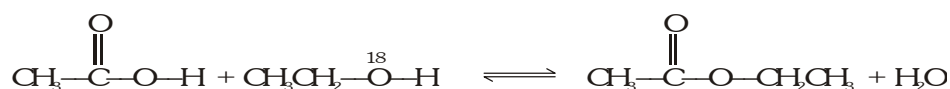
- (A)  $\text{CH}_3\text{CO}_2\text{H}$  or  $\text{CH}_2\text{FCO}_2\text{H}$   
 (B)  $\text{CH}_2\text{ClCO}_2\text{H}$  or  $\text{CH}_2\text{BrCO}_2\text{H}$   
 (C)  $\text{CH}_3\text{CH}_2\text{CHFCH}_2\text{CO}_2\text{H}$  or  $\text{CH}_3\text{CHFCH}_2\text{CO}_2\text{H}$



2. What are A and B in the following ?



3. In the following reaction, trace the position of isotopic  $\text{O}^{18}$ .



4. Carbon-oxygen bond length in formic acid are 1.23 Å and 1.36 Å but in sodium formate both the carbon-oxygen bonds have same value, i.e., 1.27 Å. Explain.

5. The second dissociation constant of fumaric acid is greater than maleic acid. Explain.

6. Which is stronger conjugate base in each pair ?

- (A)  $\bar{\text{O}}\text{H}$  or  $\text{NH}_2^-$  (B)  $\bar{\text{C}}\text{H}_3$  or  $\text{CH}_3\text{COO}^-$   
 (C)  $\text{HCOO}^-$  or  $\text{CH}_3\text{COO}^-$  (D)  $\text{CF}_3\text{COO}^-$  or  $\text{CCl}_3\text{COO}^-$

7. Write the reagents to carry out following conversions:



8.  What is A?

9. 

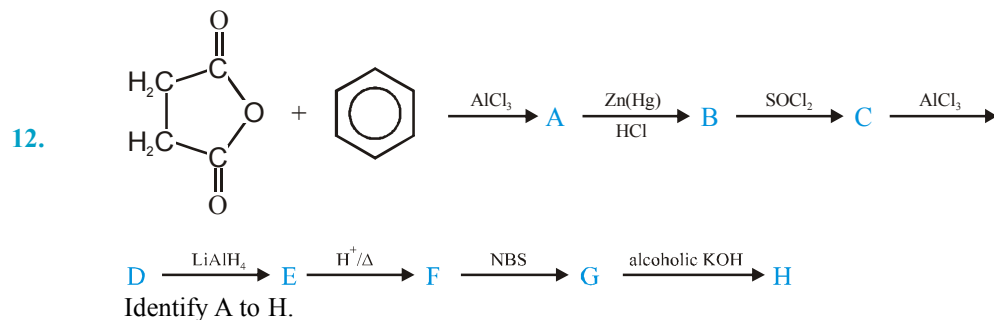
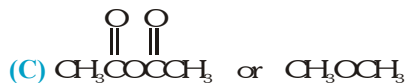
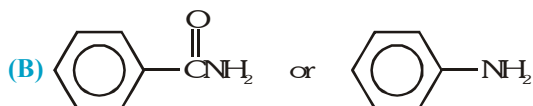
Write down the structure of A? What is the use of A?

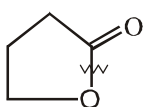
10. 

What are X and Y ?

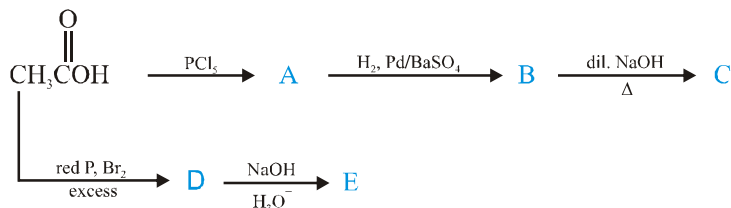
## CARBOXYLIC ACID AND THEIR DERIVATIVES

11. Which is more reactive in each pair towards  $S_N$  reaction ?

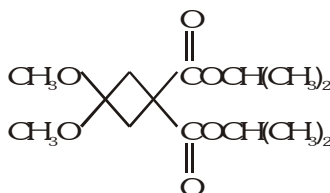


13.  reacts with :
- $\gamma$ -Butyrolactone (ester)
- (A)  $\text{NH}_3$                       (B)  $\text{LiAlH}_4$                       (C)  $\text{EtOH}, \text{H}^+$                       (D)  $\text{NaBH}_4/\text{EtOH}$
- What are the product in each case ?

14. Identify A, B, C, D and E in the following sequence of reactions:



15. When the compound shown was heated in refluxing hydrochloric acid, a compound with the molecular formula  $\text{A}(\text{C}_5\text{H}_6\text{O}_3)$  was isolated. Identify this product. Along with this product, three other carbon-containing substances are formed. What are they ?



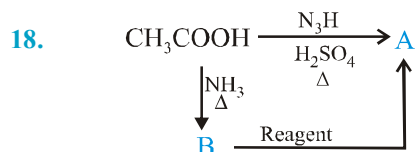
What happens when  $\text{A}(\text{C}_5\text{H}_6\text{O}_3)$  reacts with

- (A)  $\text{HCN}$  followed by hydrolysis                      (B) soda lime/ $\Delta$   
 (C)  $\text{NH}_2\text{NH}_2/\text{glycol}, \text{OH}^-$                       (D)  $\text{P}/\text{Br}_2$                       (E)  $\text{N}_3\text{H}$

16.  $\text{CH}_3\text{COO}^-$  (acetate ion) is more stable than  $\text{C}_2\text{H}_5\text{O}^-$  (ethoxide ion). Explain.

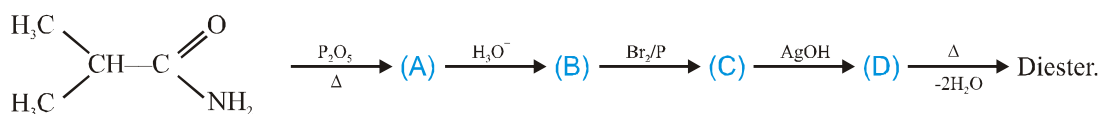
17. In case of aldehydes and ketones there is addition of nucleophile but in case of acyl compound there is nucleophilic substitution. Explain.

## CHEMISTRY FOR JEE MAIN & ADVANCED

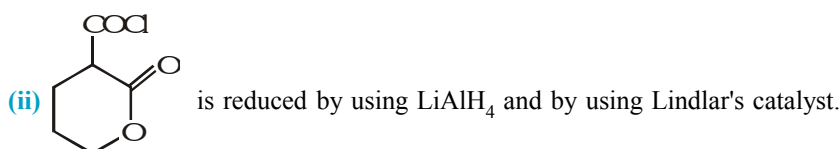
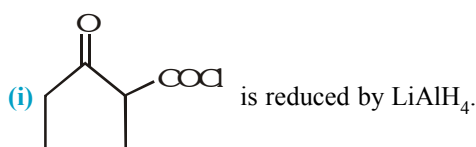


- (i) What are A & B ?  
 (ii) Which reagent will convert B into A ?

19. Complete the following sequence of reactions :



20. What happens when?



21. How will you distinguish between Benzoic acid and Ethyl benzoate?

22. Ethyl isocyanide on acidic hydrolysis generates :

23. The correct sequence of decreasing order of reactivity of hydrolysis of acid chlorides  $\text{PhCOCl}$ ,  $p\text{-O}_2\text{NC}_6\text{H}_4\text{COCl}$  and  $p\text{-CH}_3\text{OC}_6\text{H}_4\text{COCl}$  is :

24. Write Decarboxylation reaction.

25. How an acid amide may be converted to the parent acid.

26. How the acetic acid is converted into ethanamine ?

27. Which of the following acid has the smallest dissociation constant ?

- (a)  $\text{CH}_3-\underset{\text{NO}_2}{\text{CH}}-\text{COOH}$ , (b)  $\text{O}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{COOH}$ ,  
 (c)  $\text{Cl}-\text{CH}_2-\text{CH}_2-\text{COOH}$ , (d)  $\text{NC}-\text{CH}_2-\text{CH}_2-\text{COOH}$

28. Arrange the following compounds in increasing order of their acidic strength with reason.  
 Benzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic acid, 4-Methoxybenzoic acid.

29. How will you distinguish between Phenol and Benzoic acid?

30. Write a suitable chemical equation to complete each of the following transformations :

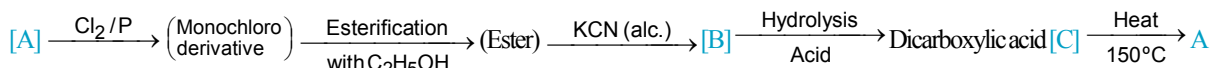
- (i) Butan-1-ol to butanoic acid  
 (ii) 4-Methylacetophenone to benzene-1,4-dicarboxylic acid.





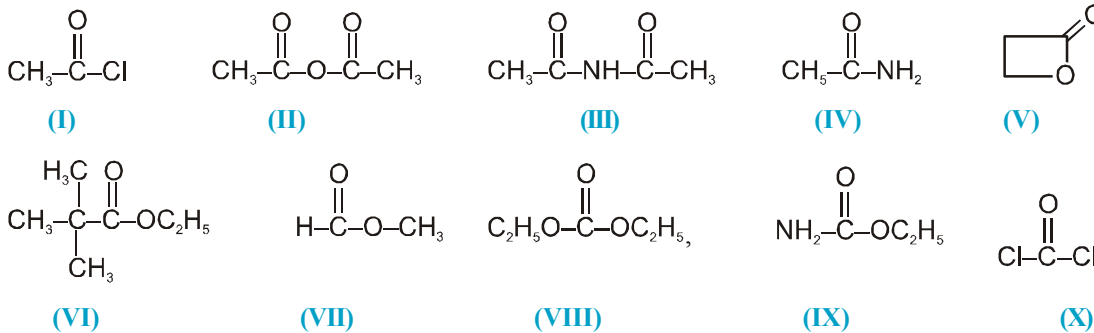
## CHEMISTRY FOR JEE MAIN & ADVANCED

44. 30 g of monobasic carboxylic acid **A** consumed 0.5 moles of NaOH for its neutralisation. **A** is subjected to following treatments :

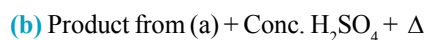
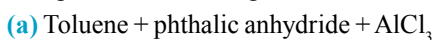


Give structures of **A**, **B**, **C** providing the sequence of reactions.

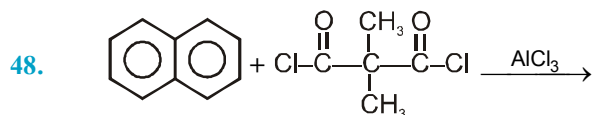
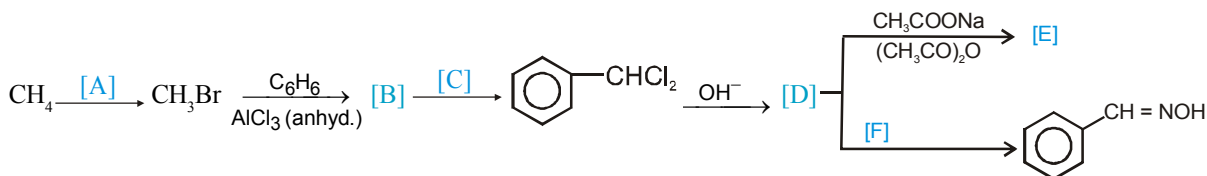
45. How many compounds out of the following are more reactive than ethyl acetate towards hydrolysis.



46. Complete the following reaction



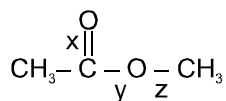
47. Complete the following by reactions. Find the unknown **A** to **F** :



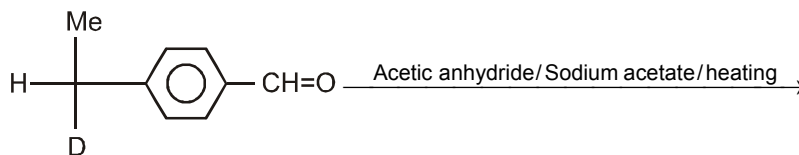
The products can be :

49. The respective boiling points and molecular weights (in/gmol) of the following amides are :  $\text{MeCONH}_2$ ,  $221^\circ\text{C}$  and 59;  $\text{MeCONHMe}$ ,  $204^\circ\text{C}$  and 73;  $\text{MeCONMe}_2$ ,  $165^\circ\text{C}$  and 87. Explain.

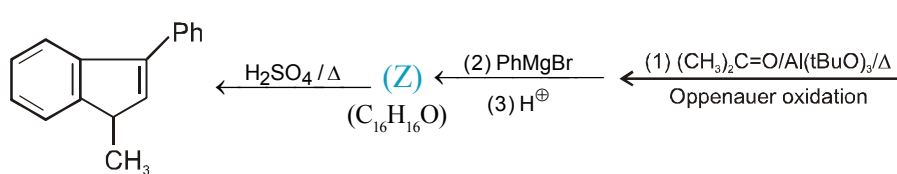
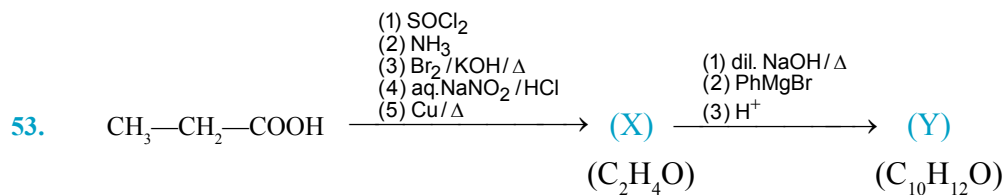
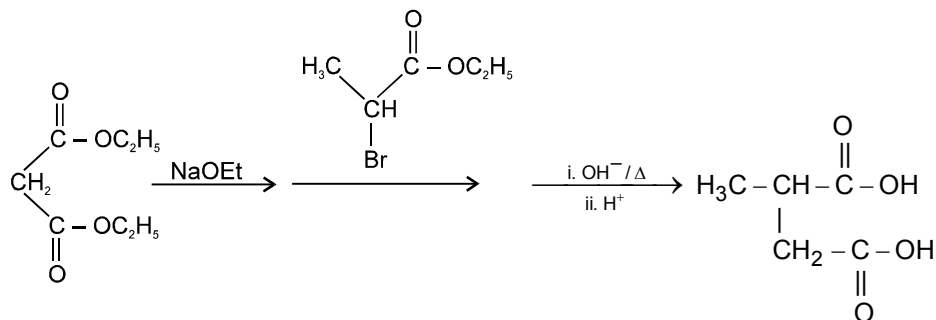
50. In the following ester there are three carbon oxygen bonds denoted by **x**, **y** and **z**. Then bond length of (i) **x**, **y** (ii) **y**, **z** and (iii) **x**, **z** orders are :



51. The number of isomeric products formed in the following reaction is :



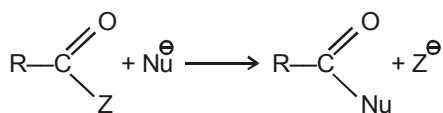
52. Explain briefly the formation of the products giving the structures of the intermediates.



Exercise # 5

Part # I [Previous Year Questions] [AIEEE/JEE-MAIN]

1. Rate of the reaction is fastest when Z is : [AIEEE-2004]



- (1) Cl (2) OCOCH<sub>3</sub> (3) OC<sub>2</sub>H<sub>5</sub> (4) NH<sub>2</sub> [AIEEE-2004]

2. Consider the acidity of the carboxylic acids : [AIEEE-2004]

- (A) PhCOOH (B) o-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>COOH  
(C) p-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>COOH (D) m-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>COOH

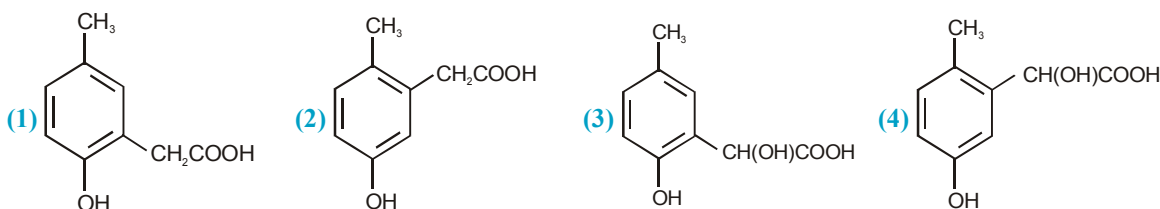
which of the following order is correct ?

- (1) a > b > c > d (2) b > c > d > a (3) b > d > a > c (4) b > d > c > a

3. On mixing ethyl acetate with aqueous sodium chloride, the composition of the resultant solution is : [AIEEE-2004]

- (1) CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub> + NaCl (2) CH<sub>3</sub>Cl + C<sub>2</sub>H<sub>5</sub>COONa  
(3) CH<sub>3</sub>COCl + C<sub>2</sub>H<sub>5</sub>OH + NaOH (4) CH<sub>3</sub>COONa + C<sub>2</sub>H<sub>5</sub>OH

4. p-cresol reacts with chloroform in alkaline medium to give the compound A which adds hydrogen cyanide to form the compound B. The latter on acidic hydrolysis gives chiral carboxylic acid. The structure of the carboxylic acid is : [AIEEE-2005]



5. An organic compound having molecular mass 60 is found to contain C = 20%, H = 6.67% and N = 46.67% while rest is oxygen. On heating it gives NH<sub>3</sub> along with a solid residue. The solid residue give violet colour with alkaline copper sulphate solution. The compound is : [AIEEE-2005]

- (1) CH<sub>3</sub>CH<sub>2</sub>CONH<sub>2</sub> (2) (NH<sub>2</sub>)<sub>2</sub>CO (3) CH<sub>3</sub>CONH<sub>2</sub> (4) CH<sub>3</sub>NCO

6. A liquid was mixed with ethanol and a drop of concentrated H<sub>2</sub>SO<sub>4</sub> was added. A compound with a fruity smell was formed. The liquid was : [AIEEE-2009]

- (1) HCHO (2) CH<sub>3</sub>COCH<sub>3</sub> (3) CH<sub>3</sub>COOH (4) CH<sub>3</sub>OH

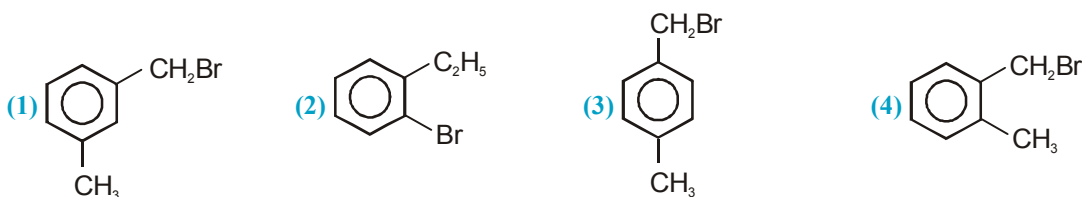
7. Sodium ethoxide has reacted with ethanoyl chloride. The compound that is produced in the above reaction is : [AIEEE-2011]

- (1) Diethyl ether (2) 2-Butanone (3) Ethyl chloride (4) Ethyl ethanoate

8. A compound with molecular mass 180 is acylated with CH<sub>3</sub>COCl to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is : [JEE(Mains) 2013]

- (1) 2 (2) 5 (3) 4 (4) 6

9. Compound (A), C<sub>8</sub>H<sub>9</sub>Br, gives a white precipitate when warmed with alcoholic AgNO<sub>3</sub>. Oxidation of (A) gives an acid (B), C<sub>8</sub>H<sub>6</sub>O<sub>4</sub>. (B) easily forms anhydride on heating. Identify the compound (A). [JEE (Mains) 2013]



## CARBOXYLIC ACID AND THEIR DERIVATIVES

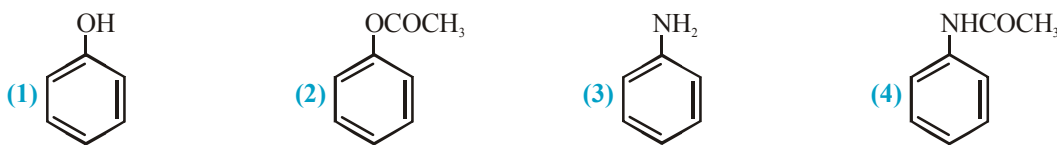
10. An organic compound **A** upon reacting with  $\text{NH}_3$  gives **B**. On heating **B** gives **C**. **C** in presence of  $\text{KOH}$  reacts with  $\text{Br}_2$  to give  $\text{CH}_3\text{CH}_2\text{NH}_2$ . **A** is : [JEE (Mains) 2013]



11. In the Hofmann bromamide degradation reaction, the number of moles of  $\text{NaOH}$  and  $\text{Br}_2$  used per mole of amine produced are : [JEE (Mains) 2016]

- (1) Four moles of  $\text{NaOH}$  and two moles of  $\text{Br}_2$   
 (2) Two moles of  $\text{NaOH}$  and two moles of  $\text{Br}_2$   
 (3) Four moles of  $\text{NaOH}$  and one mole of  $\text{Br}_2$   
 (4) One mole of  $\text{NaOH}$  and one mole of  $\text{Br}_2$

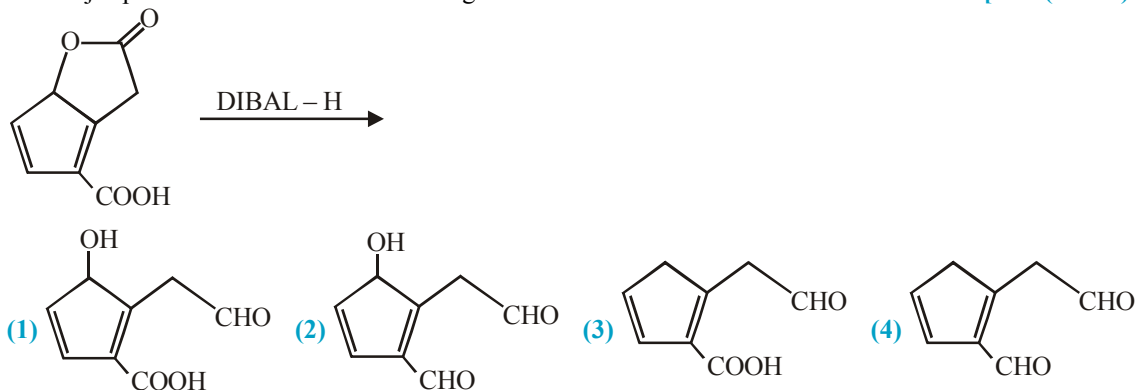
12. Which of the following compounds will form significant amount of *meta* products during mono-nitration reaction? [JEE (Mains) 2017]



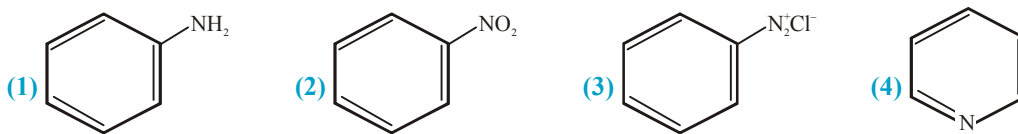
13. Sodium salt of an organic acid 'X' produces effervescence with conc.  $\text{H}_2\text{SO}_4$ . 'X' reacts with the acidified aqueous  $\text{CaCl}_2$  solution to give a white precipitate which decolourises acidic solution of  $\text{KMnO}_4$ . 'X' is : [JEE (Mains) 2017]



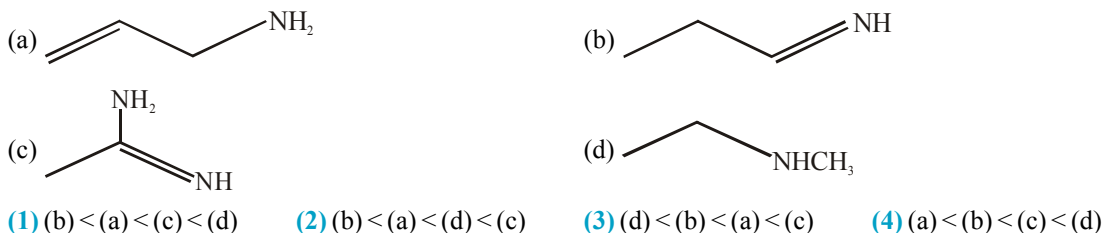
14. The major product obtained in the following reaction is [JEE (Mains) 2017]



15. Which of the following compounds will be suitable for Kjeldahl's method for nitrogen estimation ? [JEE (Mains) 2018]

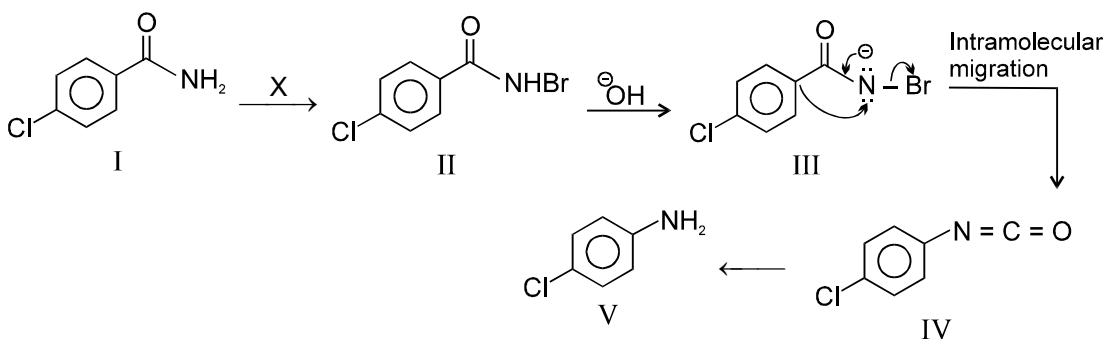


16. The increasing order of basicity of the following compounds is : [JEE (Mains) 2018]



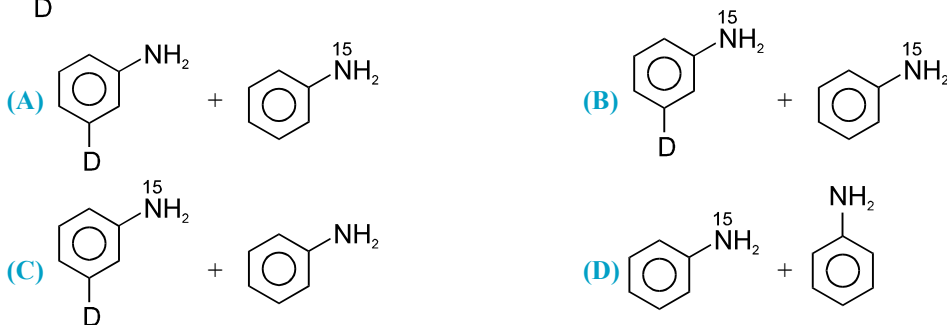
1. **Statement-1** : Acetate ion is more basic than the methoxide ion.  
**Statement-2** : The acetate ion is resonance stabilized. [JEE-2004]  
 (A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.  
 (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1  
 (C) Statement-1 is True, Statement-2 is False  
 (D) Statement-1 is False, Statement-2 is True
2. In conversion of 2-butanone to propanoic acid which reagent is used. [JEE-2005]  
 (A) NaOH, NaI / H<sup>⊕</sup>      (B) Fehling solution      (C) NaOH, I<sub>2</sub> / H<sup>⊕</sup>      (D) Tollen's reagent

Passage



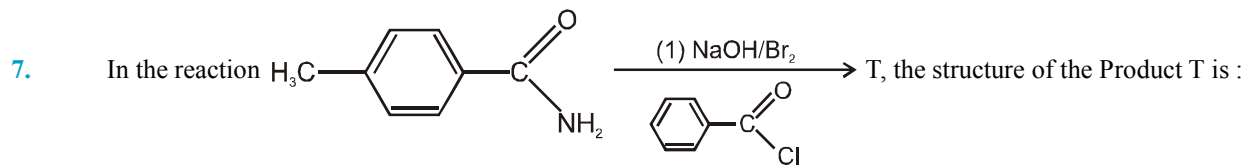
3. Which reagent (X) is used to convert I to II [JEE 2006]  
 (A) KBr / NaOH      (B) Br<sub>2</sub> / NaOH      (C) NaHCO<sub>3</sub>      (D) N-Bromo succinimide
4. Which step is rate determining step [JEE 2006]  
 (A) Formation of II      (B) Formation of III      (C) Formation of V      (D) Formation of IV

5. under Hofmann conditions will give : [JEE 2006]

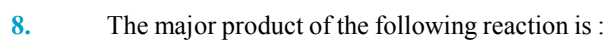
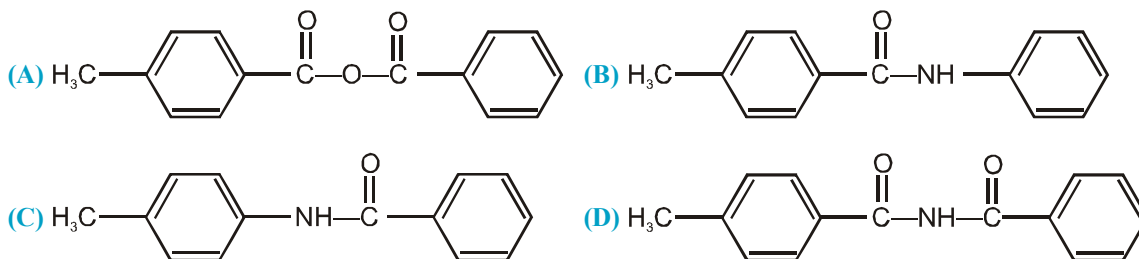


6. **Statement-1** : p-Hydroxybenzoic acid has a lower boiling point than o-hydroxybenzoic acid.  
**Statement-2** : o-Hydroxybenzoic acid has intramolecular hydrogen bonding. [JEE 2007]  
 (A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.  
 (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1  
 (C) Statement-1 is True, Statement-2 is False  
 (D) Statement-1 is False, Statement-2 is True.

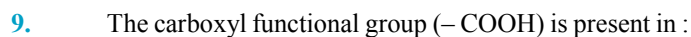
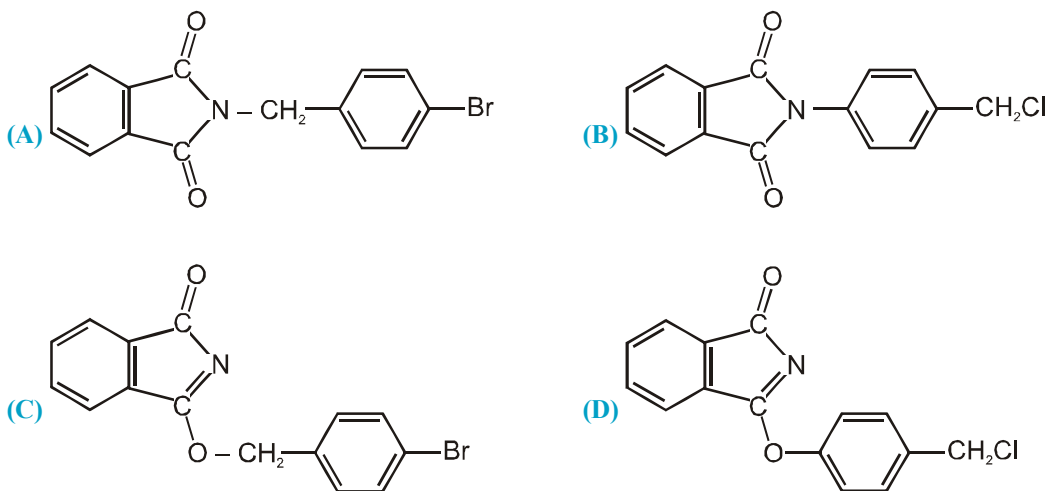
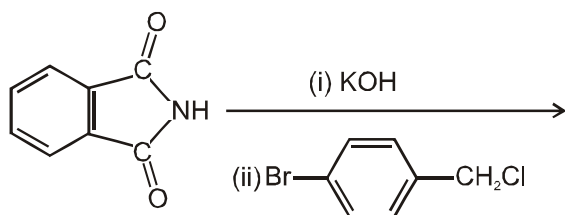
## CARBOXYLIC ACID AND THEIR DERIVATIVES



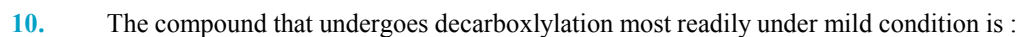
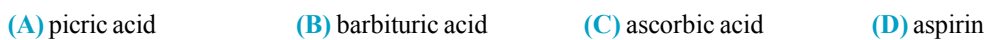
[JEE-2010]



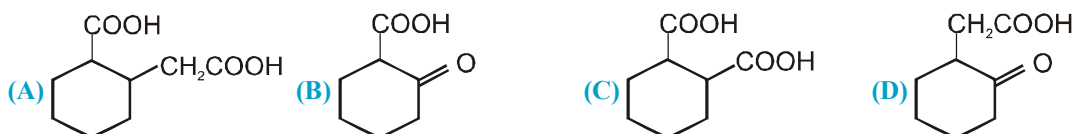
[JEE-2011]



[JEE-2012]

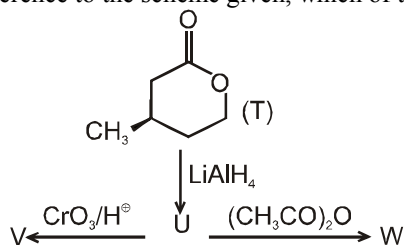


[JEE-2012]



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11. With reference to the scheme given, which of the given statements(s) about **T**, **U**, **V** and **W** is (are) correct?

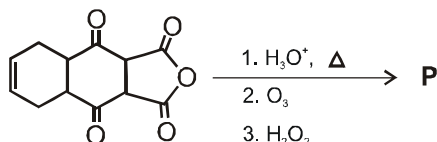


[JEE-2012]

- (A) **T** is soluble in hot aqueous NaOH  
 (B) **U** is optically active  
 (C) Molecular formula of **W** is  $\text{C}_{10}\text{H}_{18}\text{O}_4$   
 (D) **V** gives effervescence on treatment with aqueous  $\text{NaHCO}_3$

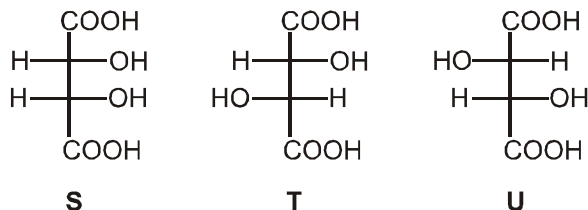
12. The total number of carboxylic acid groups in the product **P** is

[JEE(Advanced)-2013]



## Paragraph for Question 13 and 15

**P** and **Q** are isomers of dicarboxylic acid  $\text{C}_4\text{H}_4\text{O}_4$ . Both decolorize  $\text{Br}_2/\text{H}_2\text{O}$ . On heating, **P** forms the cyclic anhydride. Upon treatment with dilute alkaline  $\text{KMnO}_4$ , **P** as well as **Q** could produce one or more than one from **S**, **T** and **U**.



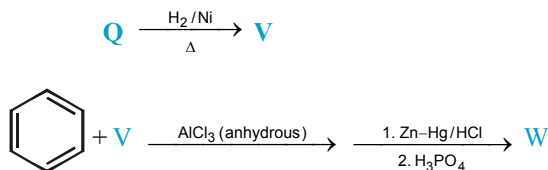
13. Compounds formed from **P** and **Q** are, respectively

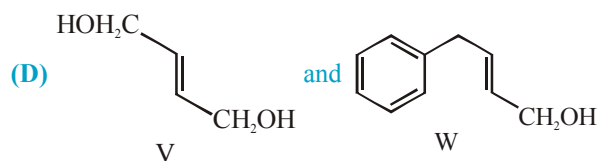
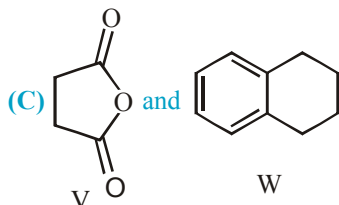
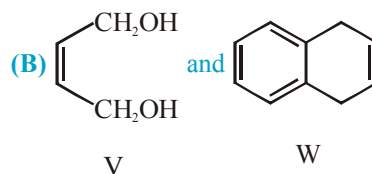
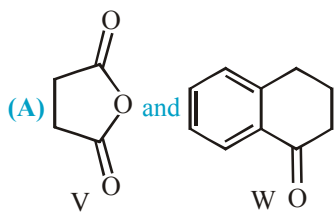
[JEE(Advanced)-2013]

- (A) Optically active **S** and optically active pair (**T**, **U**)  
 (B) Optically inactive **S** and optically inactive pair (**T**, **U**)  
 (C) Optically active pair (**T**, **U**) and optically active **S**  
 (D) Optically inactive pair (**T**, **U**) and optically inactive **S**

14. In the following reaction sequences **V** and **W** are respectively :

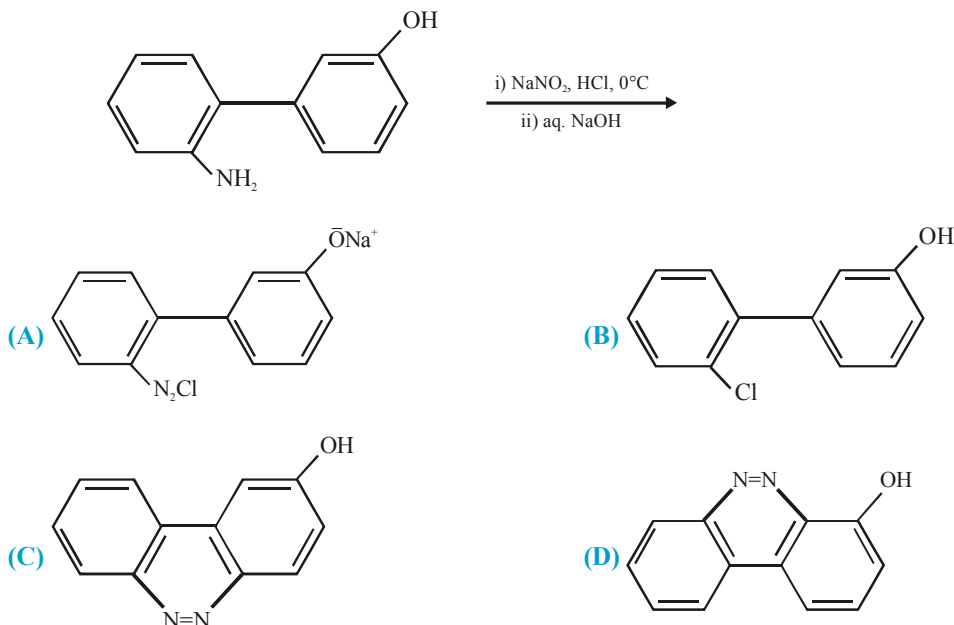
[JEE(Advanced)-2013]





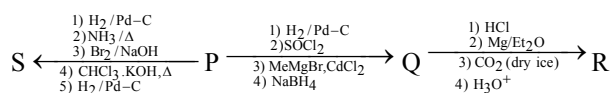
15. The major product of the following reaction is

[JEE(Advanced)-2017]



PARAGRAPH (16-17)

An organic acid P ( $C_{11}H_{12}O_2$ ) can easily be oxidized to a dibasic acid which reacts with ethyleneglycol to produce a polymer decron. Upon ozonolysis, P gives an aliphatic ketone as one of the products. P undergoes the following reaction sequences to furnish R via Q. The compound P also undergoes another set of reactions to produce S.

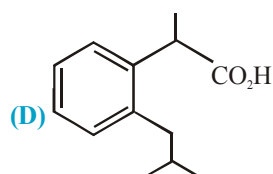
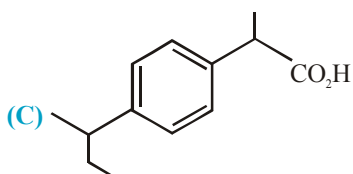
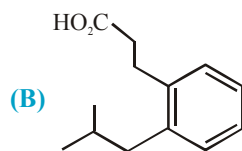
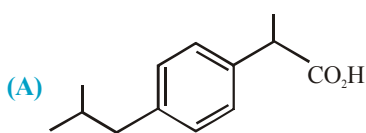


[JEE(Advanced)-2018]

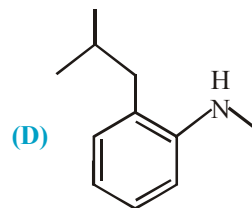
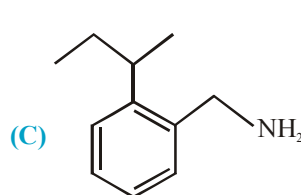
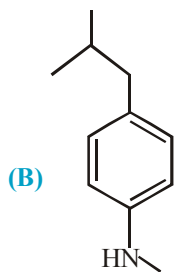
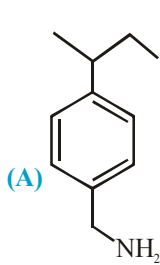


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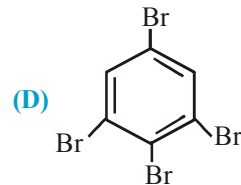
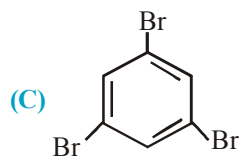
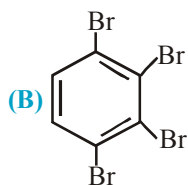
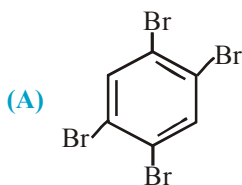
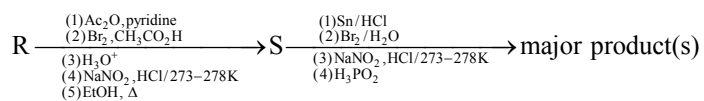
16. The compound R is



17. The compound S is



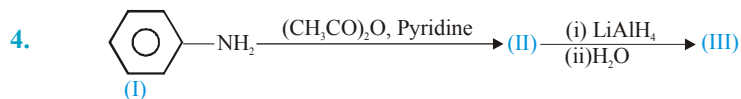
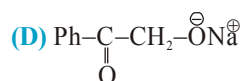
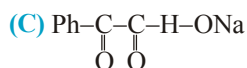
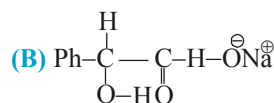
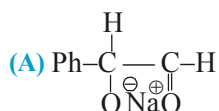
18. Aniline reacts with mixed acid (conc.  $\text{HNO}_3$  and conc.  $\text{H}_2\text{SO}_4$ ) at 288 K to give P (51%), Q (47%) and R (51%), Q (47%) and R (2%). The major product(s) of the following reaction sequence is/are [JEE(Advanced)-2018]



MOCK TEST

SECTION - I: STRAIGHT OBJECTIVE TYPE

- PhCOOH, PhMe can be separated by  
 (A) NaHCO<sub>3</sub> (B) aq. NaHCO<sub>3</sub> + n-hexane  
 (C) H<sub>2</sub>O (D) All of these
- Reactivity order towards a nucleophile is  
 (A) RCOCl > RCOOEt > (RCO)<sub>2</sub>O > RCONH<sub>2</sub> (B) RCOCl > (RCO)<sub>2</sub>O > RCOOEt > RCONH<sub>2</sub>  
 (C) (RCO)<sub>2</sub>O > RCOCl > RCOOEt > RCONH<sub>2</sub> (D) (RCO)<sub>2</sub>O > RCOOEt > RCOCl > RCONH<sub>2</sub>
- When phenyl glyoxal is kept in a solution of aq. NaOH it is converted to

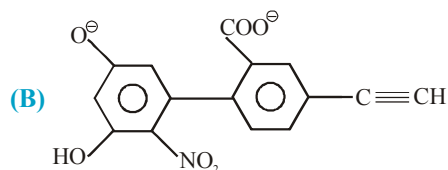
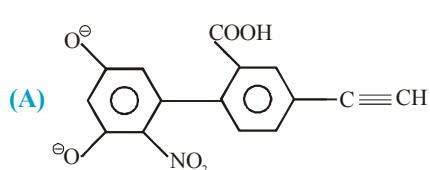
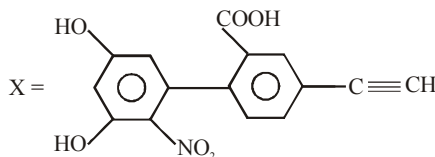


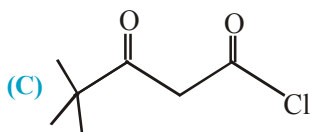
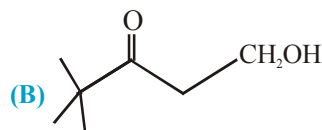
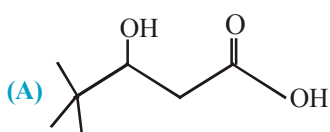
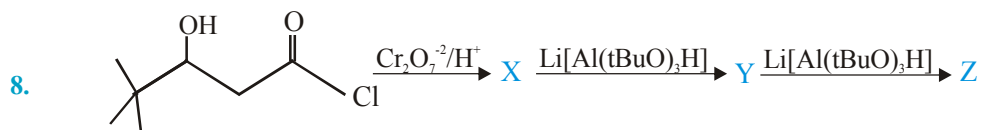
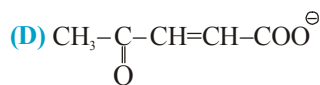
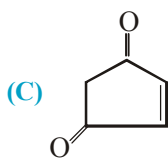
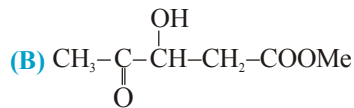
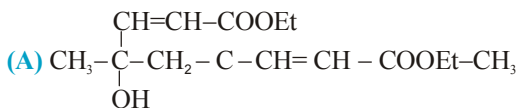
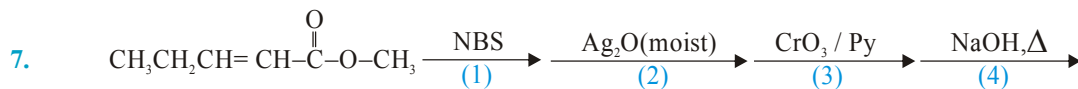
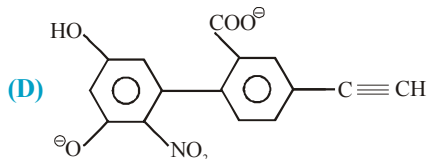
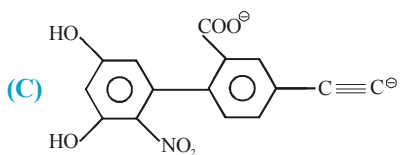
The basically order of I, II and III is

- (A) III > I > II (B) I > II > III (C) III > II > I (D) II > III > I
5.  $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2(\text{CH}_2\text{COOH}) + \text{PCl}_3 \longrightarrow \text{X} \xrightarrow{\text{AlCl}_3/\text{CS}_2} \text{Y} \xrightarrow{\text{N}_2\text{H}_4/\text{OH}^{\oplus}} \text{Z}$   
 Identify the correct set of X, Y, Z

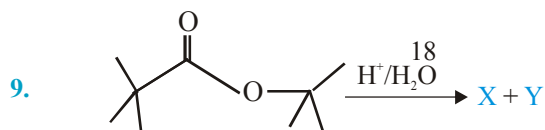
	(A)	(B)	(C)	(D)
(X)	C <sub>11</sub> H <sub>13</sub> OCl	C <sub>11</sub> H <sub>11</sub> OCl	C <sub>10</sub> H <sub>12</sub> OCl	C <sub>11</sub> H <sub>13</sub> Cl
(Y)	C <sub>11</sub> H <sub>12</sub> O	C <sub>11</sub> H <sub>10</sub> O	C <sub>10</sub> H <sub>10</sub> O	C <sub>11</sub> H <sub>12</sub> O
(Z)	C <sub>11</sub> H <sub>14</sub>	C <sub>11</sub> H <sub>12</sub>	C <sub>10</sub> H <sub>12</sub>	C <sub>11</sub> H <sub>14</sub>

6. What will be the most probable product when compound 'X' is treated with two equivalents of NaOH,

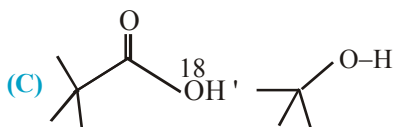
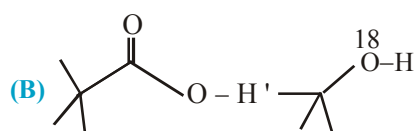
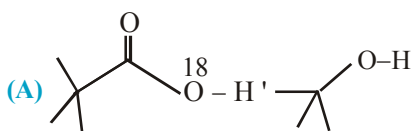




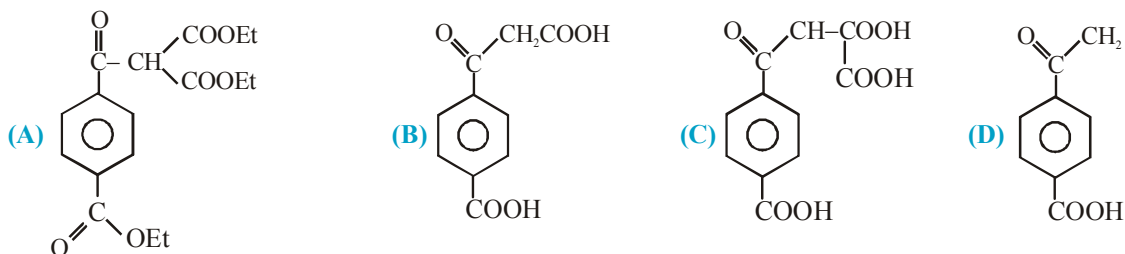
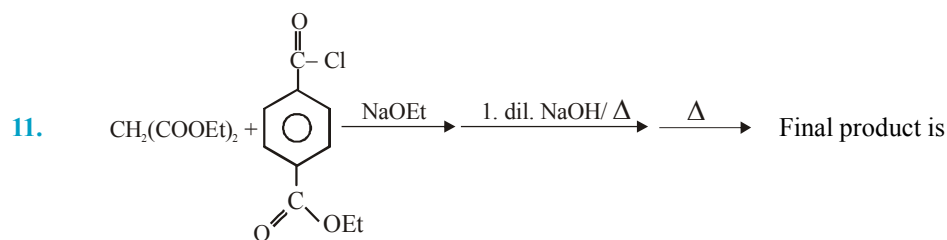
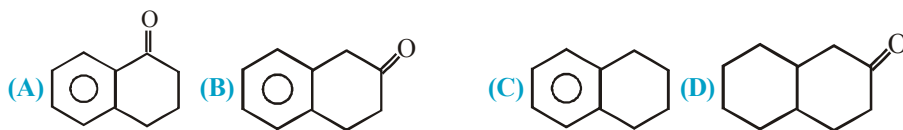
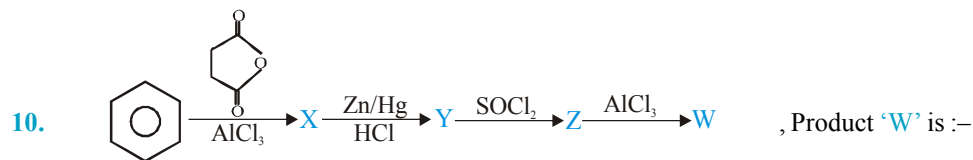
(D) None of these



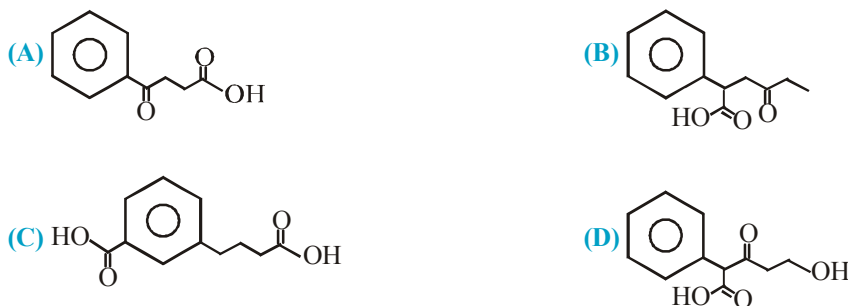
X, Y are



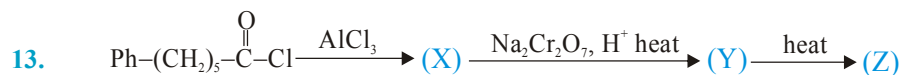
(D) All of these

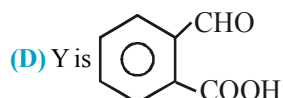
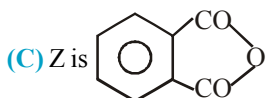


12. Which of the following undergoes decarboxylation most readily on being heated ?

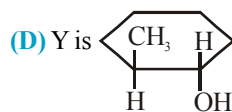
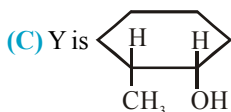
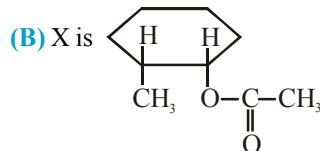
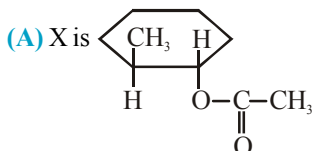
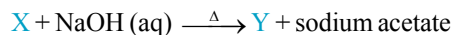


SECTION - II : MULTIPLE CORRECT ANSWER TYPE





14. trans-2-methylcyclohexanol + acetyl chloride  $\longrightarrow$  X



### SECTION - III : ASSERTION AND REASON TYPE

Read the following question and choose the correct answer :

(A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1

(B) Statement-1 is True, Statement-2 is True ; Statement-II is NOT a correct explanation for Statement-1

(C) Statement-1 is True, Statement-2 is False.

(D) Statement-1 is False, Statement-2 is True.

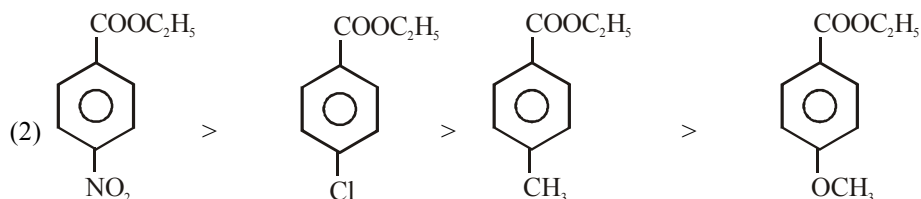
15. **Statement - 1 :** Halogen atom in a-halogeno acid is more reactive than that in alkyl halide.

**Statement - 2 :** It is due to -M effect of -COOH group.

16. **Statement - 1 :** The halogeno acids donot form Grignard reagent.

**Statement - 2 :** This is because of the presence of -COOH group (acidic H).

17. **Statement - 1 :** The base catalysed hydrolysis of easter order is



**Statement - 2 :**  $\text{S}_{\text{N}}2$  Th is sterically as well as electronically controlled reaction.

18. **Statement - 1 :** C-O bond length is shorter in an easter as compared with an anhydride.

**Statement - 2 :** A degree of cross conjugation exist in the hydride which decreases the delocalisation to each carbonyl oxygen.

19. **Statement - 1 :** Acid catalysed hydrolysis of easter is reversible while base catalysed hydrolysis is irriversible.

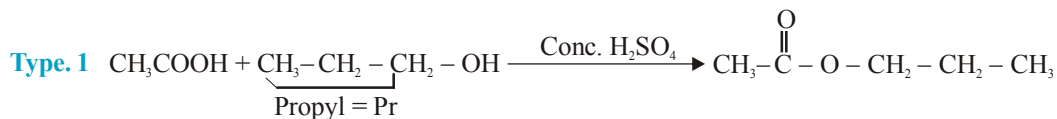
**Statement - 2 :** In acid catalysed ester hydrolysis

### SECTION - IV : COMPREHENSION TYPE

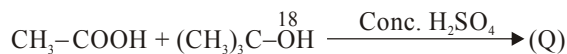
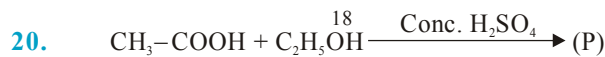
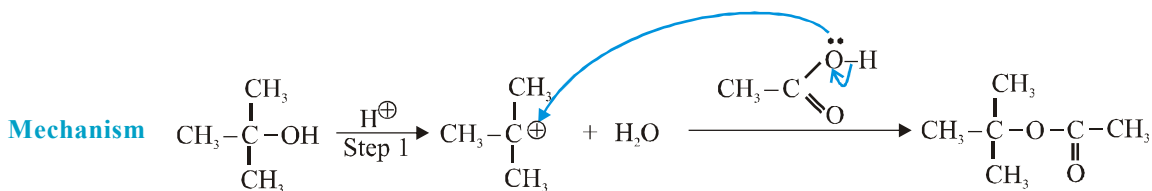
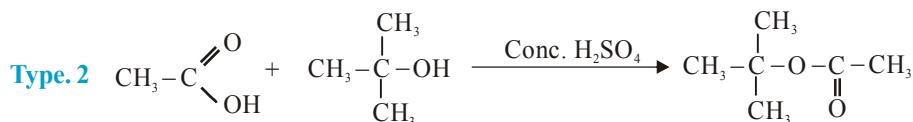
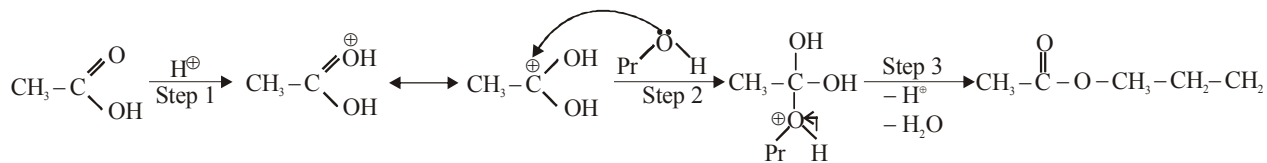
Read the following comprehensions carefully and answer the questions.

#### Comprehension # 1

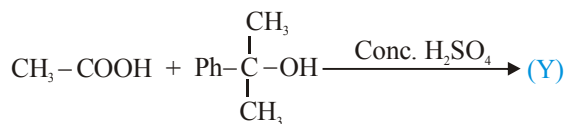
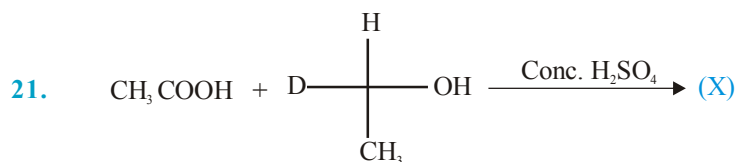
Observe the estrification mechanisms for primary and tertiary alcohols.



**Mechanism**



In the above reaction (P) and (Q) are respectively :



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- (A) (X) is optically active while (Y) is optically inactive  
 (B) Both (X) and (Y) are optically active  
 (C) Both (X) and (Y) are optically inactive  
 (D) (X) is optically inactive while (Y) is optically active

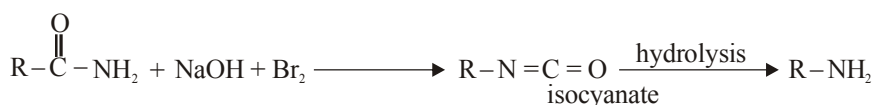
22. (+) Octan-2-ol esterifies with Acetic acid to give optically racemised product. It must have gone by  
 (A) Type I mechanism (B) Type II mechanism  
 (C) Mix type I and type II mechanism (D) More by type I and less by type II mechanism

### Comprehension # 2

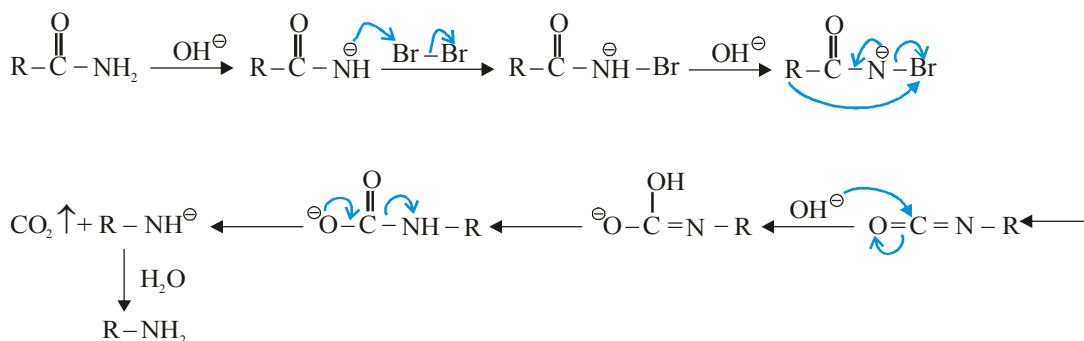
#### Hofmann rearrangement

In the Hofmann rearrangement an unsubstituted amide is treated with sodium hydroxide and bromine to give a primary amine that has one carbon lesser than starting amide.

General reaction.

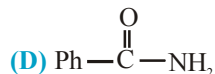
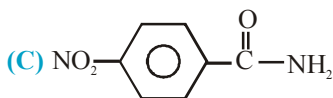
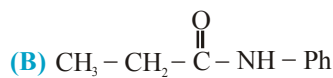
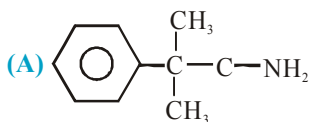


Mech :

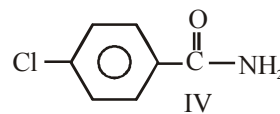
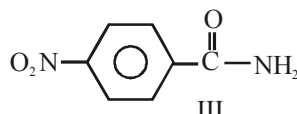
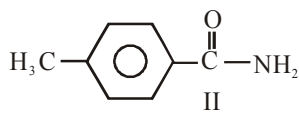
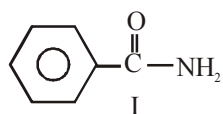


If the migrating group is chiral then its configuration is retained. Electron releasing effects in the migrating group increases reactivity of Hofmann rearrangement.

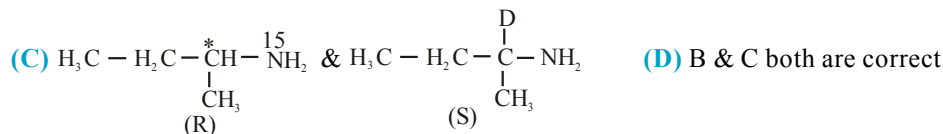
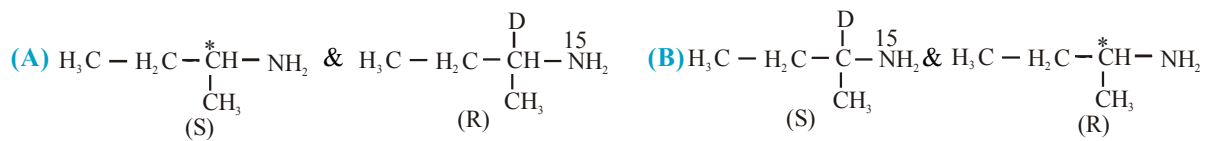
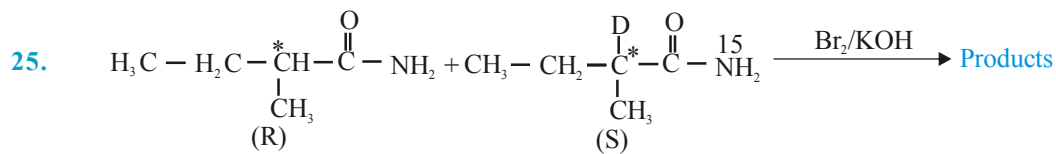
23. Which of the following compound(s) cannot give Hofmann rearrangement :



24. Arrange the following amides according to their relative reactivity when react with  $\text{Br}_2$  in excess of strong base



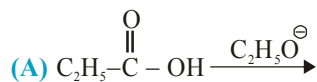
- (A)  $\text{IV} > \text{I} > \text{II} > \text{III}$  (B)  $\text{II} > \text{I} > \text{III} > \text{IV}$  (C)  $\text{II} > \text{IV} > \text{III} > \text{I}$  (D)  $\text{II} > \text{I} > \text{IV} > \text{III}$



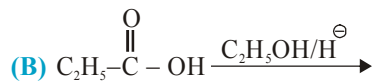
**SECTION - V : MATRIX - MATCH TYPE**

26. **Column - I**

**Column - II**



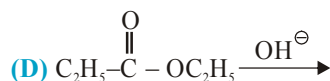
(p) Hydrolysis



(q) Esterification

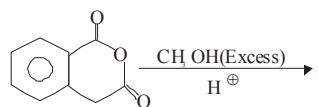
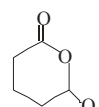
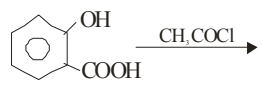
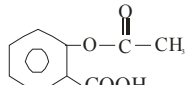
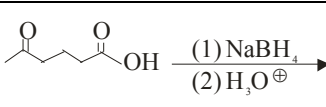
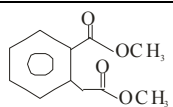
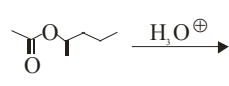
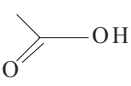


(r) Saponification



(s) Acid base reaction

27.

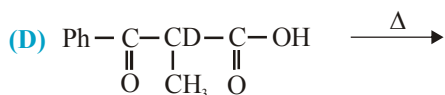
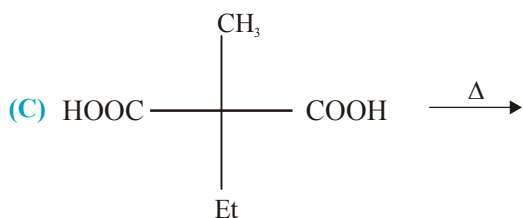
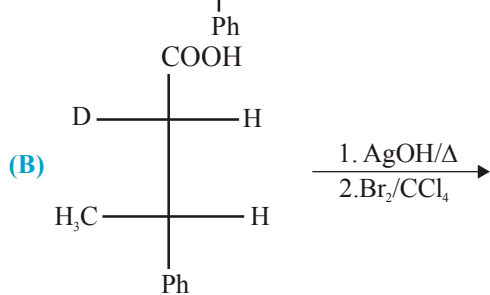
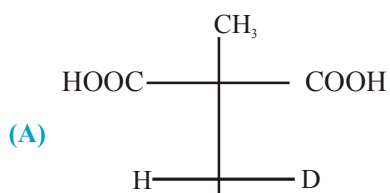
S.No.	X	Y
1		(p) 
2		(q) 
3		(r) 
4		(s) 



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28. Match the column I with column II.

## Column - I



## Column - II

(p) Diastereomer

(q) Racemic mixture

(r) Optically active

(s) CO<sub>2</sub> gas will evolve

**ANSWER KEY**

**EXERCISE - 1**

1. A 2. B 3. C 4. B 5. A 6. D 7. A 8. C 9. C 10. C 11. B 12. C 13. D  
 14. A 15. C 16. A 17. B 18. A 19. D 20. B 21. B 22. B 23. D 24. B 25. C 26. C  
 27. A 28. C 29. A 30. B 31. B 32. D 33. C 34. C 35. C 36. C 37. A 38. A 39. C  
 40. C 41. B 42. A 43. A 44. A 45. B 46. A 47. D 48. B 49. B 50. A 51. A 52. C  
 53. C 54. A 55. A 56. C 57. C 58. C 59. A 60. B 61. B 62. C 63. C 64. C 65. B  
 66. C 67. D 68. B 69. C 70. D 71. D 72. B 73. B 74. C 75. C 76. B 77. A 78. D  
 79. D 80. B 81. B 82. D

**EXERCISE - 2 : PART # I**

1. A,B,C 2. A,B 3. B,C 4. A,B,D 5. A,B,C 6. A,C 7. A,B  
 8. A,B,C,D 9. A 10. A,B,D 11. B,D 12. A,B 13. A,B,C 14. C  
 15. A,B,D 16. D 17. D 18. C 19. B 20. A,B,C 21. A  
 22. B 23. B 24. A,D 25. C,D 26. A,B,C 27. A,B,D 28. A,B,D

**PART # II**

1. C 2. A 3. C 4. D 5. C 6. A 7. A 8. A 9. A 10. C 11. A 12. E 13. E

**EXERCISE - 3 : PART # I**

1.  $A \rightarrow s, B \rightarrow r, C \rightarrow p, D \rightarrow q$   
 2.  $A \rightarrow s, B \rightarrow r, C \rightarrow q, D \rightarrow p, E \rightarrow t$   
 3.  $A \rightarrow r, B \rightarrow s, C \rightarrow p, D \rightarrow q$   
 4.  $A \rightarrow s, B \rightarrow p, C \rightarrow q, D \rightarrow r$   
 5.  $A \rightarrow s, B \rightarrow q, s, C \rightarrow p, s, D \rightarrow p, r, s$

**PART # II**

- Comprehension # 1 :** 1. B 2. D 3. B  
**Comprehension # 2 :** 1. C 2. D 3. D  
**Comprehension # 3 :** 1. B 2. A 3. B  
**Comprehension # 4 :** 1. A 2. A 3. B 4. B 5. A  
**Comprehension # 5 :** 1. B 2. B 3. A 4. C  
**Comprehension # 6 :** 1. C 2. C 3. A 4. B

**EXERCISE - 5 : PART # I**

1. 1 2. 2 3. 1 4. 3 5. 2 6. 3 7. 4 8. 2 9. 4 10. 4 11. 3 12. 3 13. 4  
 14. 2 15. 1 16. 2

PART # II

1. D 2. C 3. B 4. D 5. A 6. D 7. C 8. A 9. D 10. B 11. A,C,D 12. 2 13. B  
14. A 15. C 16. A 17. B 18. D

MOCK-TEST

1. B 2. B 3. B 4. A 5. A 6. D 7. C 8. B 9. B 10. A 11. D 12. D 13. ABC  
14. AD 15. C 16. A 17. A 18. A 19. A 20. B 21. A 22. B 23. B 24. D 25. B  
26.  $A \rightarrow s$   $B \rightarrow q$   $C \rightarrow p$   $D \rightarrow r$  27.  $1 \rightarrow r$ ,  $2 \rightarrow q$ ,  $3 \rightarrow p$ ,  $4 \rightarrow s$   
28.  $A \rightarrow p, r, s$ ;  $B \rightarrow p, r, s$ ;  $C \rightarrow q, s$ ;  $D \rightarrow q, s$