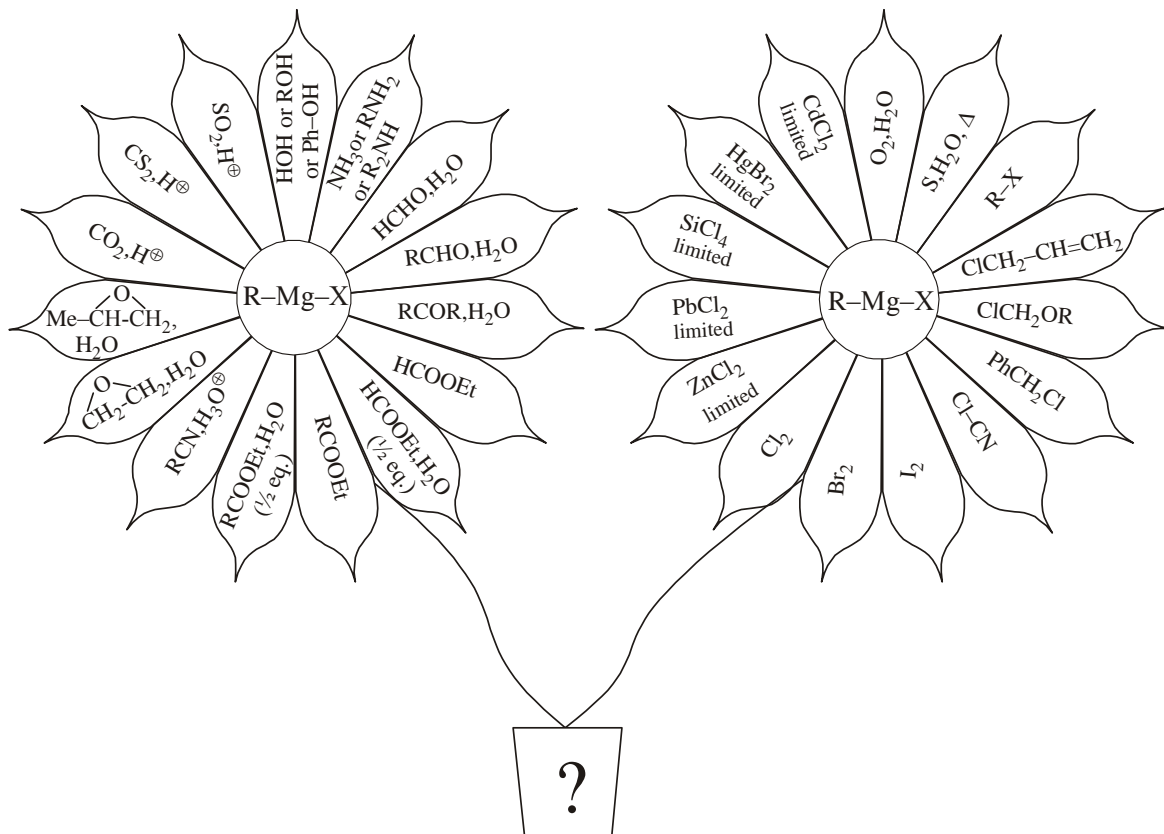


ORGANIC CHEMISTRY

TARGET IIT-ENTRANCE 2013 XII

GRIGNARD REAGENT



Hydrocarbon part of Grignard reagent ($R-Mg^+X^-$) has some carbanionic characters. So, it could act as a base as well as nucleophile both. As a nucleophile, it could show Nucleophilic substitution, Nucleophilic addition and Nucleophilic Addition-Elimination reactions.

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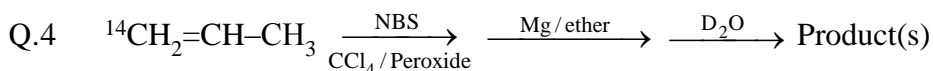
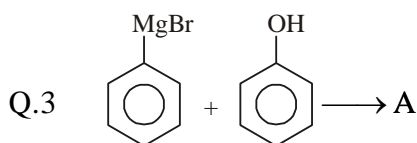
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In time of trouble, don't say "God I have a big problem." say "Hey Problem. I have a big God."

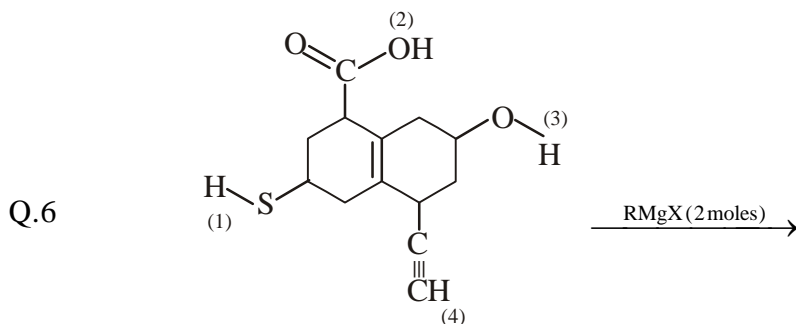
EXERCISE - I

- Q.1 Consider the given organometallic compound.
 (I) $(\text{CH}_3)_2\text{Hg}$ (II) $(\text{CH}_3)_2\text{Zn}$ (III) $(\text{CH}_3)_2\text{Mg}$ (IV) CH_3Li
 The correct decreasing order of ionic character is
 (A) $\text{I} > \text{II} > \text{III} > \text{IV}$ (B) $\text{II} > \text{I} > \text{III} > \text{IV}$ (C) $\text{I} > \text{III} > \text{II} > \text{IV}$ (D) $\text{IV} > \text{III} > \text{II} > \text{I}$
- Q.2 The order of reactivity of alkyl halide in the reaction $\text{R-X} + \text{Mg} \longrightarrow \text{RMgX}$ is
 (A) $\text{RI} > \text{RBr} > \text{RCl}$ (B) $\text{RCl} > \text{RBr} > \text{RI}$
 (C) $\text{RBr} > \text{RCl} > \text{RI}$ (D) $\text{RBr} > \text{RI} > \text{RCl}$



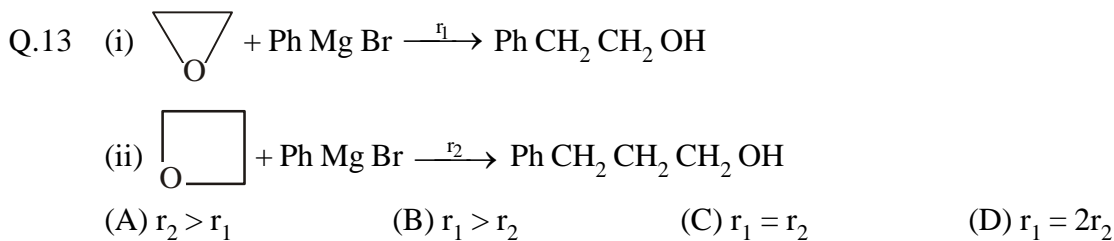
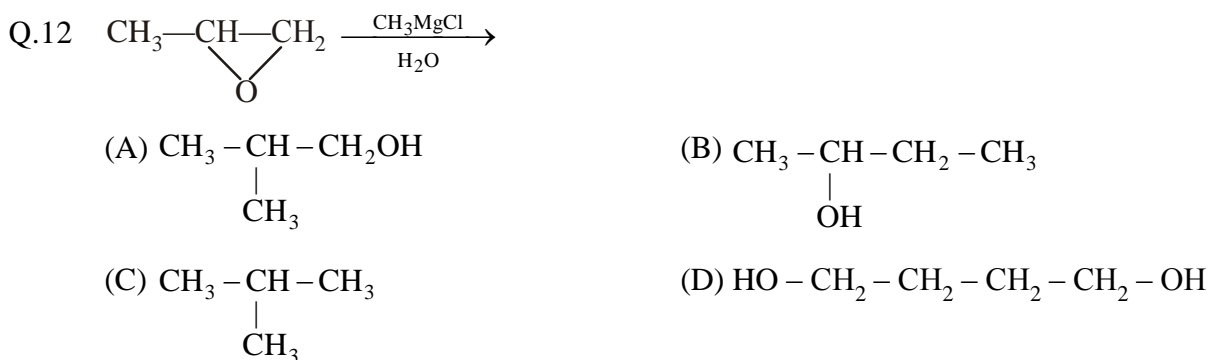
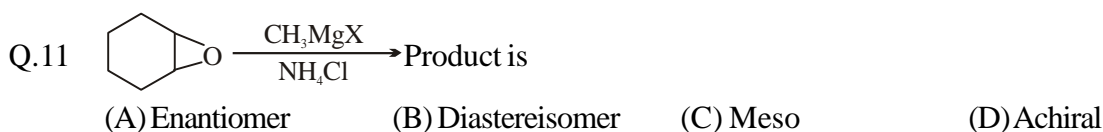
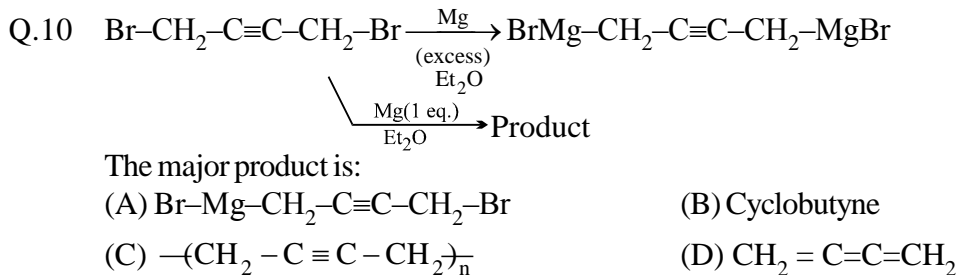
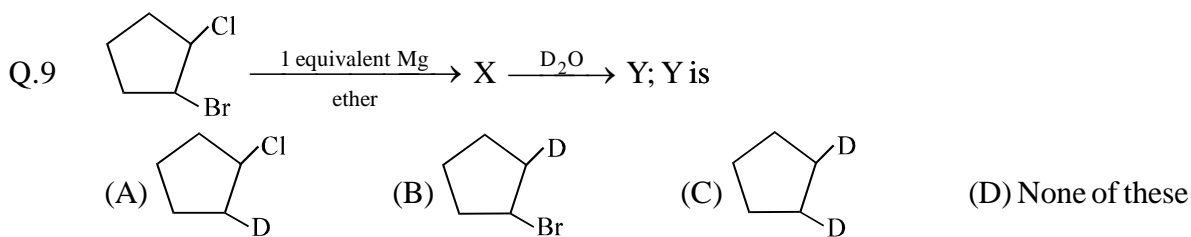
Product(s) is / are:

- (A) $^{14}\text{CH}_2=\text{CH}-\text{CH}_2-\text{D}$ (B) $\text{CH}_2=\text{CH}-^{14}\text{CH}_2-\text{D}$
 (C) Both of these (D) None of these
- Q.5 On conversion into Grignard followed by treatment with ethanol, how many alkyl halides (excluding stereoisomers) would yield 2-methyl butane.
 (A) 2 (B) 3 (C) 4 (D) 5

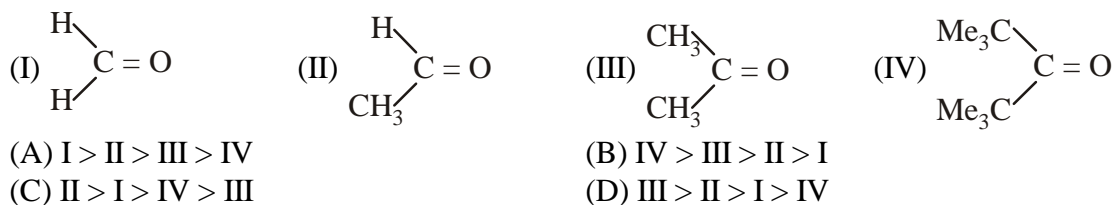


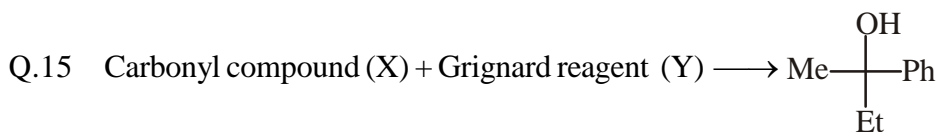
Deprotonation will occur from the following positions:

- (A) 1,2 (B) 1,3 (C) any two positions (D) 1,4
- Q.7 How many litres of methane would be produced when 0.595 g of CH_3MgBr is treated with excess of $\text{C}_4\text{H}_9\text{NH}_2$
 (A) 0.8 litre (B) 0.08 litre (C) 0.112 litre (D) 1.12 litre
- Q.8 How many litres of ethene would be produced when 2.62 g of vinyl magnesium bromide is treated with 224 ml of ethyne at STP.
 (A) 0.224 litre (B) 0.08 litre (C) 0.448 litre (D) 1.12 litre

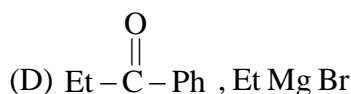
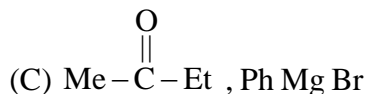
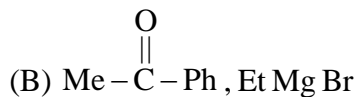
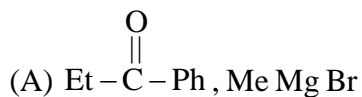


Q.14 What will be the order of reactivity of the following carbonyl compounds with Grignard's reagent?

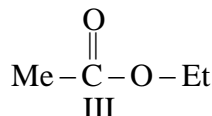
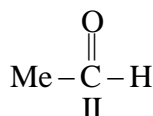
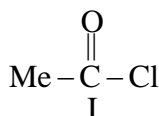




X, Y will be



Q.16 Order of rate of reaction of following compound with phenyl magnesium bromide is:



(A) I > II > III

(B) II > III > I

(C) III > I > II

(D) II > I > III

Q.17 Select the correct order of decreasing reactivity of the following compounds towards the attack of Grignard reagent

(I) Methyl benzoate

(II) Benzaldehyde

(III) Benzoylchloride

(IV) Acetophenone

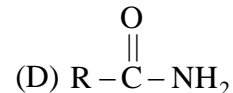
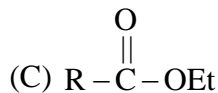
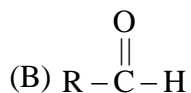
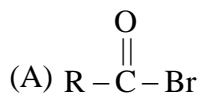
(A) II > III > I > IV

(B) III > IV > II > I

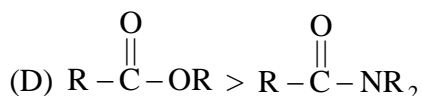
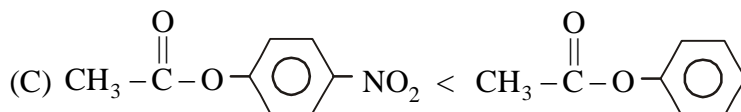
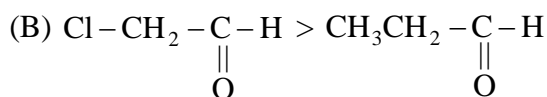
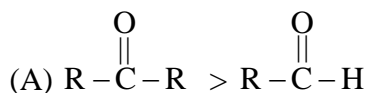
(C) III > II > IV > I

(D) II > IV > I > III

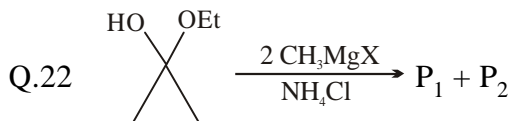
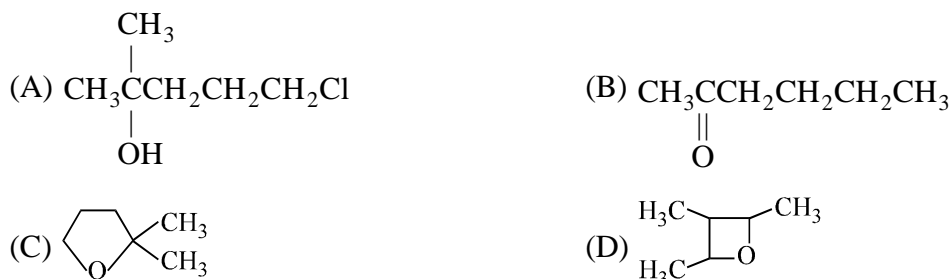
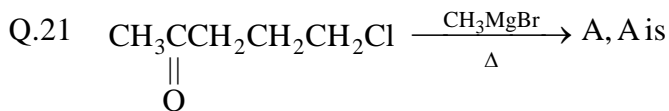
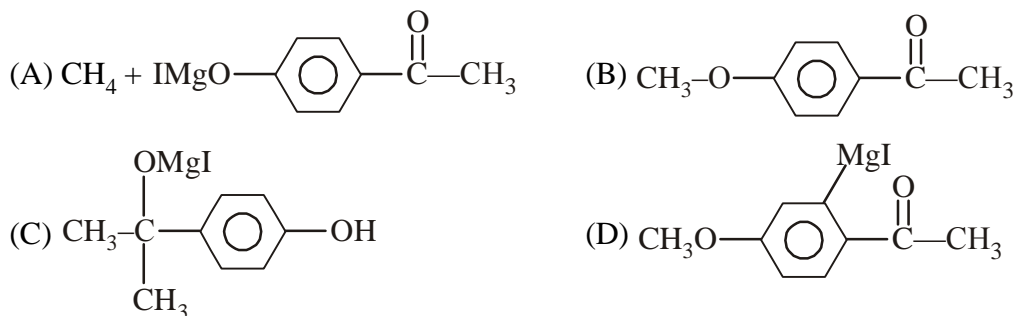
Q.18 Which of the following reacts faster with RMgX.



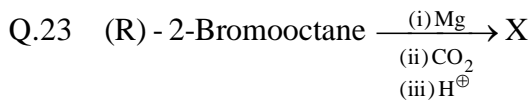
Q.19 Select the correct order of reactivity towards Grignard reagent for nucleophilic attack.



Q.20 The reaction of 1 mole each of p-hydroxy acetophenone and methyl magnesium iodide will give



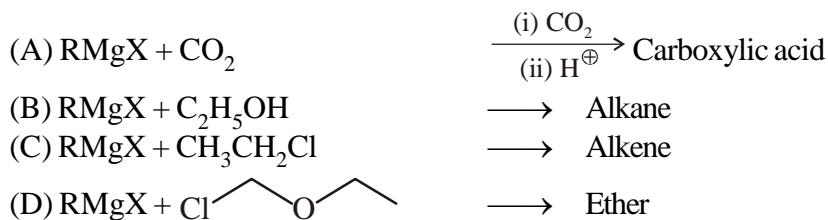
Identify P_1 & P_2 .

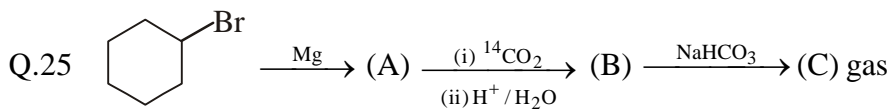


X is



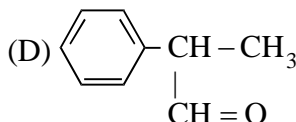
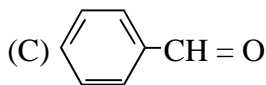
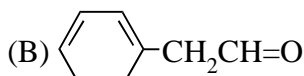
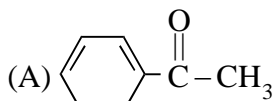
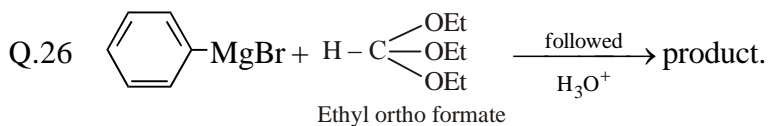
Q.24 In which one of the following reaction products are not correctly matched in



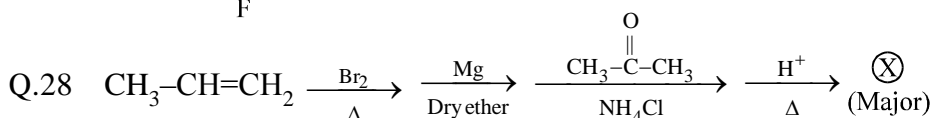
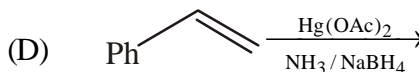
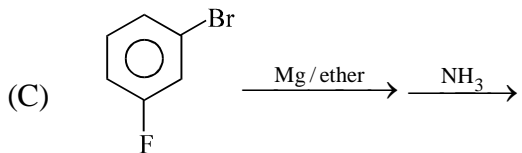
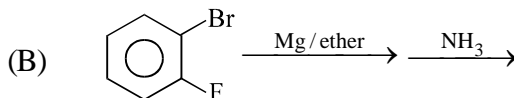
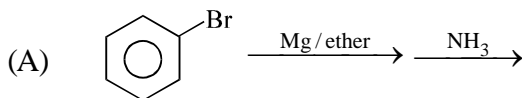


Product C is

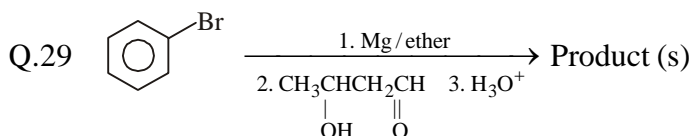
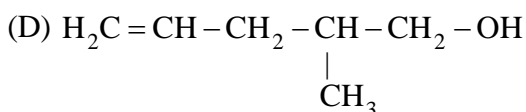
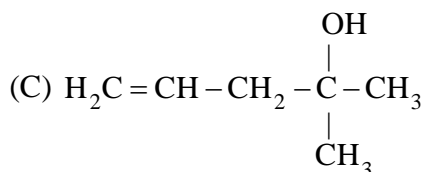
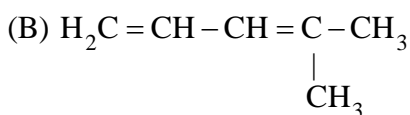
- (A) CO (B) $^{14}\text{CO}_2$
 (C) CO_2 (D) A mixture of $^{14}\text{CO}_2$ and CO_2



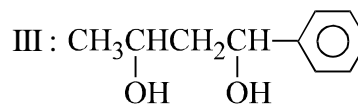
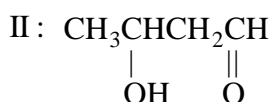
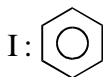
Q.27 Which reaction gives 1° aromatic amine as major product.



End product of above reaction is



Select the product from the following



(A) III

(B) I, III

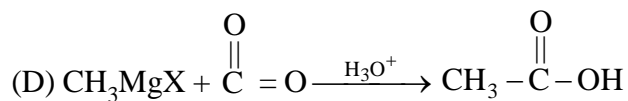
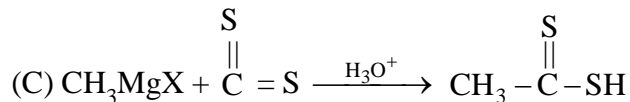
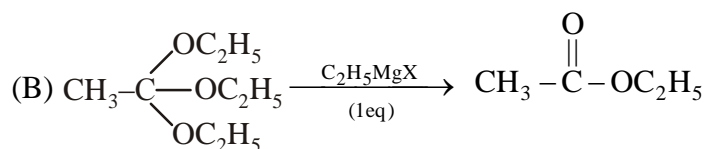
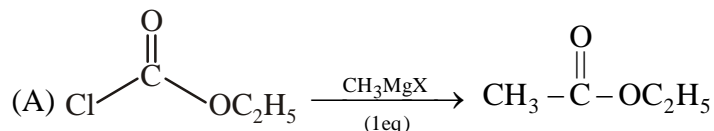
(C) I, II

(D) II, III

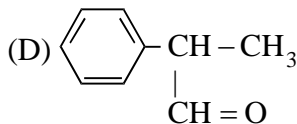
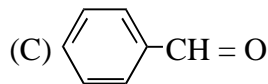
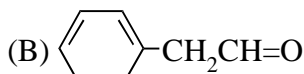
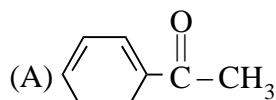
- Q.30 $\text{RMgX} \xrightarrow[\text{(ii) H}_3\text{O}^+]{\text{(i) CH}_3\text{CN}}$ (A) $\xrightarrow[\text{(ii) aq. NH}_4\text{Cl}]{\text{(i) RMgX}}$ (B) will be
 (A) 1° ROH (B) 2° ROH (C) 3° ROH (D) Alkene

- Q.31 $\text{C}_2\text{H}_5\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OC}_2\text{H}_5 \xrightarrow{2\text{CH}_3\text{MgBr}}$ A. Product A formed
 (A) is ethyl acetate
 (B) further react with $\text{CH}_3\text{MgBr}/\text{H}_2\text{O}^+$ to give acetone
 (C) further react with $\text{CH}_3\text{MgBr}/\text{H}_2\text{O}^+$ to give t-butyl alcohol
 (D) Can give pinacol when treated with Mg followed by H_2O

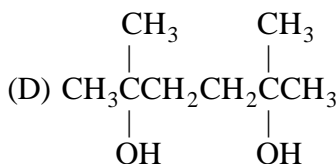
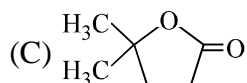
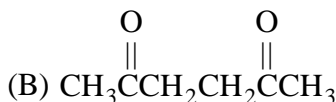
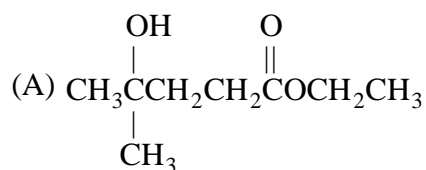
- Q.32 Which of the following is incorrect.

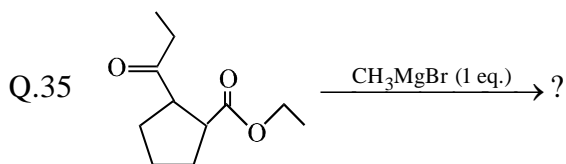


- Q.33 $\text{C}_6\text{H}_5\text{MgBr} + \text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl} \longrightarrow$ product.

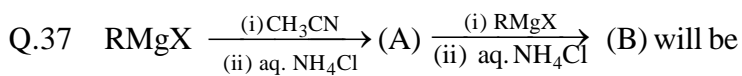
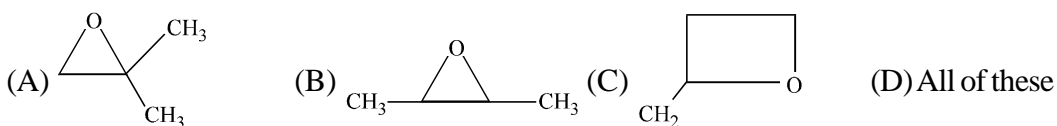
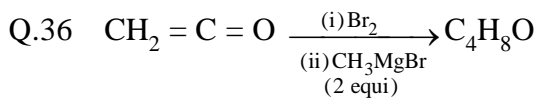
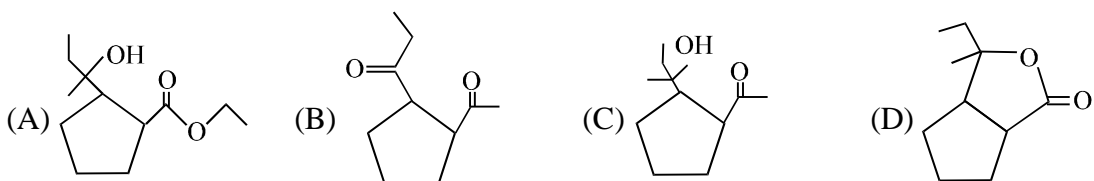


- Q.34 $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}\text{CH}_2\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}\text{OCH}_2\text{CH}_3 \xrightarrow[\text{(ii) H}_3\text{O}^+]{\text{(i) CH}_3\text{MgBr (one mol)}}$ A, A formed in this reaction is

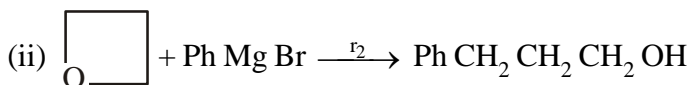




The product is:



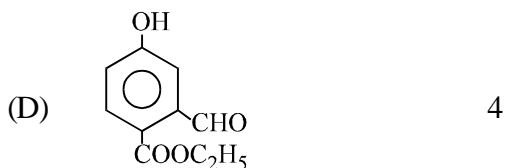
(A) 1° ROH (B) 2° ROH (C) 3° ROH (D) Alkene



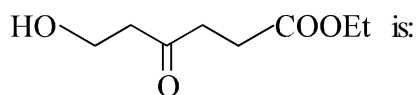
(A) $r_2 > r_1$ (B) $r_1 > r_2$ (C) $r_1 = r_2$ (D) $r_1 = 2r_2$

Q.39 Compounds are shown with the no. of RMgX required for complete reaction, select the incorrect option

- (A) $\text{CH}_3\text{COOC}_2\text{H}_5$ 1
 (B) CH_3COCl 2
 (C) $\text{HOCH}_2\text{COOC}_2\text{H}_5$ 3

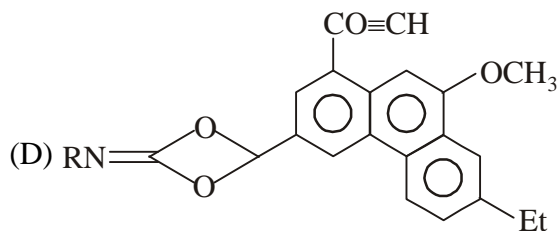
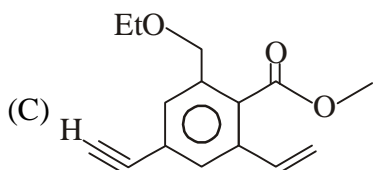
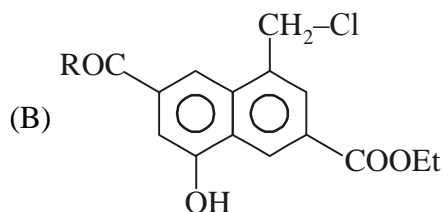
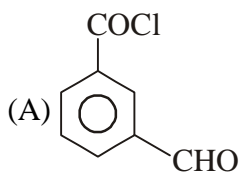


Q.40 The number of moles of grignard reagent consumed per mole of the compound

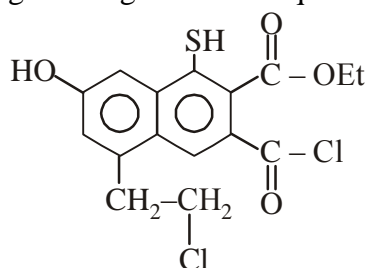


(A) 4 (B) 2 (C) 3 (D) 1

Q.41 Which of the following reacts with 4 moles of RMgX .



Q.42 How many moles of Grignard reagent will be required by one mole of given compound?



(A) 7

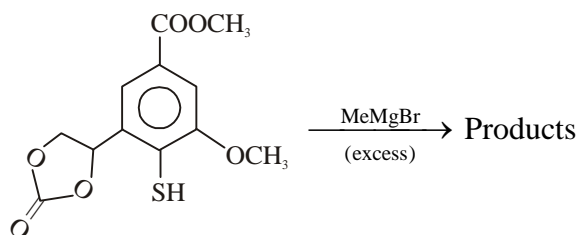
(B) 6

(C) 8

(D) 5

For Q. No.43 to Q. No. 45

Consider the given reaction and answer the following questions



Q.43 No. of RMgX consumed in the reaction is

(A) 4

(B) 5

(C) 6

(D) 7

Q.44 How many product will be formed in given reaction (excluding stereo)

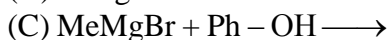
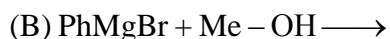
(A) 2

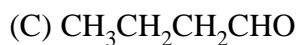
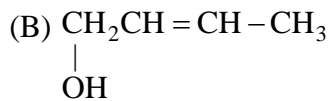
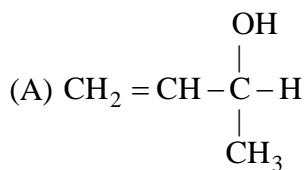
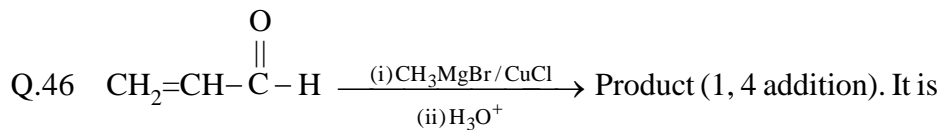
(B) 3

(C) 4

(D) 5

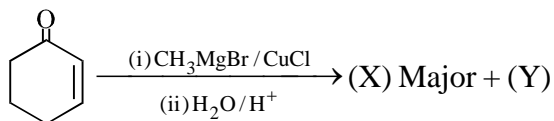
Q.45 Which of the following reaction will give the same Hydrocarbon formed as one of the product in the above reaction.



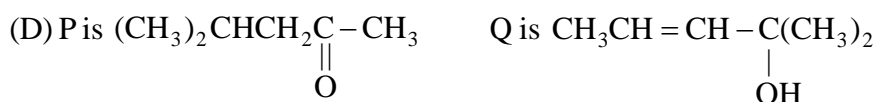
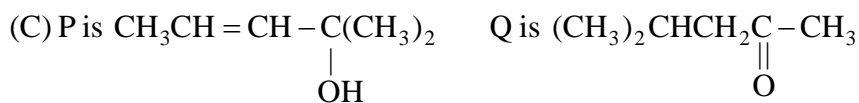
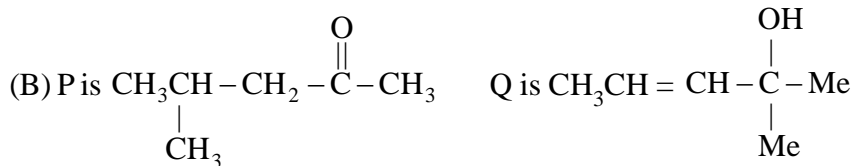
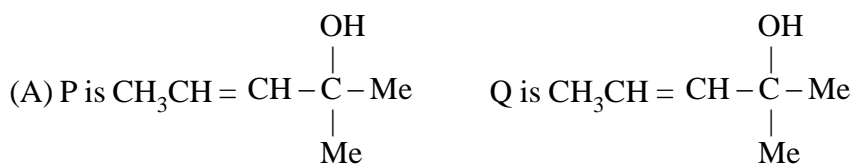
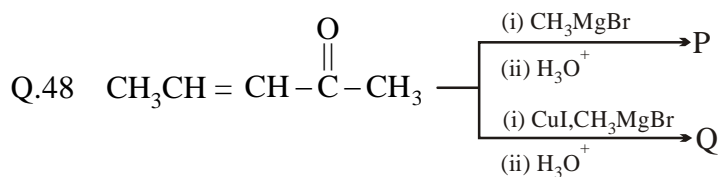
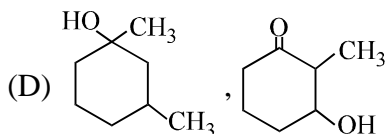
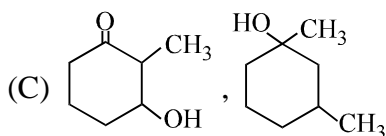
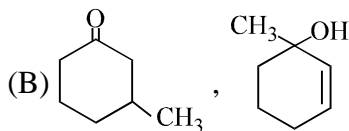
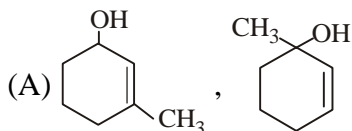


(D) none

Q.47 In the reaction sequence:



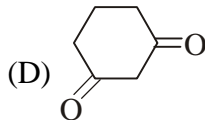
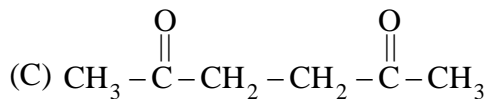
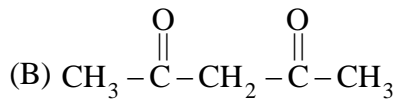
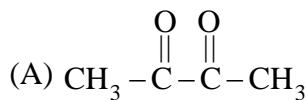
(X) & (Y) respectively are



EXERCISE - II

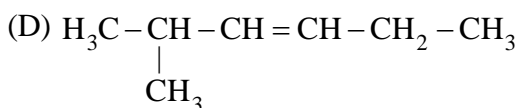
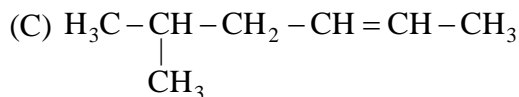
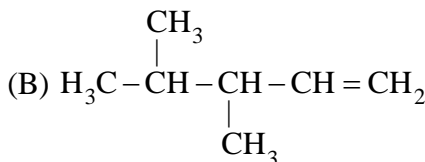
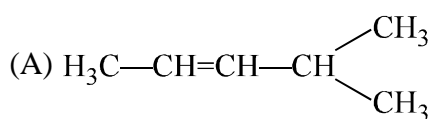
- Q.1 Which of the following reacts with Grignard reagent to give alkane?
 (A) nitro ethane (B) acetyl acetone
 (C) acetaldehyde (D) acetone

- Q.2 Nucleophilic addition of Grignard reagent cannot occur in



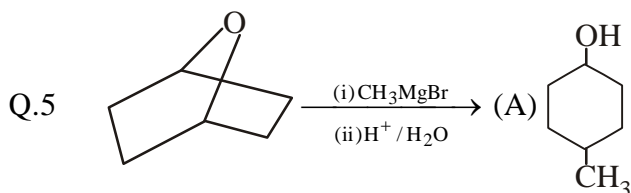
- Q.3 $\text{H}_3\text{C} - \text{CH}_2 - \text{CH}_2 - \underset{\text{OH}}{\text{CH}_2} \xrightarrow[\Delta]{\text{conc. H}_2\text{SO}_4} \text{X} + \text{Y} \xrightarrow[\text{CCl}_4/\text{peroxide}]{\text{NBS}} \xrightarrow{(\text{CH}_3 - \underset{\text{CH}_3}{\text{C}})_2\text{CuLi}} \text{Product(s)}$

Product(s) are:

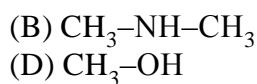
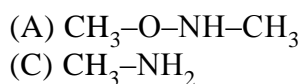
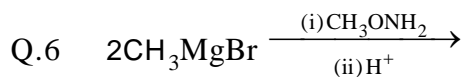


- Q.4 Select the **correct** statement:

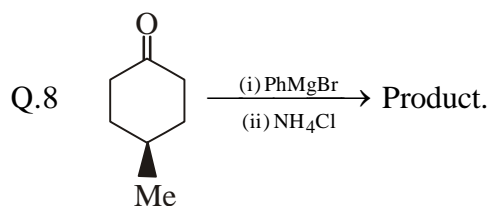
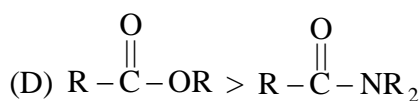
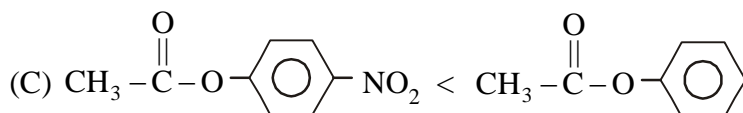
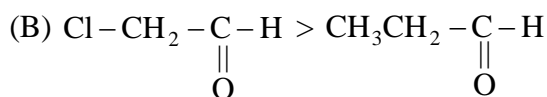
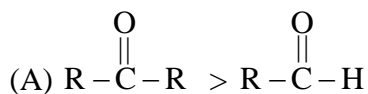
- (A) 1,4-dibromobutane react with excess of magnesium in ether to generate di-Grignard reagent.
 (B) 1,2-dichlorocyclohexane treated with excess of Mg in ether produces cyclohexene.
 (C) Vicinal dihalides undergo dehalogenation to give alkene when heated with Zn dust or Mg.
 (D) 1,3-dichloropropane by treatment with Zn dust or Mg forms cyclopropane.



- (A) The product is optically active
 (B) The product contains plane of symmetry
 (C) The product shows geometrical isomerism.
 (D) The product shows optical isomerism.

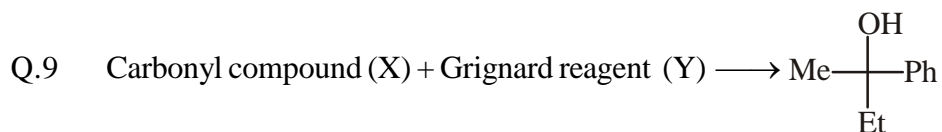


Q.7 Select the correct order of reactivity towards Grignard reagent for nucleophilic attack.

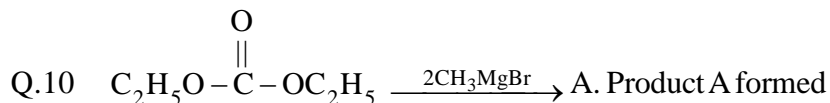
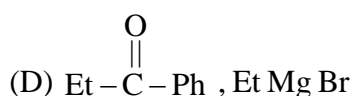
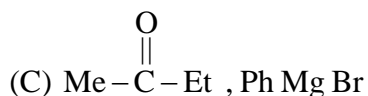
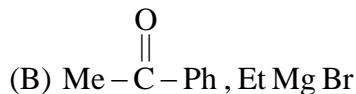
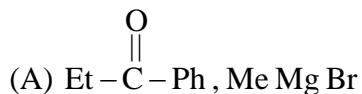


Products in this reaction will be

- (A) Stereoisomers (B) Enantiomer (C) Diastereomers (D) Geometrical isomers

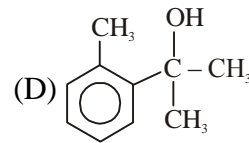
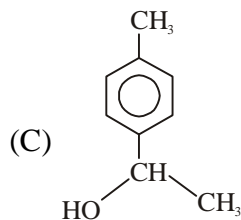
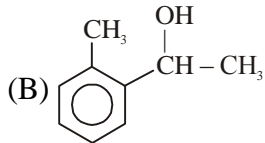
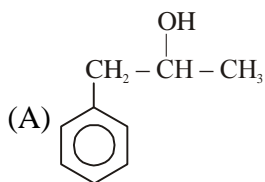
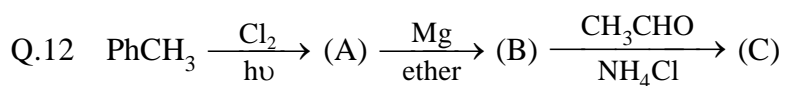
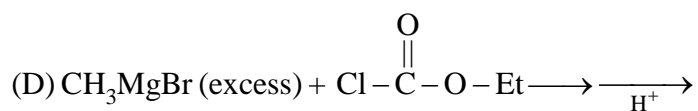
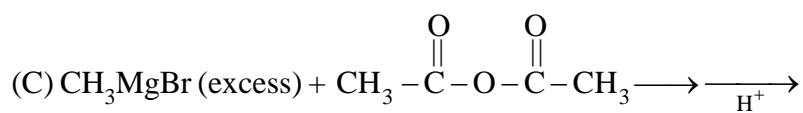
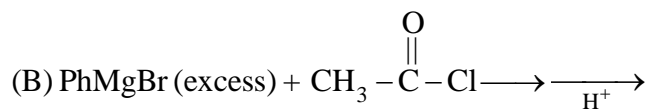
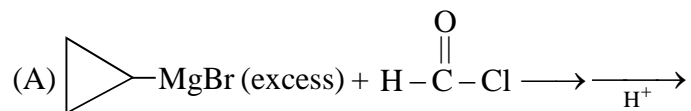


X, Y will be

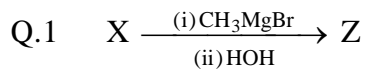


- (A) is ethyl acetate
(B) further react with $\text{CH}_3\text{MgBr}/\text{H}_2\text{O}^+$ to give acetone
(C) further react with $\text{CH}_3\text{MgBr}/\text{H}_2\text{O}^+$ to give t-butyl alcohol
(D) Can give pinacol when treated with Mg followed by H_2O

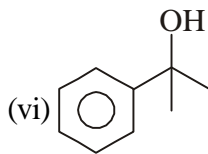
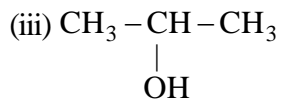
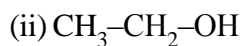
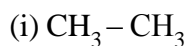
Q.11 In which of the following reactions 3° alcohol will be obtained as a product.



EXERCISE-III

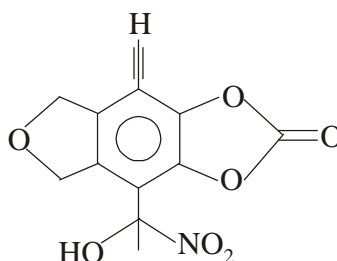


What can be used as X if Z is

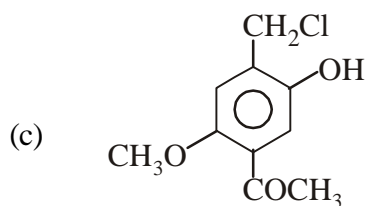
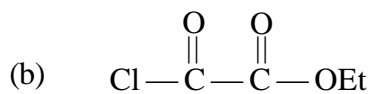


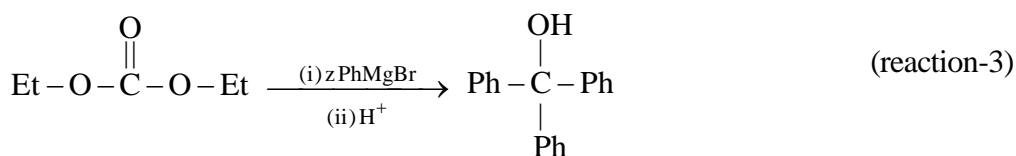
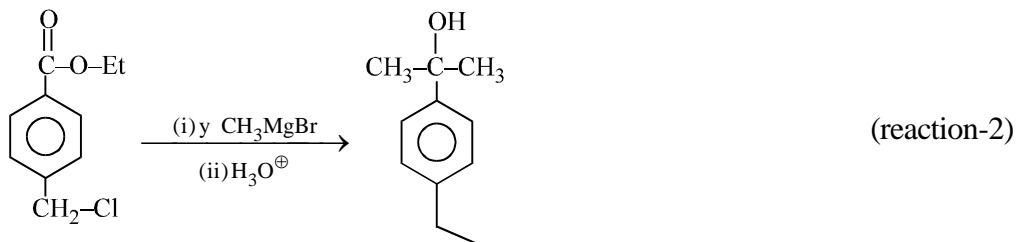
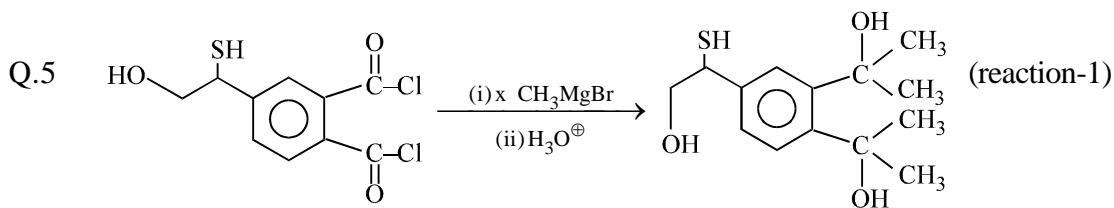
Q.2 4.6 g of a polyhydric alcohol was treated with an excess of methyl magnesium bromide to produce 3.36 litre of CH_4 at STP. Calculate number of $-\text{OH}$ group present in the alcohol.
(molecular weight of alcohol = 92)

Q.3 Calculate number of molecules of Grignard reagent consumed by 1 molecule of following compound.



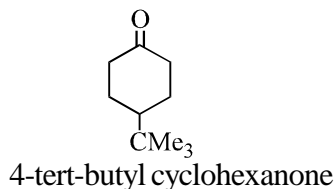
Q.4 Number of RMgX consumed per molecule with the following reactant.



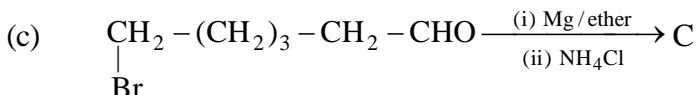
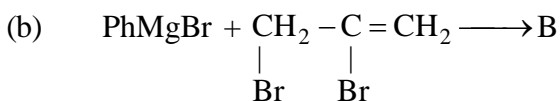
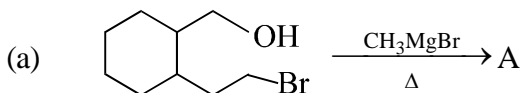


What is the value of $x + y + z = ?$

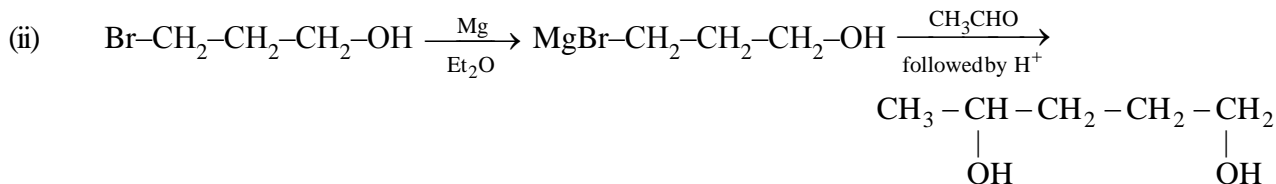
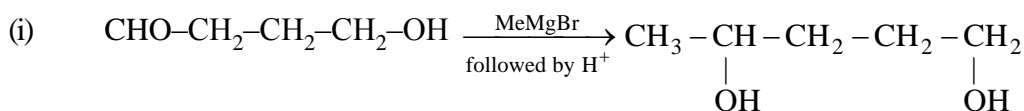
- Q.6 How many cycloalkyl chloride (without considering stereoisomers) would yield 1,3-dimethyl-cyclohexane on conversion into the Grignard reagent followed by treatment with ethanol.
- Q.7 How many grams of benzene would be produced when 135.5 gms of phenyl magnesium chloride is treated with 224 ml of ethyne at STP?
- Q.8 Addition of phenyl magnesium bromide to 4-tert-butyl cyclohexanone gives two isomeric tertiary alcohol as product. Both alcohol yield same alkene when subjected to acid-catalyzed dehydration. Suggest a reasonable structure for these two alcohol.



- Q.9 Organic halide having carbonyl, cyanide, epoxy, OH, $-NH_2$, $-NHR$, $-CO_2H$, $-SO_3H$, $-SH$, $-C\equiv CH$ group cannot be used to prepare grignard reagent. Explain why?
- Q.10 What is the product in the following reactions.



Q.11 Neither of these methods of making pentan-1,4 diol will work. Explain why not – what will happen instead?



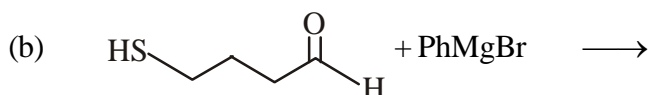
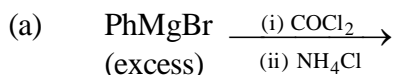
Q.12 Conversion : $\text{HC}\equiv\text{CH} \longrightarrow \text{CH}_3-\text{C}\equiv\text{CD}$
 $\text{Ph}-\text{Br} \longrightarrow \text{Ph}-\text{D}$

Q.13 (a) Unlike other esters which react with Grignard reagents to give tertiary alcohols, ethyl formate

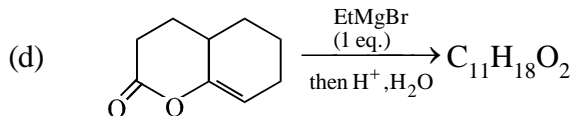
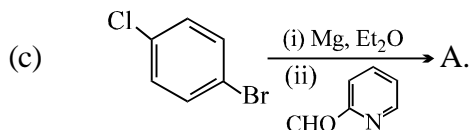
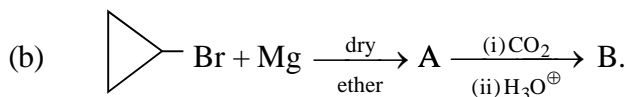
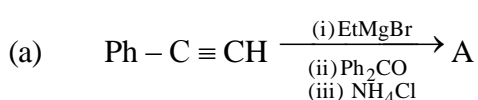
$\text{HCOCH}_2\text{CH}_3$ yields a different class of alcohols on treatment with Grignard reagents. What kind of alcohol is formed in this case and why?

(b) Diethyl carbonate ($\text{CH}_3\text{CH}_2\text{OCOCH}_2\text{CH}_3$) reacts with excess Grignard reagent to yield alcohols of a particular type. What is the structural feature that characterizes alcohols prepared in this way?

Q.14 What are the products ?



Q.15 What products would be formed in these reactions ?

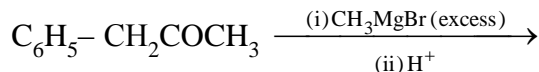


EXERCISE-IV

Q.1 Write the structural formula of main organic product formed when ethyl acetate is treated with double the molar quantity of methyl magnesium bromide and the reaction mixture is poured into water. [JEE 1981]

Q.2 Identify the major product. [JEE 1993]
 $C_6H_5COOH + CH_3MgI \longrightarrow ? + ?$

Q.3 Predict the major product. [JEE 1994]



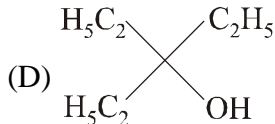
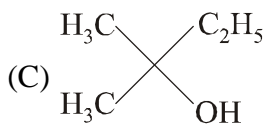
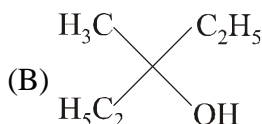
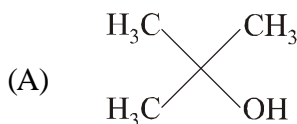
Q.4 Which of the following is an organometallic compound? [JEE 1997]

- (A) Lithium methoxide (B) Lithium acetate
 (C) Lithiumdimethylamide (D) Methyl lithium

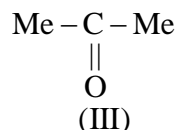
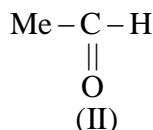
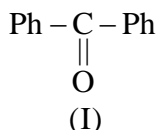
Q.5 $(CH_3)_3CMgCl$ on treatment with D_2O produces [JEE 1997]

- (A) $(CH_3)_3CD$ (B) $(CH_3)_3COD$ (C) $(CD)_3CD$ (D) $(CD)_3COD$

Q.6 Ethyl ester $\xrightarrow[(excess)]{CH_3MgBr}$ P, the product 'P' will be [JEE 2003]

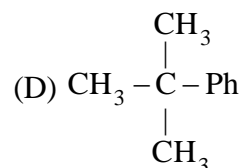
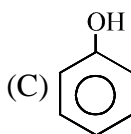
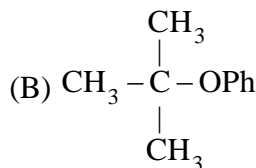
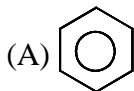


Q.7 Order of rate of reaction of following compounds with phenyl magnesium bromide is: [JEE 2004]

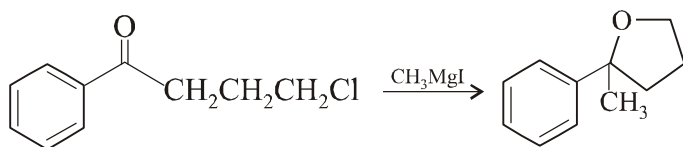


- (A) I > II > III (B) II > III > I (C) III > I > II (D) II > I > III

Q.8 $Ph-MgBr + CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH \longrightarrow A$ [JEE 2005]



Q.9 Identify the reaction mechanism: [(II-7-b)JEE 2011]



ANSWER KEY

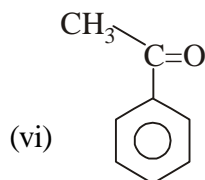
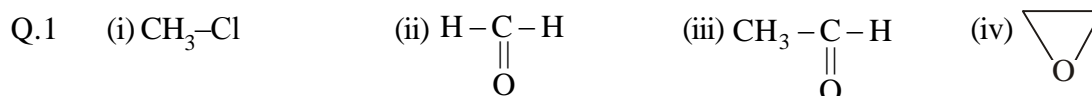
EXERCISE - I

Q.1	D	Q.2	A	Q.3	A	Q.4	C	Q.5	C	Q.6	A	Q.7	C
Q.8	C	Q.9	D	Q.10	D	Q.11	A	Q.12	B	Q.13	B	Q.14	A
Q.15	ABC	Q.16	A	Q.17	C	Q.18	D	Q.19	BD	Q.20	A	Q.21	C
Q.22	AB	Q.23	C	Q.24	C	Q.25	C	Q.26	C	Q.27	B	Q.28	B
Q.29	C	Q.30	C	Q.31	CD	Q.32	B	Q.33	C	Q.34	C	Q.35	D
Q.36	A	Q.37	C	Q.38	B	Q.39	A	Q.40	A	Q.41	D	Q.42	A
Q.43	C	Q.44	C	Q.45	C	Q.46	A	Q.47	B	Q.48	C		

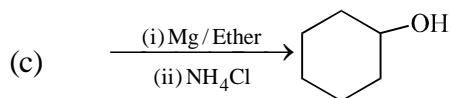
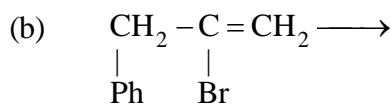
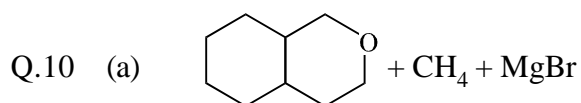
EXERCISE - II

Q.1	AB	Q.2	BD	Q.3	BC	Q.4	ACD	Q.5	BC
Q.6	CD	Q.7	BD	Q.8	ACD	Q.9	ABC	Q.10	CD
Q.11	BCD	Q.12	ABC						

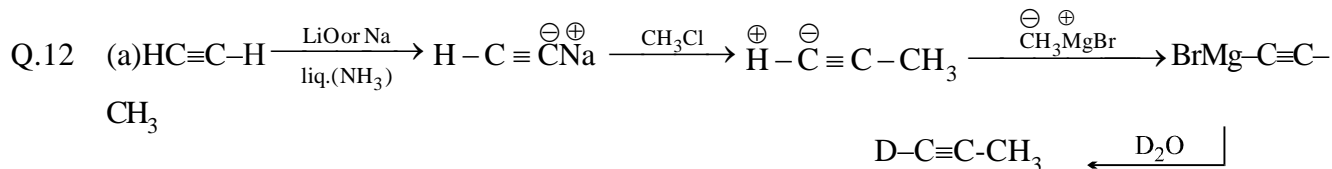
EXERCISE-III



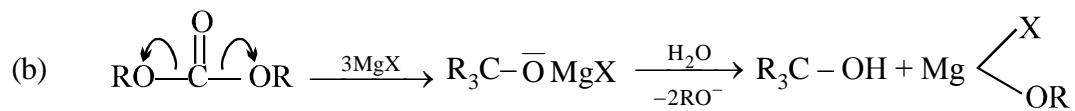
Q.2	3	Q.3	5	Q.4	1434	Q.5	12	Q.6	5
Q.7	1.56 gms	Q.8	Geometrical isomer will formed	Q.9	Not required				



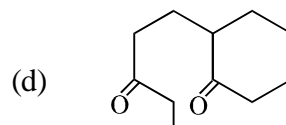
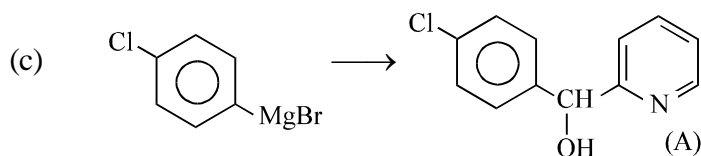
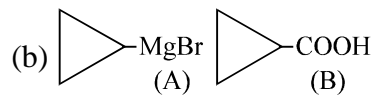
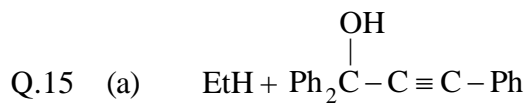
Q.11 Due to acidic hydrogen



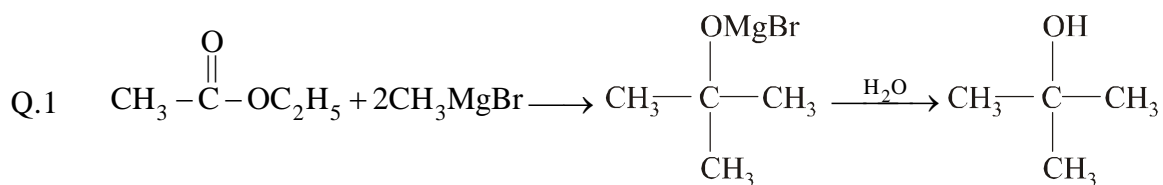
Q.13 (a) Formate gives aldehydes & other esters gives ketones.



Q.14 (a) $\text{Ph}_3\text{C}-\text{OH}$ (b) PhH



EXERCISE-IV



Q.4 D Q.5 A Q.6 A Q.7 B Q.8 A

Q.9 Nucleophilic substitution & Nucleophilic addition