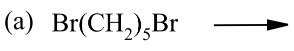
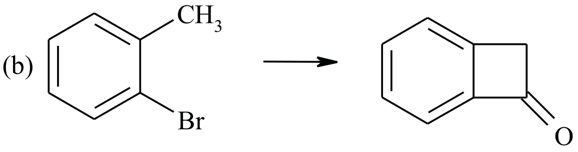
ALDEHYDES AND KETONES

PROBLEM 1013 Synthesize 3-pentanone using alkyl bromide containing not more than two carbons.

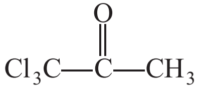




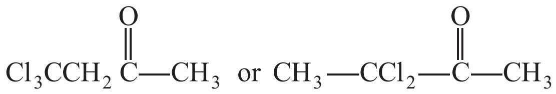
PROBLEM 1014 Convert:

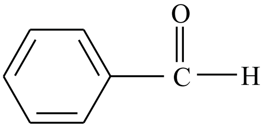
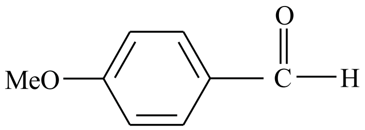
PROBLEM 1015 A hydrocarbon *A*(C_7H_{14}) exist in two stereomeric forms. *A* on reductive ozonolysis yields *B*(C_3H_6O) and *C*(C_4H_8O). *B* on catalytic hydrogenation yields *D*(C_3H_8O) that can't be resolved into enantiomers whereas *C* on catalytic hydrogenation yields *E*($C_4H_{10}O$), which can be resolved into enantiomers. *B* on treatment with HCN followed by hydrolysis of product yields *F*($C_4H_8O_3$) which can be resolved into enantiomers. *C* on treatment with HCN followed by hydrolysis of product yields *G*($C_5H_{10}O_3$), which is also resolvable. Identify *A* to *G* and show the stereomeric structures of *A*.

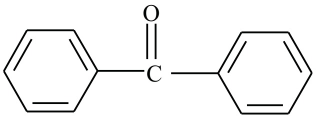
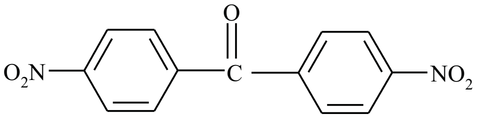
PROBLEM 1016 Which of the following pairs has larger equilibrium constant for addition of water?

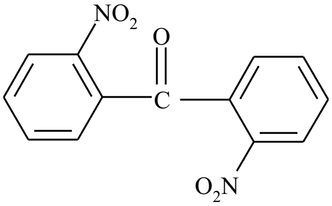
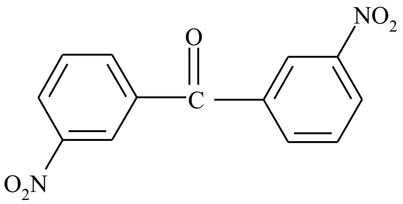


(a) Cl_3CCHO or $Cl_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

(b) 
$Cl_3CCH_2\overset{O}{\overset{\|}{C}}—CH_3$ or $CH_3—CCl_2—\overset{O}{\overset{\|}{C}}—CH_3$

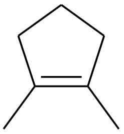
(c)  or 

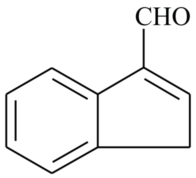
(d)  or 

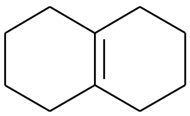
(e)  or 

Problem 1017 An organic compound $A(C_6H_{10})$ on catalytic hydrogenation with H_2/Pt yields C_6H_{12}. A on ozonolysis followed by work-up with Zn-H_2O yields $B(C_6H_{10}O_2)$. B on refluxing with dilute NaOH solution gives C (C_6H_8O). C on catalytic reduction yields $D(C_6H_{12}O)$. D on treatment with chromic acid yields E $(C_6H_{10}O_2)$ which on heating with soda lime yields $F(C_5H_{10})$. F on monochlorination yields a single isomer. Identify A to F.

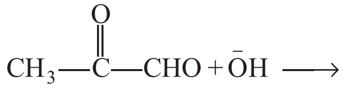
Problem 1018 Predict products in the following reactions:

(a)  $+$ cold,dil, alk $KMnO_4 \longrightarrow A \xrightarrow{HIO_4} B \xrightarrow{^{-}OH} C$

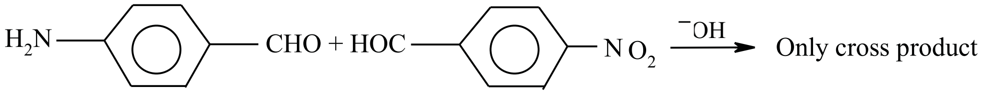
(b) $A + OsO_4 \xrightarrow{H_2O_2} B \xrightarrow{HIO_4} C \xrightarrow{^{-}OH}$ 

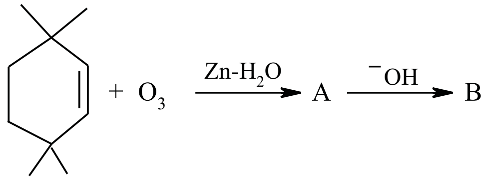
(c)  $\xrightarrow[Zn\text{-}H_2O]{O_3} A \xrightarrow[\Delta]{^{-}OH} B$

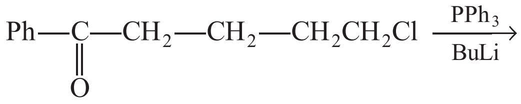
Problem 1019 Predict products in the following Cannizzaro reactions:

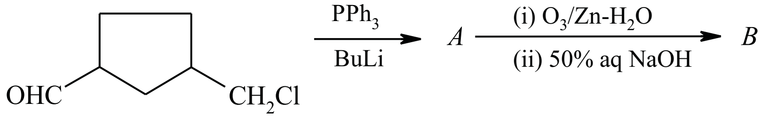
(a) 
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CHO+\bar{O}H \longrightarrow$$

Problem 1020 Write products in the following reactions:

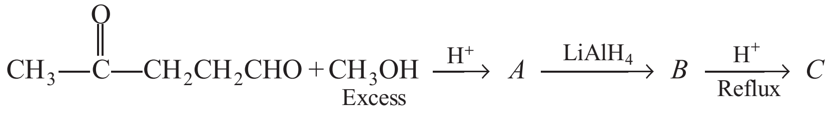
(b) 

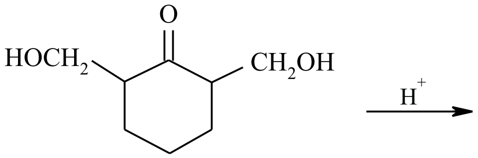
(c) 

(a) 
$$Ph-\underset{\underset{\displaystyle O}{\|}}{C}-CH_2-CH_2-CH_2CH_2Cl \xrightarrow[BuLi]{PPh_3}$$

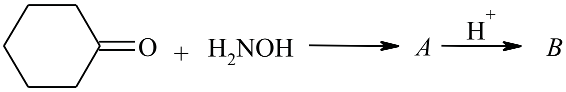
(b) 

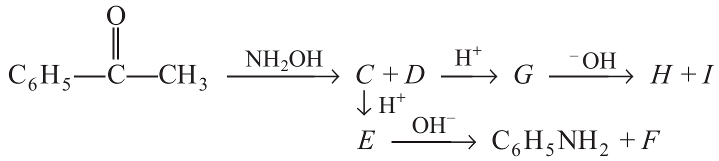
Problem 1021 Predict product in the following reactions

(a) 
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_2CHO+\underset{Excess}{CH_3OH} \xrightarrow{H^+} A \xrightarrow{LiAlH_4} B \xrightarrow[Reflux]{H^+} C$$

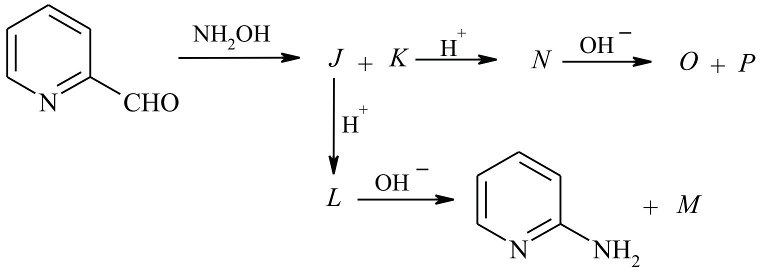
(b) 

Problem 1022 Predict products in the following reactions:

(a) 

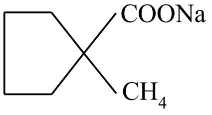
(b) 
$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow{NH_2OH} C+D \xrightarrow{H^+} G \xrightarrow{^-OH} H+I$$
$$C+D \;\downarrow H^+$$
$$E \xrightarrow{OH^-} C_6H_5NH_2+F$$

(c)



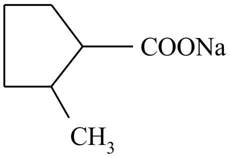
Problem 1023 An organic compound *A* has molecular formula $C_{11}H_{14}O$. *A* on treatment with hydroxyl amine yields two stereomers *B* and *C* with their molecular formula $C_{11}H_{15}NO$. *B* on treatment with concentrated sulphuric acid solution yields *D*, an isomer of *B* where *C* on treatment with concentrated sulphuric acid solution yields *E*, another isomer of *C*. *D* on alkaline hydrolysis yields a white crystalline solid and an optically active amine $F(C_4H_{11}N)$. *E* on alkaline hydrolysis produces aniline as one product. Identify *A* to *F*.

Problem 1024 When 2-chloro-6-methyl cyclohexanone is treated with NaOH, ring contraction occurs and compound (i) is formed not (ii) explain through mechanism.



(i)

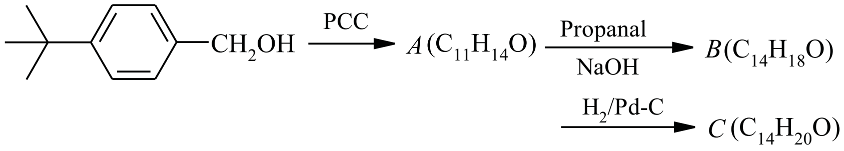
not



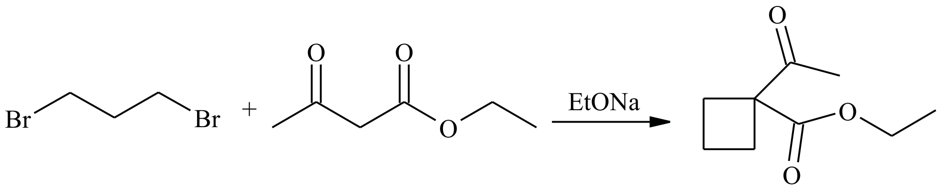
(ii)

Problem 1025 Synthesize (a) 5-nonanone from 1-butanol as only starting organic compound.
(b) 2-butanone from ethyl bromide.

Problem 1026 Outlined below is a synthesis of a compound used in perfumes. Provide all missing structures.



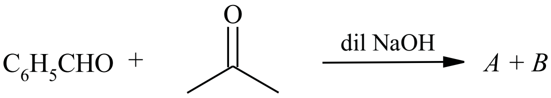
Problem 1027 Show mechanism of the following reaction



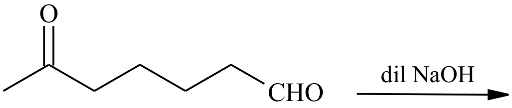
Problem 1028 An organic compound $A(C_{12}H_{20})$ decolourise bromine water, and on reductive ozonolysis produces two molecules of $B(C_6H_{10}O)$. *B* on aldol condensation followed by dehydration of product gives *C*($C_{12}H_{18}O$) which on reduction with N_2H_4/OH^- regenerate *A*. *B* on reduction with Zn(Hg)/C·HCl produces C_6H_{12}(*D*) which on monochlorination gives $C_6H_{11}Cl$(*E*) as a sole product. Identify *A* to *E*.

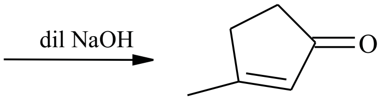
Problem 1029 Complete the following reactions:

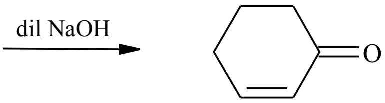
(b) $C_6H_5CHO + C_6H_5COCH_3 \xrightarrow{\text{dil. NaOH}} A + B$

(a) 

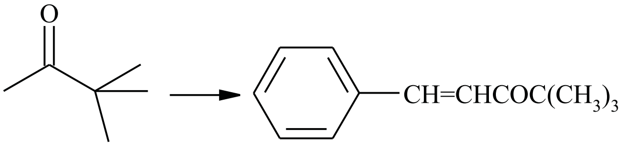
(c) $C_6H_5CHO + CH_3NO_2 \xrightarrow{\text{dil. NaOH}}$

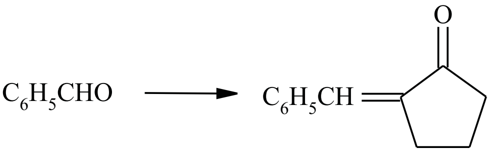
(d) 

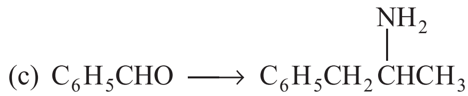
(e) ? 

(f) ? 

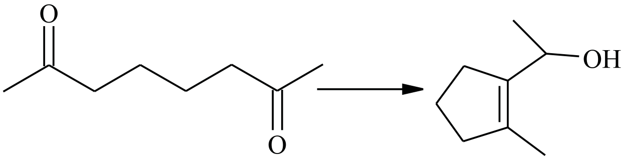
Problem 1030 Carry out the following transformations:

(a) 

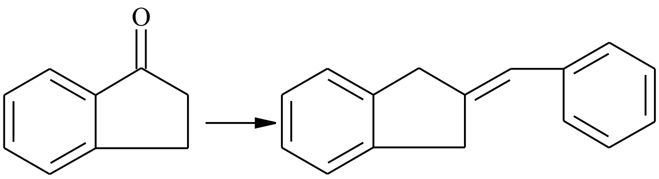
(b) 

(c) 

$$C_6H_5CHO \longrightarrow C_6H_5CH_2\overset{\overset{NH_2}{|}}{C}HCH_3$$

(d) 

(e)



PROBLEM 1031 An alkene (*A*) on reductive ozonolysis yields acetone and an aldehyde. The aldehyde is easily oxidised to an acid *B*. *B* when treated with Br_2/P yields a compound *C* which on hydrolysis gives *D*. *D* can also be obtained from acetone by reaction with HCN/H_2O. Identify *A* to *D*.

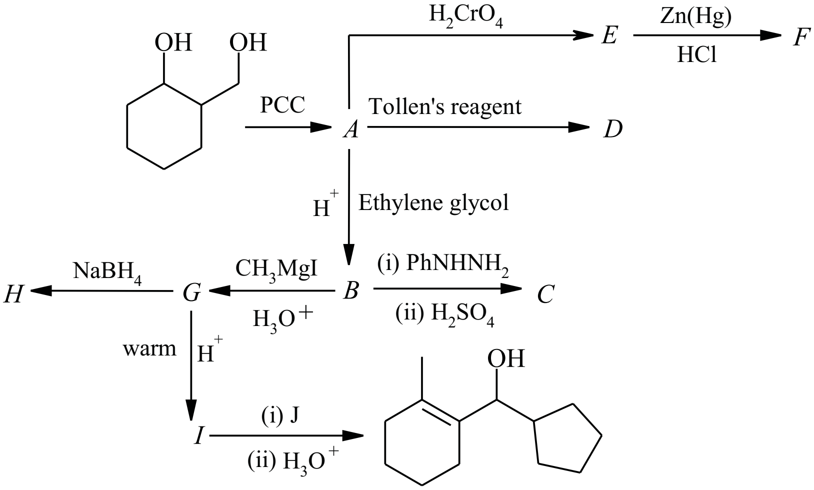
PROBLEM 1032 A hydrocarbon *A* containing C = 88.24% (MW=68) when reacted with Na followed by *n*-propylbromide, produces a compound *B*(C_8H_{14}). It gave a ketone $C_5H_{16}O$(*C*) with Hg^{2+}/H_2SO_4. *B* on refluxing with H^+/$KMnO_4$ gave two isomeric acid *D* and *E*. Identify *A* to *E*.

PROBLEM 1033 A compound having molecular formula C_6H_{12} is treated with Cl_2 in CCl_4 to form a compound *B*($C_6H_{12}Cl_2$). B is treated with alcoholic KOH followed by $NaNH_2$ resulting in the formation of *C* (C_6H_{10}). *C* when treated with Pt/H_2 gave 2-methyl pentane. Compound *C* does not react with $NaNH_2$ and with NH_4OH/$AgNO_3$. On ozonolysis *A* gave two aldehydes *D* and ethanal. Deduce the structure of *A* to *D*.

PROBLEM 1034 Compound *A*($C_7H_{16}O$) can be resolved into enantiomers and it reacts with $Na_2Cr_2O_7$/H_2SO_4 to give *B*($C_7H_{14}O$). When *B* is treated with NaOD at 25°C for several hours and then analyzed by mass spectroscopy, it is found to have MW = 116. Identify *A* and *B*.

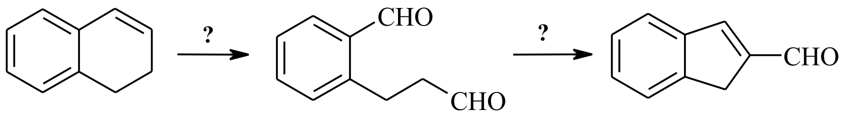
PROBLEM 1035 An organic compound *A*(C_7H_6O) on treatment with hydroxyl amine produces two isomeric compounds *B* and *C* with molecular formula C_7H_7NO. *B* and *C* on acidification rearranges to *D* and *E* respectively. *D* on alkaline hydrolysis produces a white crystalline solid *F*($C_7H_6O_2$) and ammonia gas whereas alkaline hydrolysis of *E* produces *G* and formic acid. Identify *A* to *G* describing mechanism of their formation.

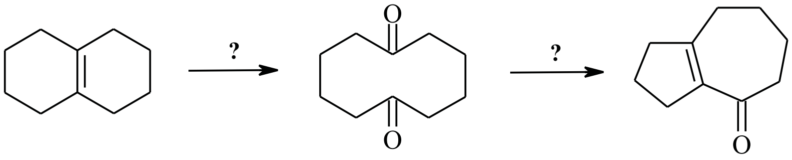
PROBLEM 1036 The following road-map problem centers on the structure and properties of *A*, a key intermediate in these reaction. Give structures for the compounds *A* through *J*:

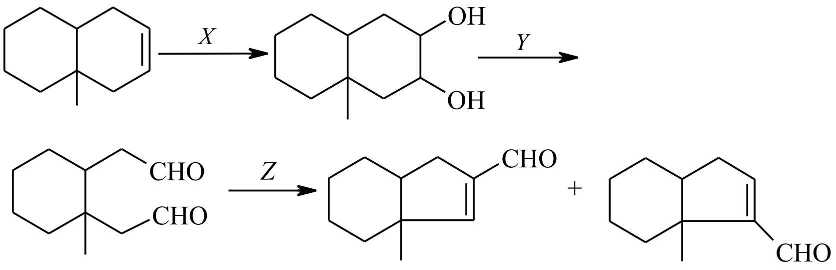


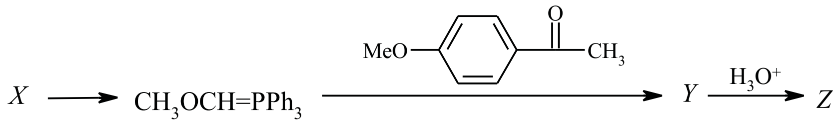
Problem 1037 An optically active alcohol *A*($C_5H_{12}O$) on oxidation with PCC gives an optically active aldehyde *B*($C_5H_{10}O$). *B* on treatment with dilute OH^- gives *C*($C_{10}H_{20}O_2$). *C* on heating with H_2SO_4 gives *D*($C_{10}H_{18}O$) which after reductive ozonolysis gives *E*($C_6H_{10}O_2$) and *F*(C_4H_8O). *F* on treatment with I_2/OH^- gives an yellow precipitate. Identify *A* to *F*.

Problem 1038 Provide reagents in the following transformations

(a)


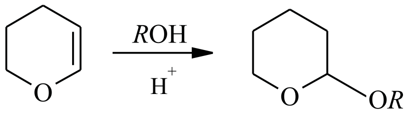
(b)


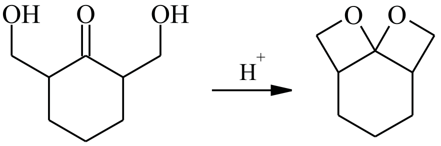
(c)


(d)


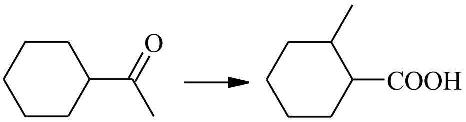
$X \longrightarrow CH_3OCH{=}PPh_3 \xrightarrow{\text{MeO-}C_6H_4\text{-}COCH_3} Y \xrightarrow{H_3O^+} Z$

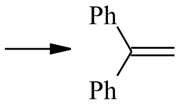
Problem 1039 Propose mechanism of the following reactions:

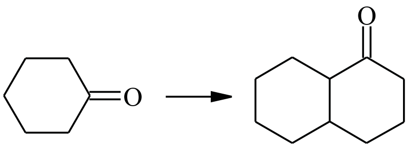
(a)


(b)


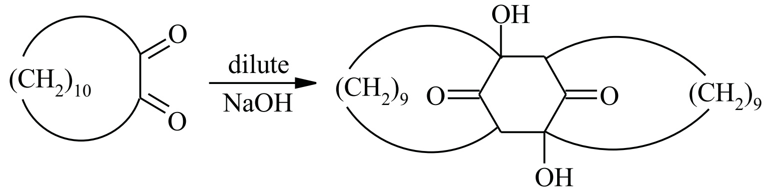
Problem 1040 Synthesize the compounds from indicated starting material:

(a)


(b) PhCHO


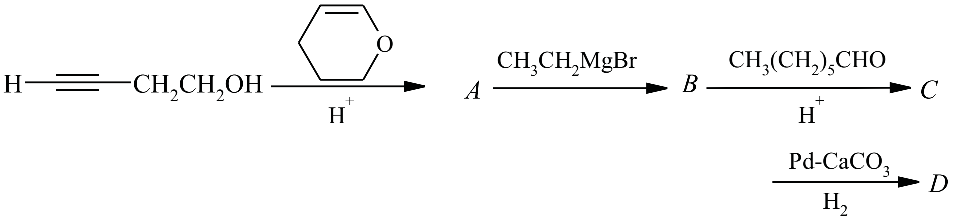
(c)


Problem 1041 Predict mechanism of the following reaction:

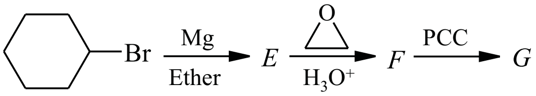


Problem 1042 Give the structures for the indicated compounds in the following reactions:

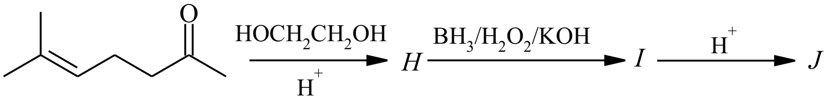
(a)



(b)

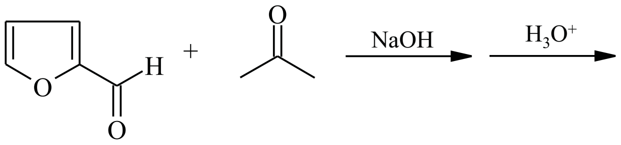


(c)

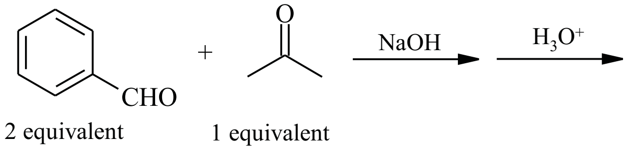


Problem 1043 Complete the following equations.

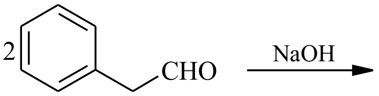
(a)



(b)

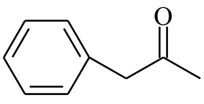


(c) 2

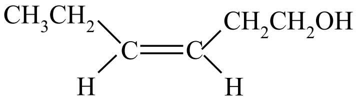


Problem 1044 Plan a synthesis for each of the following compounds through shortest route. You have been supplied bromobenzene and any organic reagents containing three or fewer carbon atoms and any inorganic reagents you need.

(a)

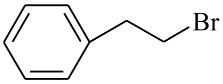


(b)

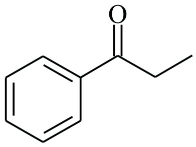


$$\begin{matrix} CH_3CH_2 & & CH_2CH_2OH \\ & C{=}C & \\ H & & H \end{matrix}$$

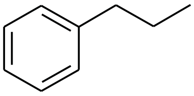
(c)



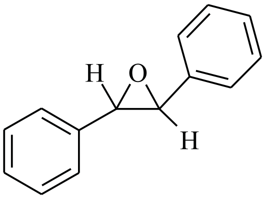
(d)



(e)

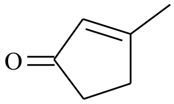


(f)



Problem 1045 A neutral, resolvable organic compound *A* has molecular formula ($C_8H_{16}O_2$). *A* on treatment with $LiAlH_4$ gives isomeric *B* and *C* ($C_4H_{10}O$) of which only *B* is optically active. *B* on treatment with acidified dichromate solution gives C_4H_8O(*D*) which on refluxing with dilute NaOH followed by acidification of product gave *E*($C_8H_{14}O$). *E* on heating with N_2H_4 in alkaline medium affords *F*(C_8H_{16}). *F* on treatment with $B_2H_6/H_2O_2/OH^-$ produced a resolvable *G*($C_8H_{18}O$). *G* on treatment with acidified dichromate solution produced *H*($C_8H_{16}O$) which on treatment with "*m*-chloroperbenzoic acid" produces *A*. Deduce structures of *A* to *H*.

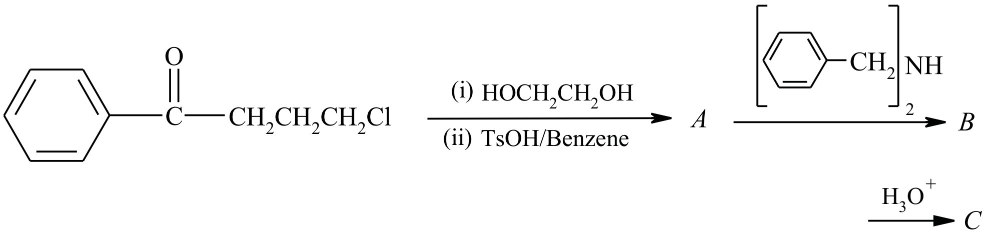
Problem 1046 An organic compound *A* has molecular formula ($C_7H_{12}O$) and does not decolourise Bayer's reagent and evolves no gas with Na-metal. *A* also does not react with either ammonical silver nitrate solution or phenyl hydrazine solution. *A* on refluxing with methanol in presence of trace amount of H_2SO_4 produces a non-resolvable *B*($C_8H_{16}O_2$). *B* on treatment with CrO_3/pyridine produced *C*($C_8H_{14}O_2$) which is non-resolvable. *C* on refluxing in HI solution produced another non-resolvable compound *D*($C_7H_{11}OI$). *D* on treatment with alcoholic KOH followed by oxidative ozonolysis of product produced *E*($C_7H_{10}O_4$) which does not show optical activity. *E* on simple heating produced $C_6H_{10}O_2$ which on refluxing with dilute NaOH gave:

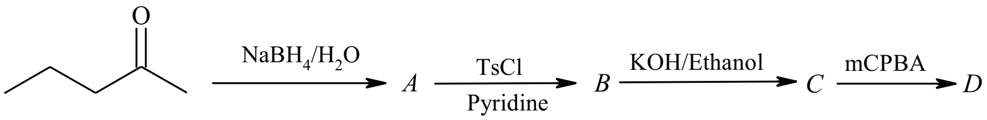


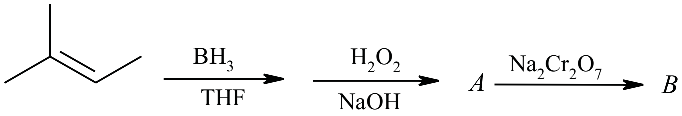
Deduce structures of *A* to *E*.

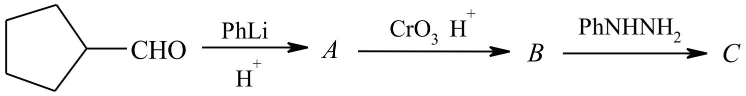
Problem 1047 Predict the structure of the products in the following reactions and show stereochemistry when it is known:

(a)

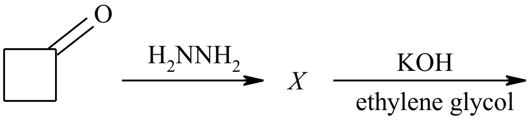


(b) 

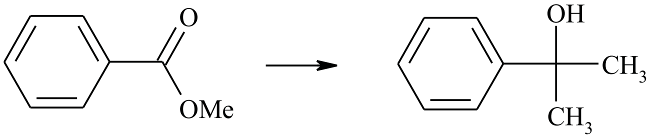
(c) 

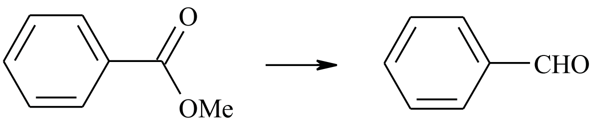
(d) 

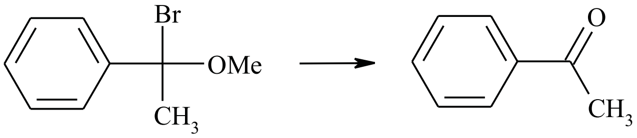
(e) $HC \equiv CH \xrightarrow{NaNH_2} D \xrightarrow{C_6H_5CH_2Br} E \xrightarrow{CH_3CH_2MgBr} F$

(f) 

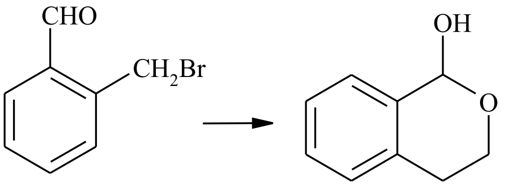
PROBLEM 1048 Bring about the following conversions:

(a) 

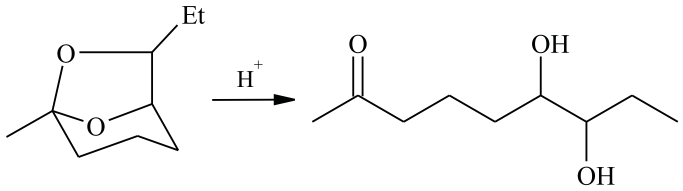
(b) 

(c) 

PROBLEM 1049 (a) Bring about the following transformation:

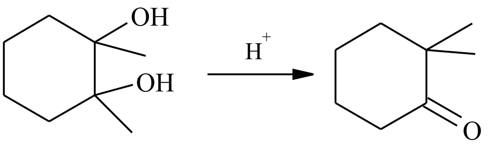


(b) Propose mechanism

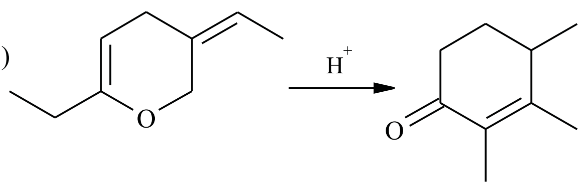


PROBLEM 1050 Propose mechanism:

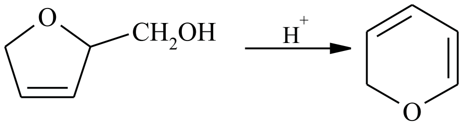
(a)



(b)

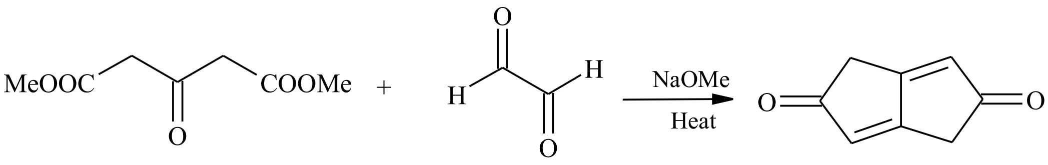


(c)

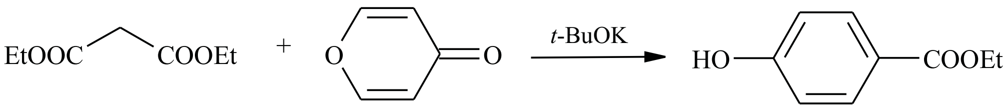


PROBLEM 1051 Propose mechanism:

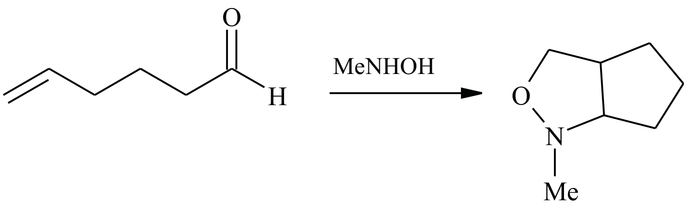
(a)



(b)

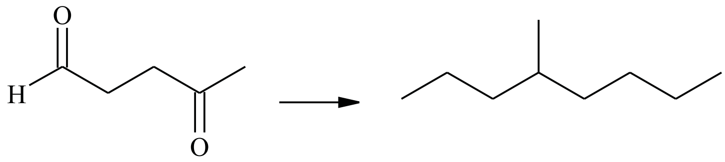


(c)

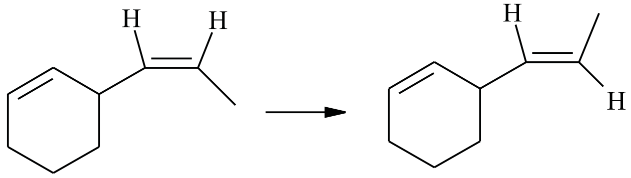


PROBLEM 1052 Bring about the following conversions:

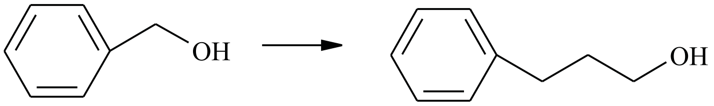
(a)



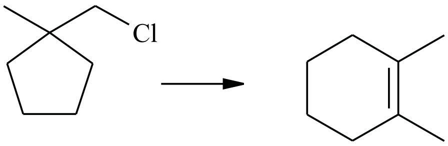
(b)



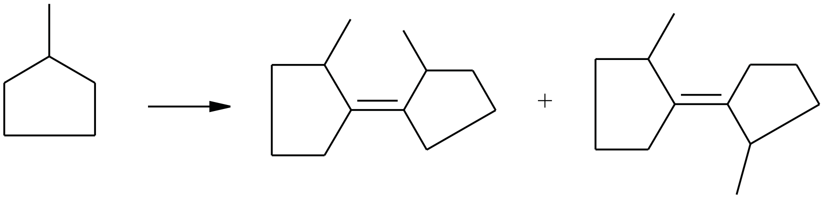
(c)



(d)

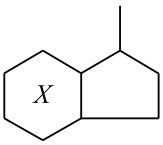


(e)



PROBLEM 1053 An optically active compound *A* has molecular formula $C_{10}H_{12}O$. *A* decolourises Bayer's reagent as well as it forms salt with NaOH. *A* on treatment with HBr forms $B(C_{10}H_{13}OBr)$ as major product which is still enantiomeric. *B* on treatment with alcoholic solution of KOH gives a stereomeric *C* that is also an isomer of *A*. *A* on treatment with acidic solution of $KMnO_4$ gives ortho hydroxy benzoic acid as one of the product. *A* on treatment with $B_2H_6/H_2O_2/NaOH$ produces $D(C_{10}H_{14}O_2)$ which on refluxing with dilute sulphuric acid produced $E(C_{10}H_{12}O)$, *E* neither decolourises Br_2-H_2O solution nor forms any salt with NaOH. Deduce structures of *A* to *E*.

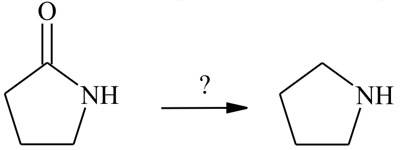
PROBLEM 1054 An organic compound has molecular formula $C_{10}H_6(A)$. *A* on treatment with $HgSO_4/H_2SO_4$ gives $B(C_{10}H_{10}O_2)$ which forms an insoluble precipitate with 2,4-DNP but fail to react with ammonical solution of $AgNO_3$. *B* on refluxing with dilute NaOH solution produced $C(C_{10}H_8O)$. *C* on further treatment with alkaline solution of N_2H_4 gives $D(C_{10}H_{10})$ which decolourises Br_2-H_2O solution. *D* on treatment with H_2/Pt produced the adjoining compound *X*.



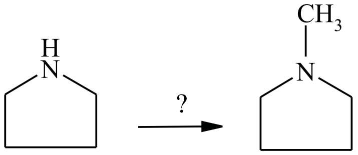
Deduce structures of *A* to *D*.

Problem 1055 Complete the followings:

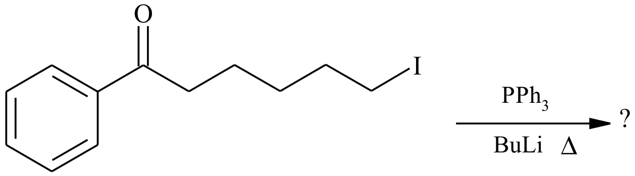
(a)



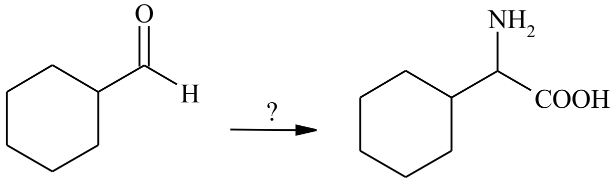
(b)



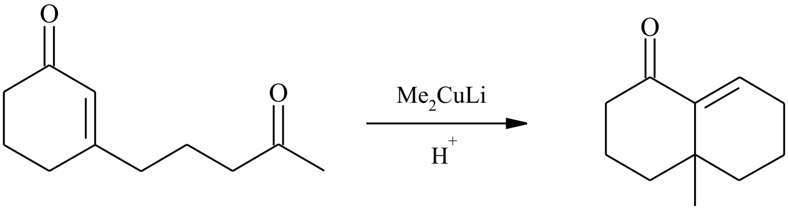
(c)



(d)



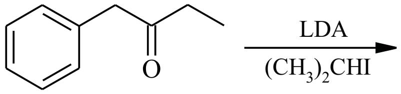
(e)



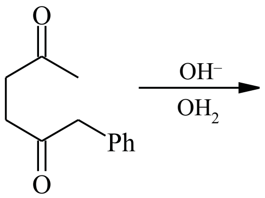
(Propose mechanism)

Problem 1056 Provide products in the following reactions:

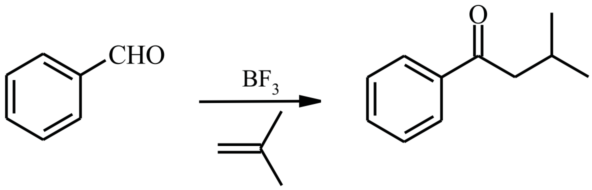
(a)



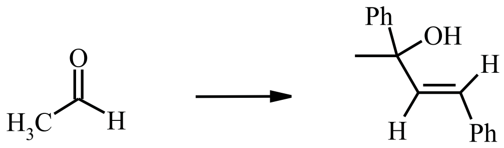
(b)



Problem 1057 Propose mechanism:

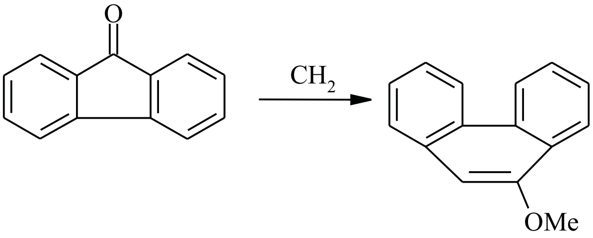


PROBLEM 1058 Convert:

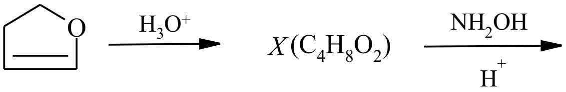


PROBLEM 1059 Propose mechanism:

(a)

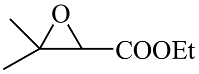


(b)

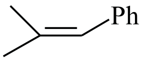


PROBLEM 1060 Starting from propanone, suggest synthesis of the following compounds:

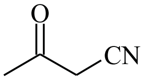
(a)



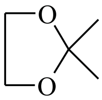
(b)



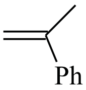
(c)



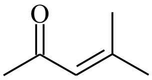
(d)



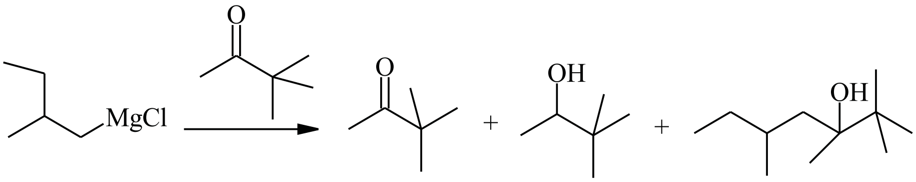
(e)



(f)

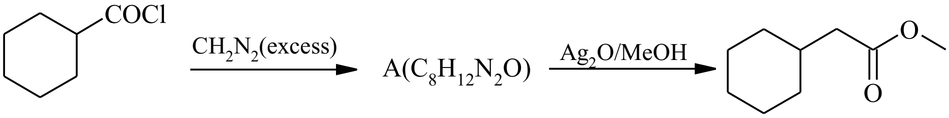


PROBLEM 1061 Offer mechanistic explanation for the formation of products in the following reaction:

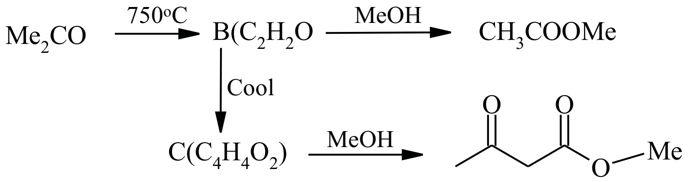


PROBLEM 1062 Propose mechanism of formation of final products in the following reactions and identify the labelled product:

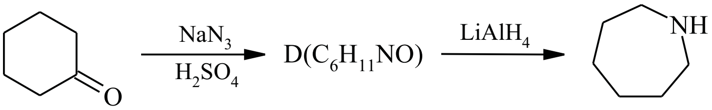
(a)



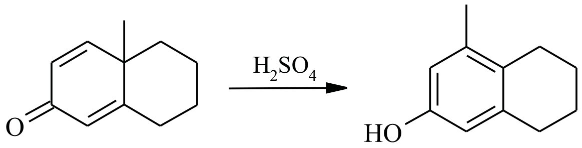
(b)



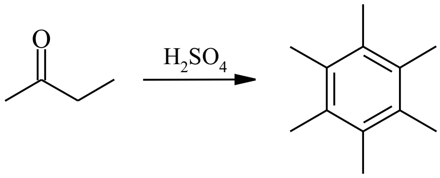
(c)



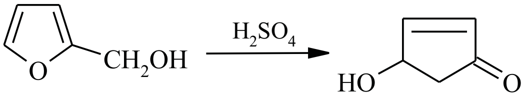
(d)



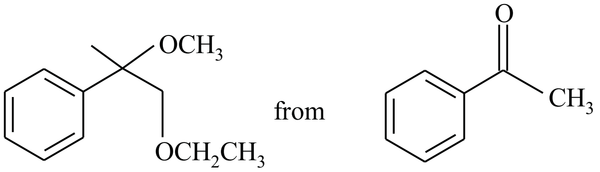
(e)



(f)



Problem 1063 Supply a suitable technique for the synthesis of following compound from indicated starting material:



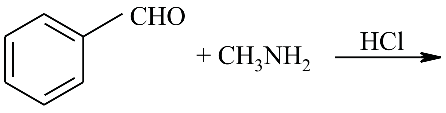
Problem 1064 A sweeting smelling organic compound A has molecular formula "$C_9H_{12}O_3$" and it does not change colour of moistened litmus paper. A on acidic hydrolysis yields an optically active compound B with their molecular formula "$C_9H_{14}O_4$". B does not decarboxylate on simple heating. B on heating with soda-lime (NaOH/CaO) yields an optically inactive compound C "$C_8H_{14}O_2$". C does not reduce Tollen's reagent but yields a bright orange crystalline substance on treatment with 2,4-dinitrophenylhydrazine. C on oxidation with acidified $K_2Cr_2O_7$ followed by heating of product with soda-lime yielded D "$C_7H_{12}O$" which is still non-resolvable. D on heating with alkaline solution of hydrazine yielded methyl cyclohexane. Identify A to D.

Problem 1065 An organic compound A has molecular formula "C_9H_{12}" and decolourises bromine-water solution. A on treatment with H_2/Pt gave an optically active hydrocarbon. A on treatment with acidified solution of $KMnO_4$ yields B"$C_9H_{12}O_7$" which can be resolved into enantiomers as well as gives bright orange crystalline substance with 2,4-dinitrophenyl hydrazine. B on simple heating gives an optically inactive C($C_7H_{12}O_3$) which evolves a gas with aqueous $NaHCO_3$ and gives a yellow precipitate with NaOH/I_2. C on treatment with $NaBH_4$ yields a resolvable D"$C_7H_{14}O_3$". D on heating with H_2SO_4 yields E"$C_7H_{12}O_2$" which does not change the colour of moistened litmus paper. Identify A to E.

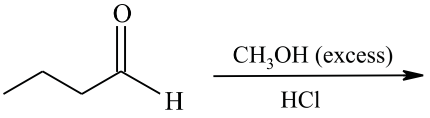
Problem 1066 An organic compound A has molecular formula "$C_9H_{16}O$" and it gives an yellow precipitate on treatment with alkaline solution of iodine. A on treatment with hydroxyl amine (H_2NOH) yields two stero-isomeric compound B and C with their molecular formula "$C_9H_{17}NO$". B on treatment with concentrated sulphuric acid undergo rearrangement to yield a stable product D which is an isomer of B. C on similar treatment undergo similar type of rearrangement to yield a stable product E which is an isomer of C. Hydrolysis of E in acid medium yields F($C_7H_{15}N$) as one of the product. F on treatment with nitrous acid followed by oxidation with acidified dichromate solution yields G($C_7H_{12}O_2$). G on heating with sodalime yields a product C_6H_{12} which on heating with nitric acid affords a single mono-nitro derivative. Identify A to G.

Problem 1067 Predict all products of the following reactions and show stereochemistry where important.

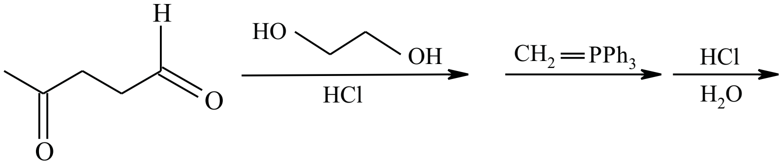
(a)



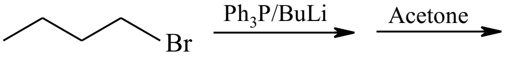
(b)



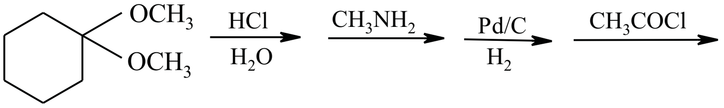
(c)



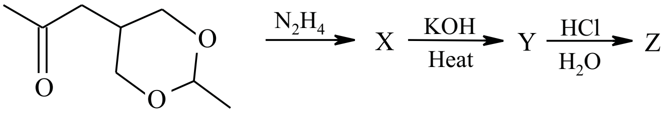
(d)



(e)

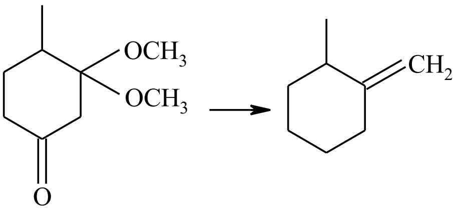


(f)

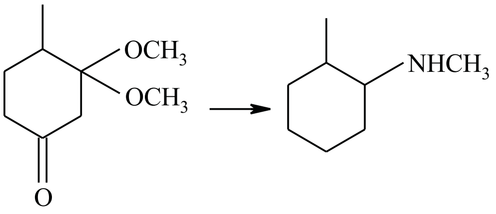


Problem 1068 Provide reagents for the following transformations :

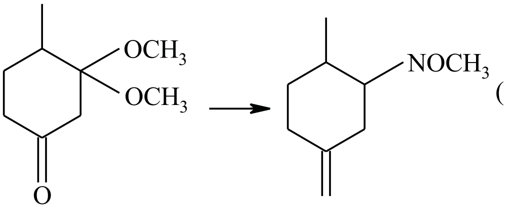
(a)



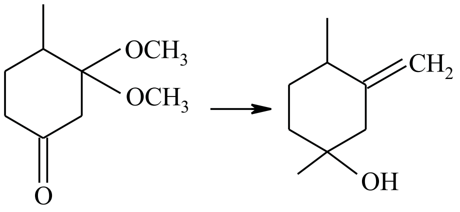
(b)



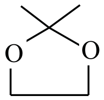
(c)



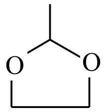
(d)



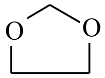
Problem 1069 Arrange the following acetals/ketals in increasing ease of their hydrolysis in acidic medium—(provide mechanistic reasoning).



I

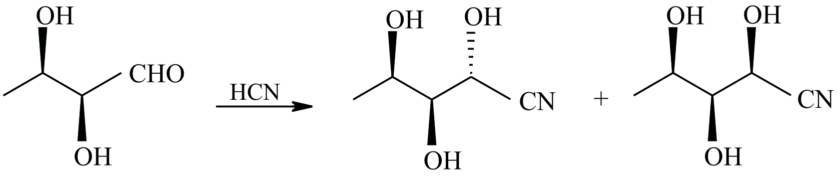


II



III

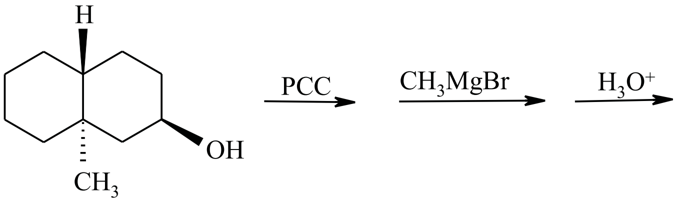
Problem 1070 The reaction of aldehyde A with HCN gives two cyanohydrin products B and C. Explain why C in produced in greater amount than B.



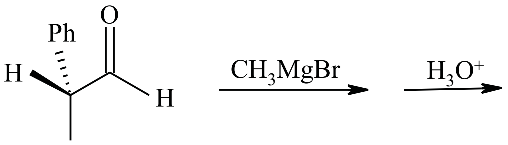
A B C

Problem 1071 Write the structures of major and minor stereo-isomers of product explaining reasons for your choice.

(a)

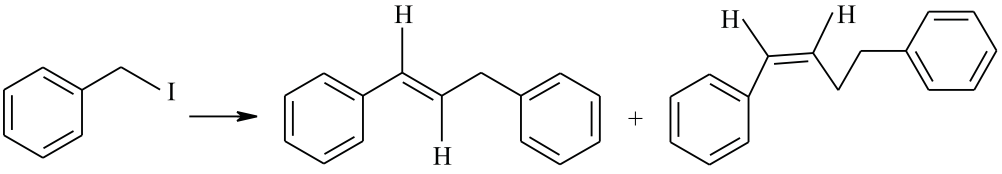


(b)

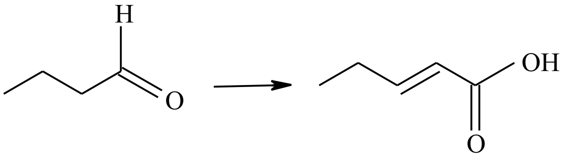


Problem 1072 Bring about the following transformations:

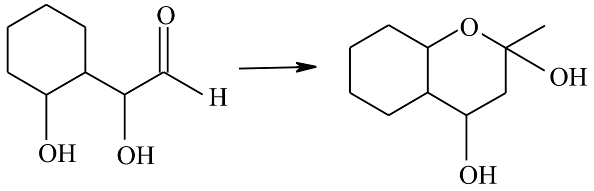
(a)



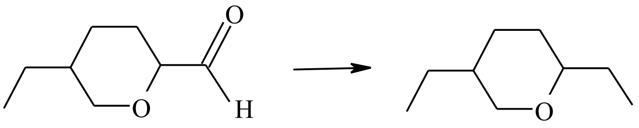
(b)



(c)

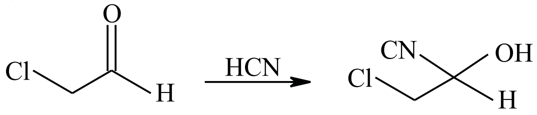


(d)

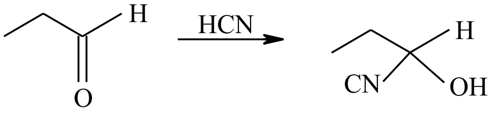


Problem 1073 Draw the product of the reaction A and B and predict which one proceeds more efficiently and why?

A :

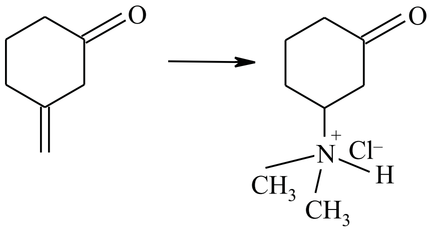


B :

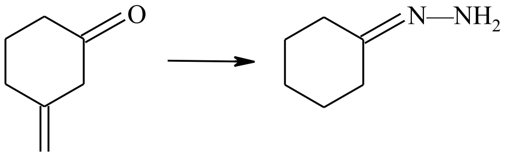


Problem 1074 Bring about the following transformations:

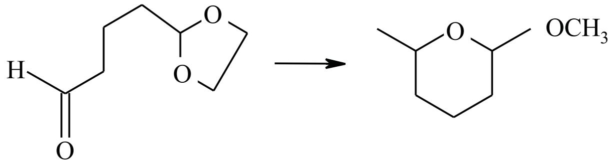
(a)



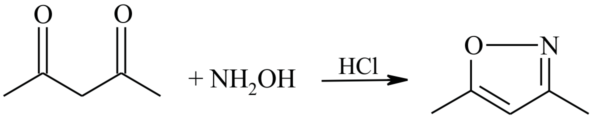
(b)



(c)

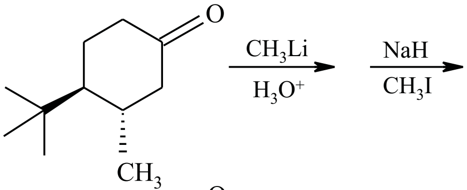


Problem 1075 Provide a mechanistic explanation for the reaction:

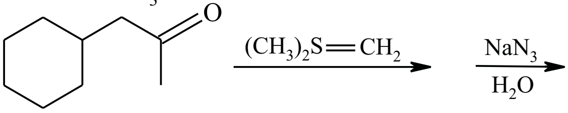


Problem 1076 Predict products in the following reaction. Provide stereoisomers where appropriate.

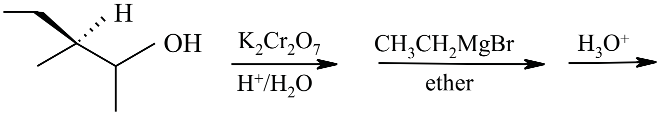
(a)



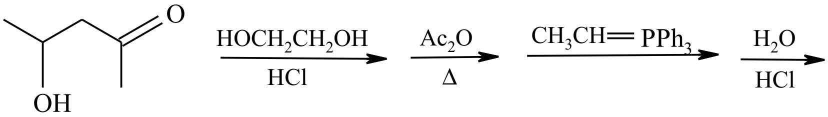
(b)



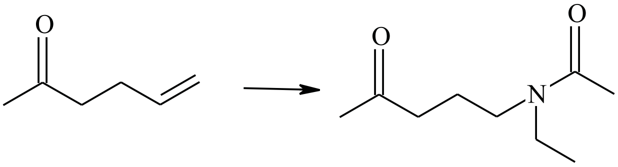
(c)



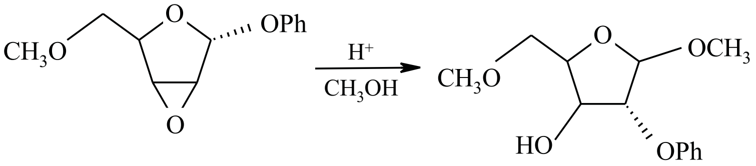
(d)



Problem 1077 Bring about the following transformations:

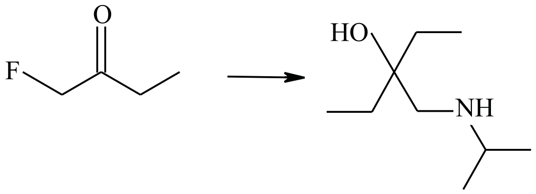


Problem 1078 Propose mechanism for the reaction:

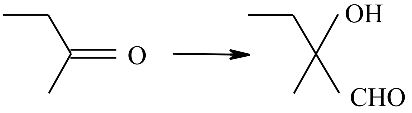


PROBLEM 1079 Bring about the following transformations:

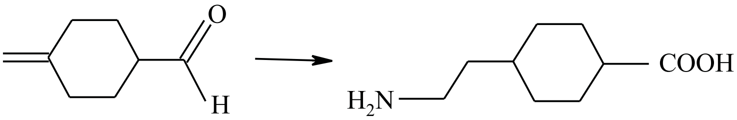
(a)



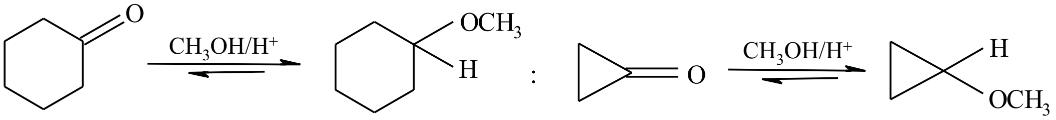
(b)



(c)



PROBLEM 1080 The equilibrium established when cyclohexanone is treated with methanol and HCl lies in the favour of ketone. In contrast, the same reaction with cyclopropanone lies heavily in favour of hemiacetal. Explain.

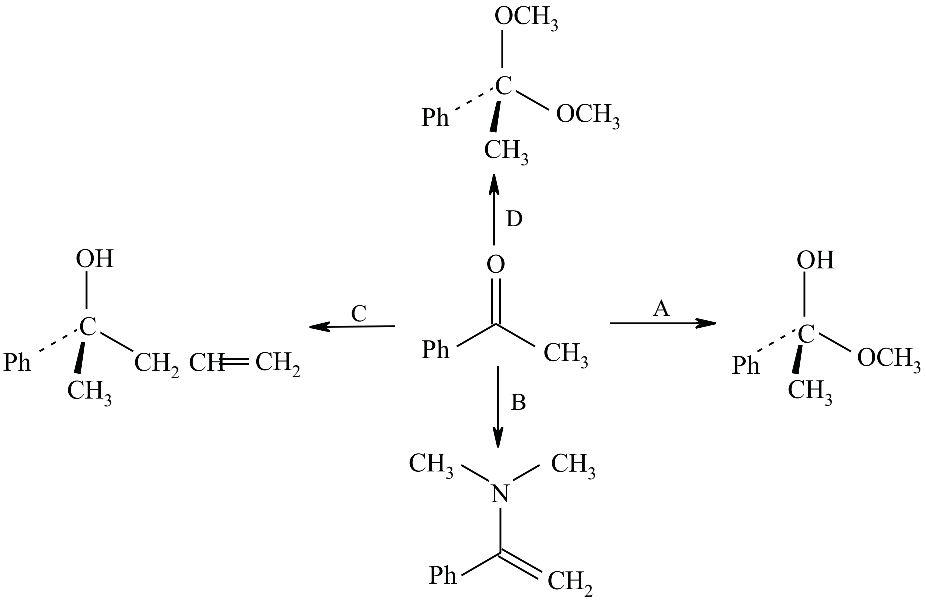


PROBLEM 1081 Within each set, select the compound which is more reactive in nucleophilic addition at carbonyl carbon:

(a) $CH_3COCH_2CH_2Br$ or CH_3COCH_2Br (b) CH_3CHO or CH_3COCH_3

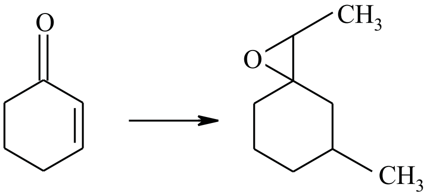
(c) CH_3COCH_3 or $CH_3—CO—CF_3$ (d) PhCHO or CH_3CHO

PROBLEM 1082 Provide reagents for accomplishing the following transformations:

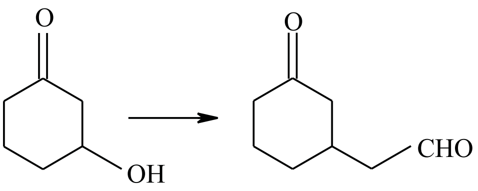


Problem 1083 Bring about the following transformations:

(a)



(a)

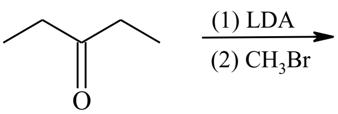


Problem 1084 Treatment of trans 2-chlorocyclohexanol with NaOH yields 1,2-epoxycyclohexane while reaction of *cis* isomer under the same condition yields cyclohexanone. Propose mechanistic explanation.

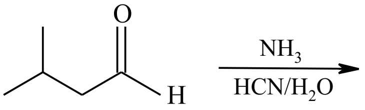
Problem 1085 When 4-hydroxybutanal is treated with methanol in the presence of acid catalyst, 2-methoxy tetrahedrofuran is formed. Provide mechanism.

Problem 1086 Give products of the following reactions (major):

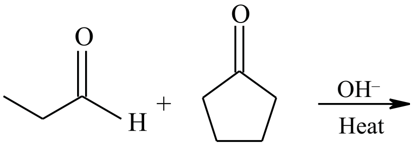
(a)



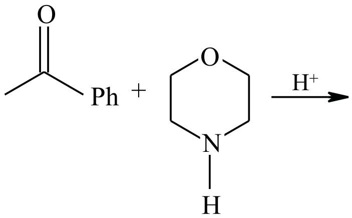
(b)



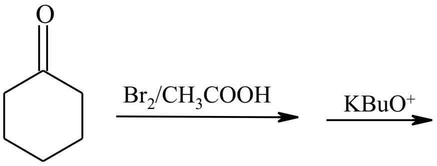
(c)



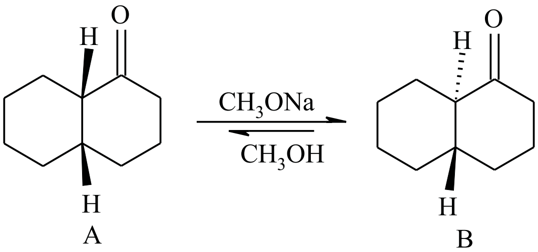
(d)



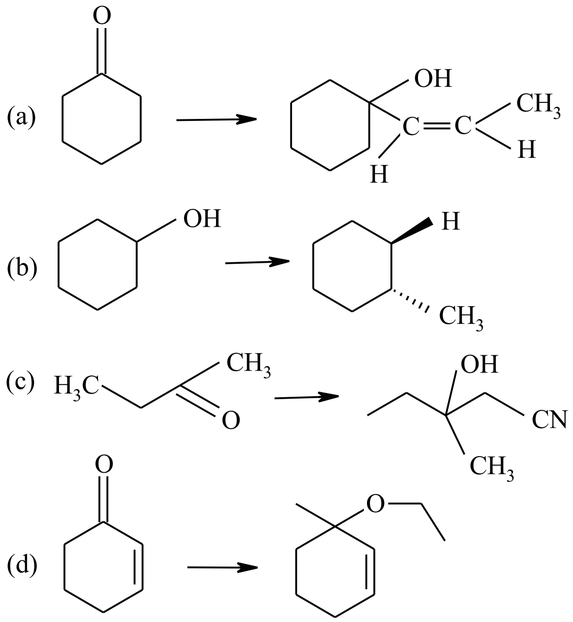
(e)



Problem 1087 When compound A is treated with CH_3ONa in CH_3OH, isomerization to compound B occurs. Provide mechanism and explain why equilibrium favour product B?

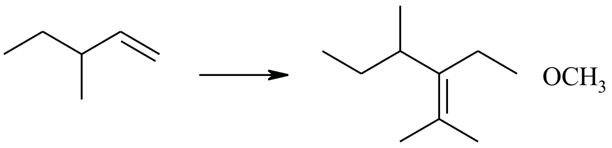


Problem 1088 Bring about the following transformations:

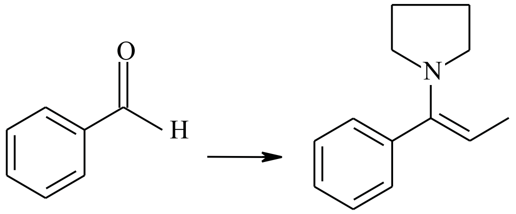


Problem 1089 Provide synthesis of the compounds from indicated starting materials:

(a)



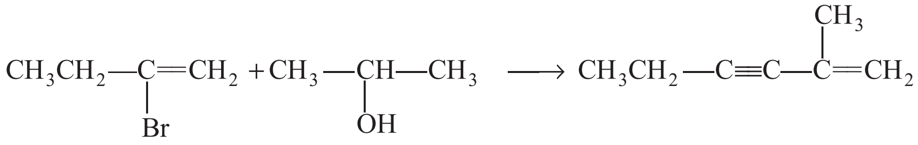
(b)



Problem 1090 An optically active organic compound A($C_4H_8O_2$) gives an orange precipitate with 2,4-dinitrophenylhydrazine and a silver mirror with ammonical silver nitrate solution. A is converted into B(C_4H_6O) on treatment with concentrated sulphuric acid. B may exist as *cis* or *trans* isomers. B reacts with HCl to give C(C_4H_7OCl) as major product and with chlorine to give D($C_4H_6OCl_2$). Reduction of C with Sn/HCl gives E(C_4H_9OCl) which on hydrolysing with aqueous alkali yields F($C_4H_{10}O_2$). F gives a yellow precipitate with I_2 and NaOH solution but A does not. Identify A to F.

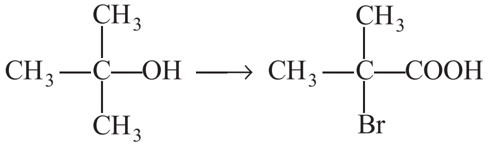
Problem 1091 Synthesize products from indicated reactants and other inorganic reagents needed:

(a)



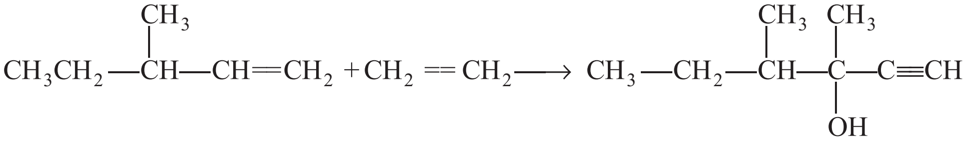
$$CH_3CH_2-\underset{\underset{Br}{|}}{C}=CH_2 + CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \longrightarrow CH_3CH_2-C\equiv C-\overset{\overset{CH_3}{|}}{C}=CH_2$$

(b)



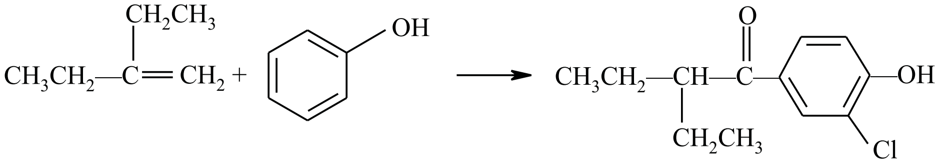
$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}-COOH$$

(c)

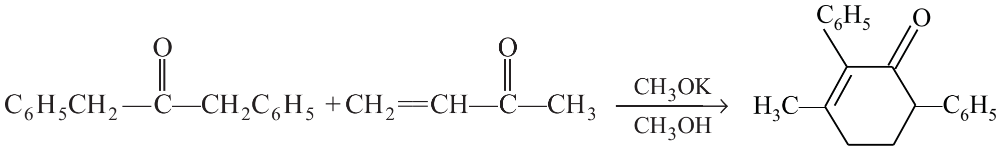


$$CH_3CH_2-\overset{\overset{CH_3}{|}}{CH}-CH=CH_2 + CH_2=CH_2 \longrightarrow CH_3-CH_2-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-C\equiv CH$$

(d)

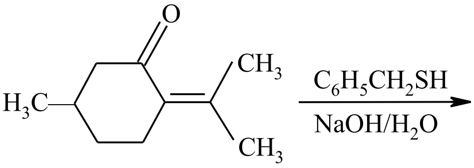


PPROBLEM 1092 Propose mechanism:

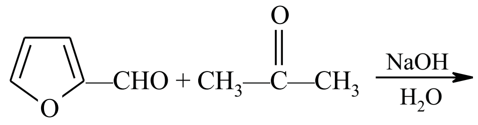


PROBLEM 1093 Predict product in each of the following showing stereochemistry where appropriate:

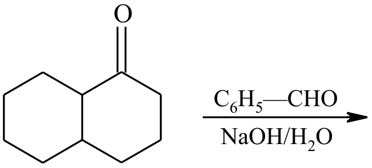
(a)



(b)

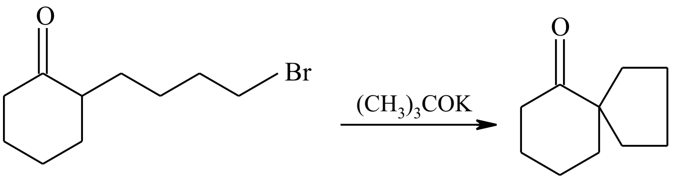


(c)

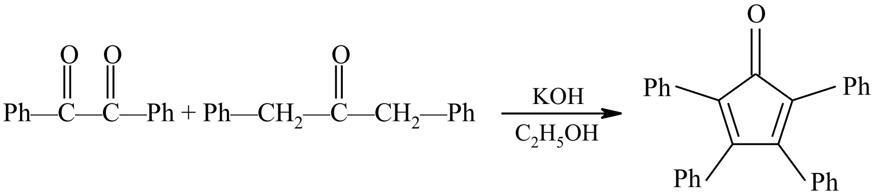


PROBLEM 1094 Propose mechanism:

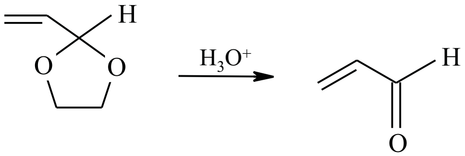
(a)



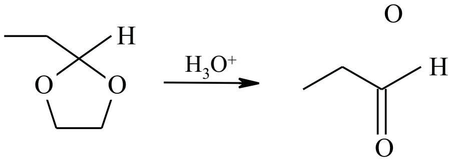
(b)



PROBLEM 1095 The acid catalyzed hydrolysis of two acetals shown below occurs at much different rates. Provide a brief explanations with structures of key intermediate to illustrate why these two acetals undergo hydrolysis at such different rates.

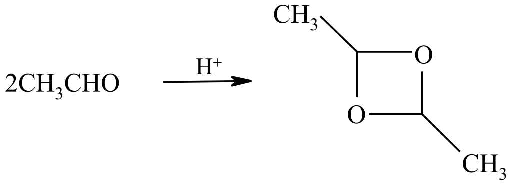


Reaction is complete in 1.0 hour at 20°C

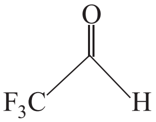


Reaction is complete in 24 hour at 60°C

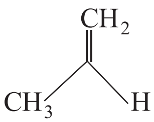
PROBLEM 1096 Provide a stepwise mechanism for the following acid catalyzed reaction:



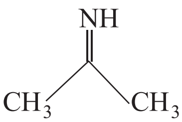
PROBLEM 1097 Rank the following compounds in increasing order of electrophilicity:



I

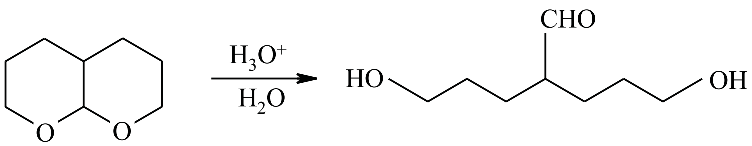


II

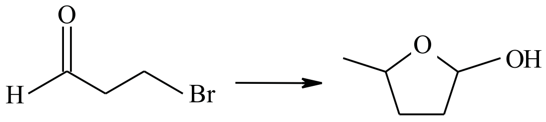


III

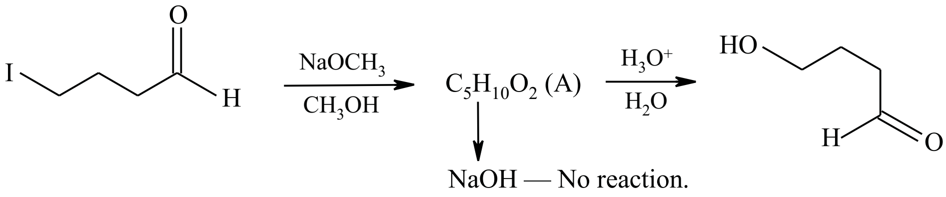
PROBLEM 1098 Provide a stepwise mechanism for the following acid catalyzed reaction:



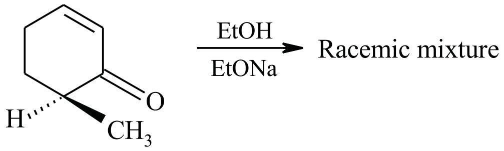
PROBLEM 1099



Problem 1100 Identify A in the following reaction and propose mechanism of its formation:

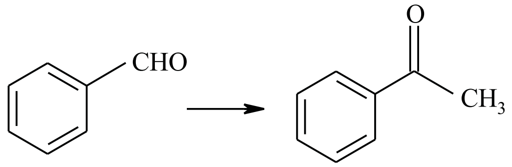


Problem 1101 The enantiomerically pure cyclic ketone, shown below, loses optical activity upon standing in a solution of EtONa/EtOH. Provide mechanistic explanation.

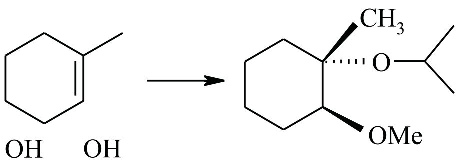


Problem 1102 Bring about the following transformations:

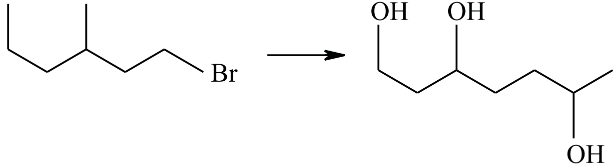
(a)



(b)



(c)



Problem 1103 An organic compound A has molecular formula $C_6H_{12}O$. A does not decolourize bromine water solution but evolves a gas on heating with NaH. A can be resolved into distereomers and it also change colour of acidified dichromate solution from orange to blue green. A on heating with concentrated sulphuric acid yields B(C_6H_{10}) as a major product which can't be resolved into enantiomers. B on oxidation with ozone followed by work-up with Zn—H_2O yields C($C_6H_{10}O_2$). C on refluxing with dilute solution of NaOH gives D–an isomer of C. D also evolves a gas wtih NaH. D on heating dehydrate to yield E(C_6H_8O). E on heating with H_2 gas in presence of platinum catalyst at high temperature and pressure yields F(C_6H_{12}) which gives single monochloro derivative on free radical chlorination. Identify A to F.

Problem 1104 An organic compound A has molecular formula $C_7H_{14}O_2$ and it can be resolved into enantiomers. A on treatment with H_2CrO_4 yields B($C_7H_{12}O_2$) which can't be resolved into enantiomers.

Refluxing B with dilute alkali solution yields “C” which is an isomer of B. C evolves a gas with NaH but does not change colour of acidified dichromate solution. C on heating with concentrated sulphuric acid yields D($C_7H_{10}O$) which on heating with Pt at high pressure yields methyl cyclohexane. Identify A to D.

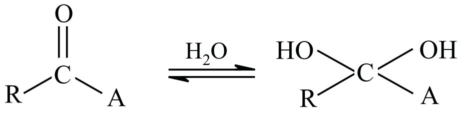
Problem 1105 An organic compound a has molecular formula $C_{11}H_{22}$. A on treatment with concentrated solution of $KMnO_4$ in acidic medium yields B(C_3H_6O) and C($C_8H_{16}O$), both form orange colour precipitate with 2,4-dinitrophenyl hydrazine but neither gives positive Tollen’s test. C on treatment with $LiAlH_4$ yields D($C_8H_{18}O$) which on heating with concentrated sulphuric acid solution gives E(C_8H_{16}). E on further treatment with acidified permanganate solution yielded B and 2,2-dimethyl propanoic acid. Identify A to E.

Problem 1106 Identify the compounds labeled A to F:

$$A(C_8H_{10}) \xrightarrow[h\nu/CCl_4]{NBS} B(C_8H_9Br) \xrightarrow[(CH_3)_3COH]{(CH_3)_3COK} C \xrightarrow[Zn-H_2O]{O_3} D(C_7H_6O) \xrightarrow{MeMgBr}$$

$$\xrightarrow[H_2O]{H_3O^+} E \xrightarrow[CH_2Cl_2]{PCC} F \xrightarrow[OH^-/\Delta]{N_2H_4} A$$

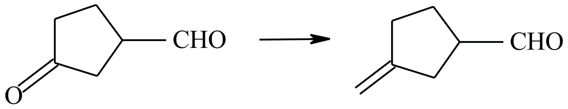
Problem 1107 Arrange the following hydrates in order of increasing K_{eq}:



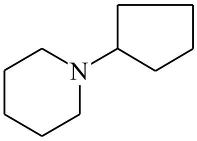
A : H, $(CH_3)_2CH$—, $ClCH_2$— Ph—.

Problem 1108 Propose a reasonable synthesis of the product in the following reactions starting from the indicated materials.

(a)

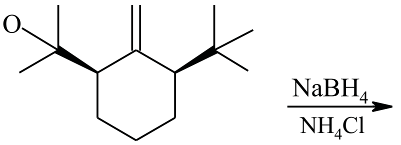


(b) Compound containing 5 or less carbons ⟶

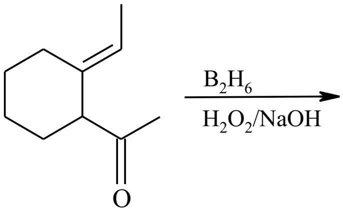


Problem 1109 Give structures of all the products in the following reactions:

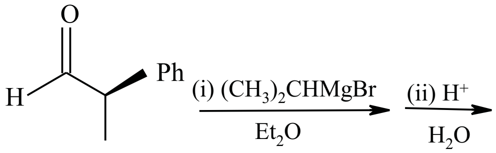
(a)



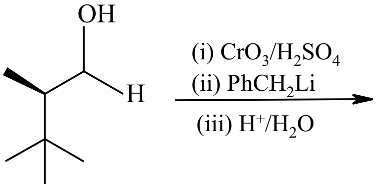
(b)



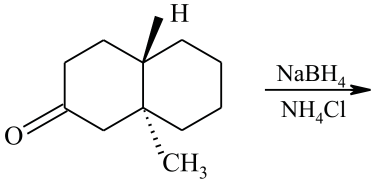
(c)



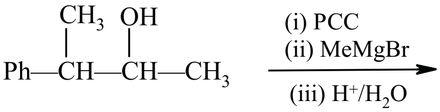
(d)



(e)

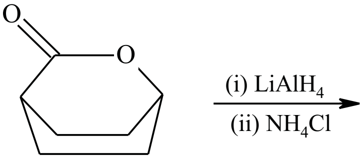


(f)



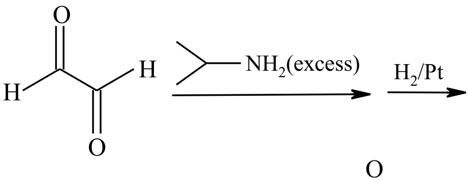
$\mathrm{Ph{-}\overset{CH_3}{\overset{|}{C}H}{-}\overset{OH}{\overset{|}{C}H}{-}CH_3}$

(g)

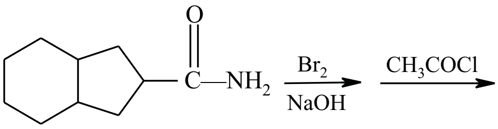


Problem 1110 Complete the following reactions:

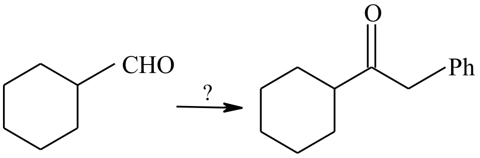
(a)



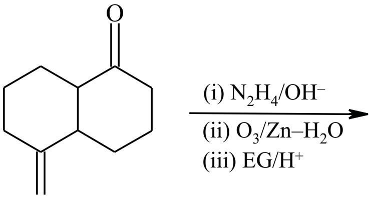
(b)



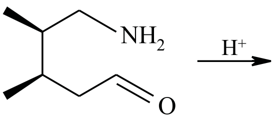
(c)



(d)

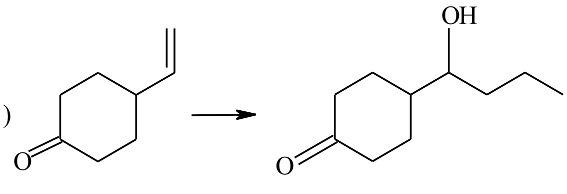


(e)

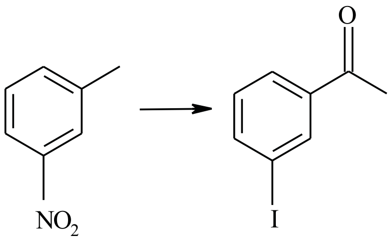


Problem 1111 Bring about the following transformations:

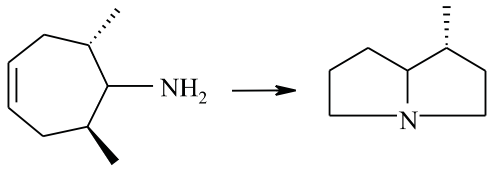
(a)



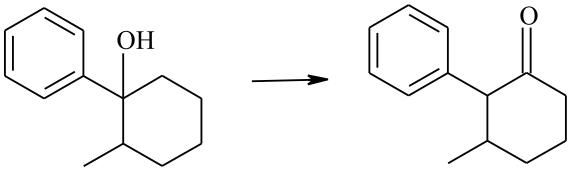
(b)



(c)



PROBLEM 1112 Propose mechanism:



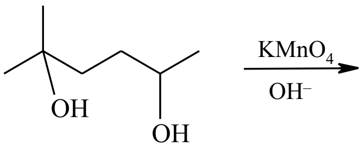
PROBLEM 1113 (a) Draw all the enol forms possible 4-methyl-1,3-cyclopentandione.

(b) Give product of the reaction of above diketo compound with:

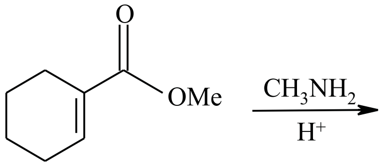
(i) Excess of D_2O/H^+, (ii) One mole of Br_2/H^+, (iii) LDA/THF then CH_3I.

PROBLEM 1114 Complete the following reactions:

(a)

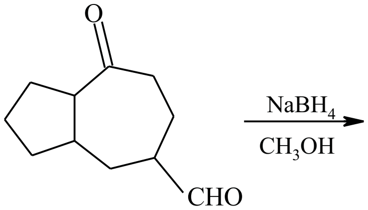


(b)

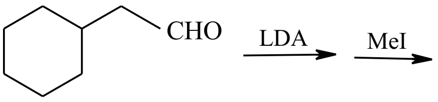


(c) $2PhCH_2CHO \xrightarrow[\text{Warm}]{HO^-}$

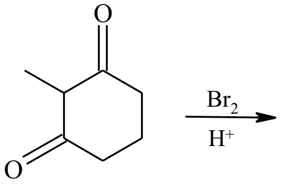
(d)



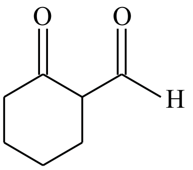
(e)



(f)



PROBLEM 1115 Consider the compound shown below:

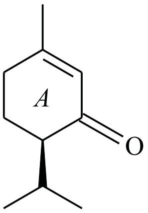


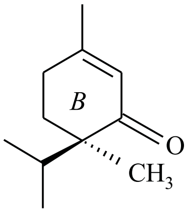
(a) Give the product of its reaction with excess of D_2O.

(b) Give product of reaction with one mole of Br_2 in dilute acidic medium.

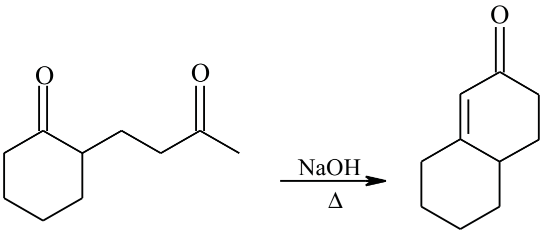
(c) Give product of its reaction with one mole of C_6H_5CHO in presence of strong base EtONa.
(d) Write structure of its most stable enol form.

PROBLEM 1116 Of the two compounds *A* and *B* shown below, *A* losses its optical activity upon standing an enantiomerically pure form of it in a solution of NaOEt but no such loss of optical activity is observed on similar treatment to *B*. Explain:

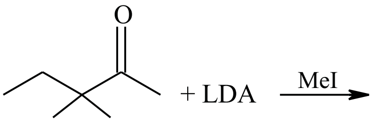


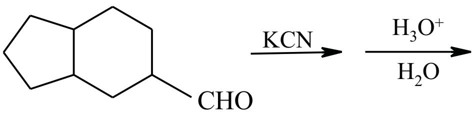


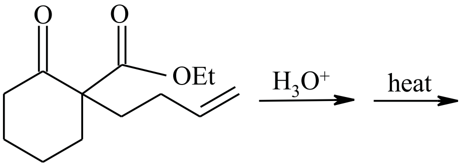
PROBLEM 1117 Give a complete stepwise mechanism for the reaction:

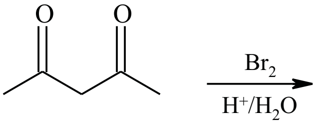


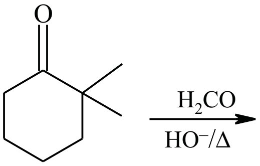
PROBLEM 1118 Complete the following reactions:

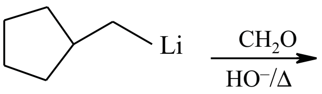
(a)


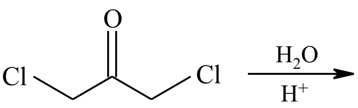
(b)


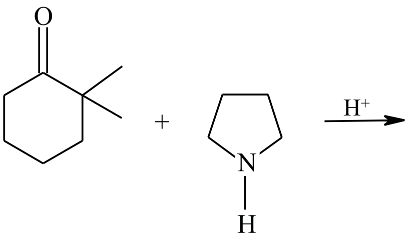
(c)


(d)


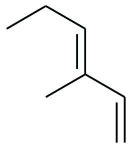
(e)


(f)


(g)


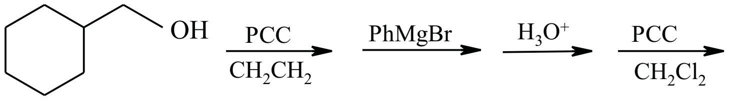
(h)


PROBLEM 1119 Synthesize the following compound starting from alcohols of three or less carbons:

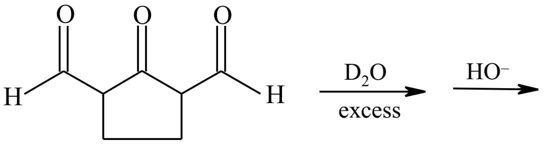


PROBLEM 1120 Write product in the following reactions:

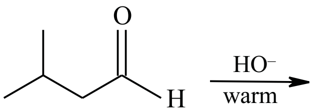
(a)



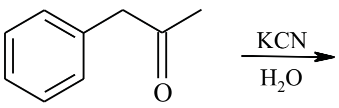
(b)



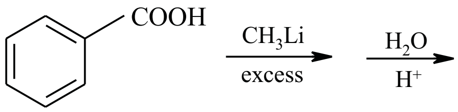
(c)



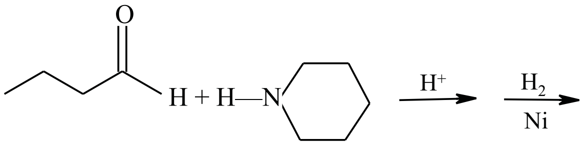
(d)



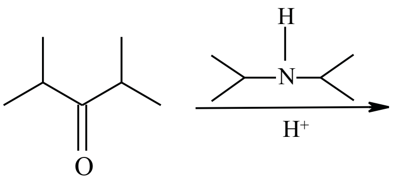
(e)



(f)

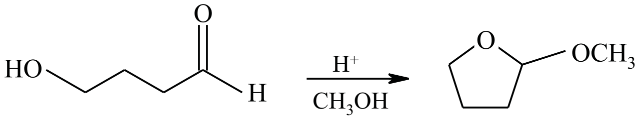


(g)

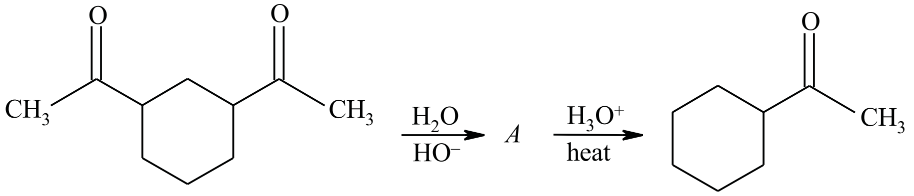


PROBLEM 1121 Give a complete, stepwise mechanism of the following reactions:

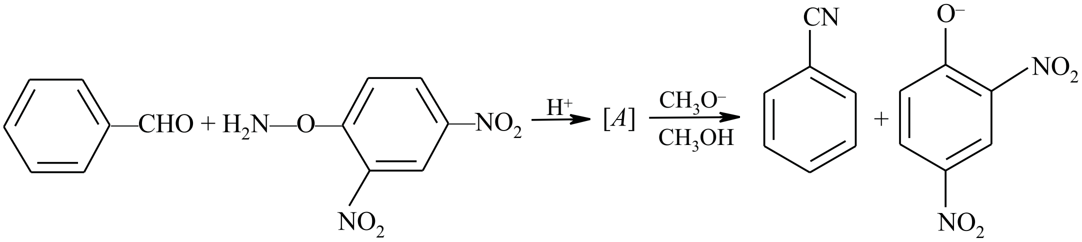
(a)



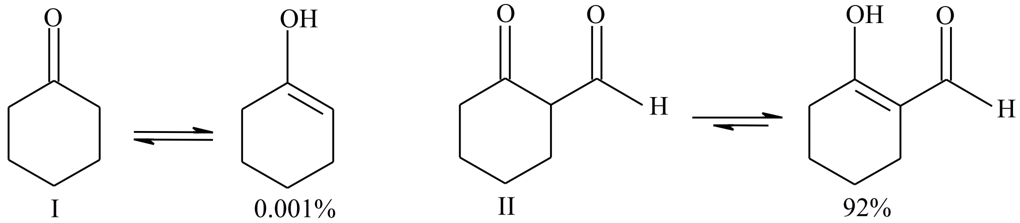
(b)



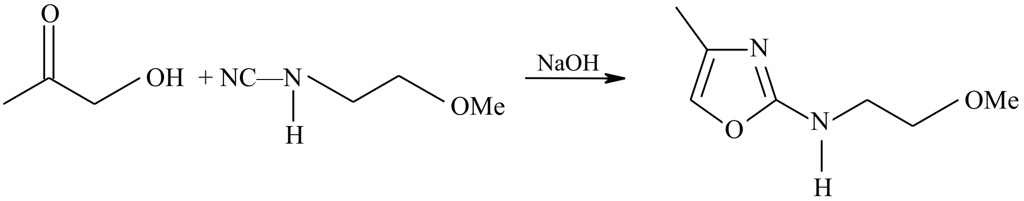
(c)



Problem 1122 Rationalize the difference in enol contents shown below:

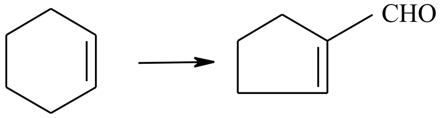


Problem 1123 Propose mechanism of the following reaction:

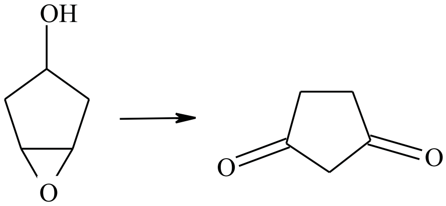


Problem 1124 Bring about the following transformations:

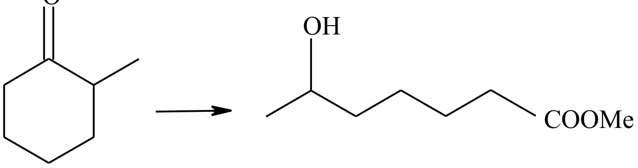
(a)



(b)

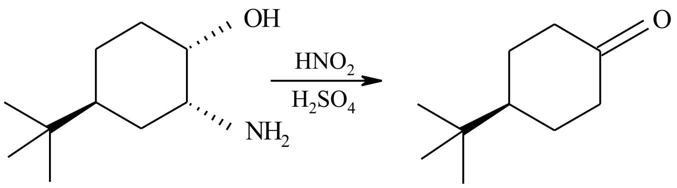


(c)

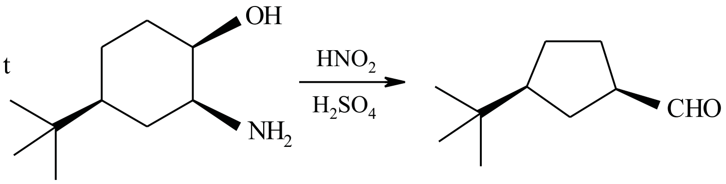


Problem 1125 Explain, with the aid of mechanism, the differing outcome in the following pair of reactions:

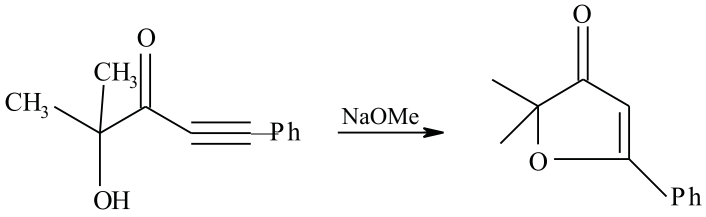
(a)



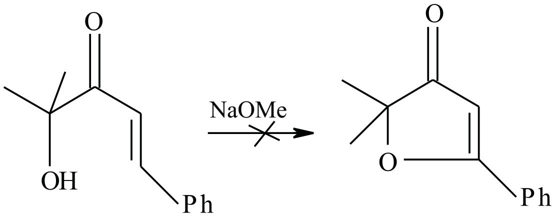
but



(b)

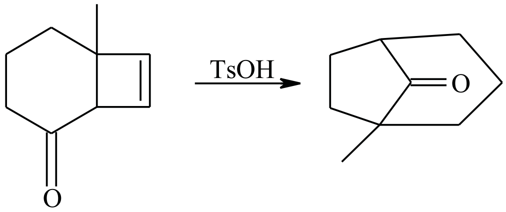


but

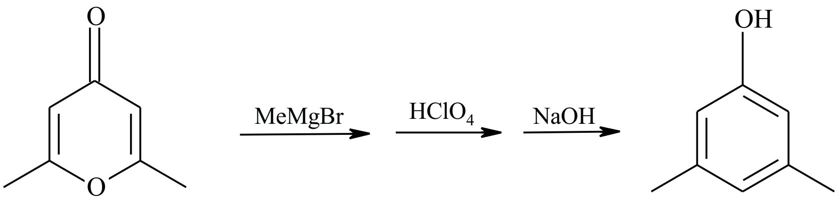


Problem 1126 Propose mechanism:

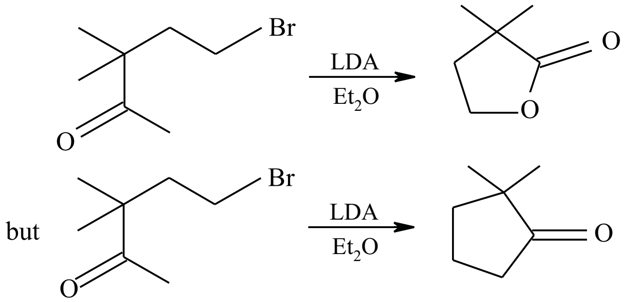
(a)



(b)



Problem 1127 Explain the following observation:



Problem 1128 An organic compound *A* has molecular formula $C_9H_{18}O$ and it can be resolved into enantiomers. *A* evolves a colourless gas on heating with Na-metal, but does not change the colour of acidified dichromate solution or bromine water solution. *A* on heating with concentrated sulphuric acid undergo dehydration to yield three isomeric products *B*, *C* and *D* all having molecular formula C_9H_{16}. *B* shows cis-trans isomerism and on ozonolysis followed by work-up with Zn—H_2O produced $E(C_7H_{12}O)$ as one product. *E* formed an yellow precipitate on treatment with alkaline solution of iodine. Ozonolysis of *C* followed by work-up with Zn—H_2O produced $F(C_5H_8O)$ which did not produce yellow precipitate with alkaline NaOH but produced a single isomer $G(C_5H_9NO)$ on treatment with H_2NOH. Also *D* on ozonolysis followed by work-up with Zn—H_2O produced nonan-2,7-dione. Identify *A* to *G*.

Problem 1129 An organic compound *A* has molecular formula C_8H_{16}. *A* on treatment with aqueous $(CH_3COO)_2Hg$ followed by reduction with $NaBH_4$ yields yields $B(C_8H_{18}O)$ which cannot be resolved into enantiomers. *A* on treatment with B_2H_6/H_2O_2 in alkaline medium yields *C*, an isomer of *B*, but it can be resolved into enantiomers. Ozonolysis of *A*, followed by work-up with dimethylsulphide, yields $D(C_6H_{12}O)$ as one product which is non-resolvable. On catalytic reduction with $LiAlH_4$, *D* yields $E(C_6H_{14}O)$ which can be resolved into enantiomers. *E* on heating with concentrated H_2SO_4 yields two isomeric alkenes *F* and *G*, of which *F* is stereo-isomeric while *G* is not. Deduce structures of *A* to *G*.

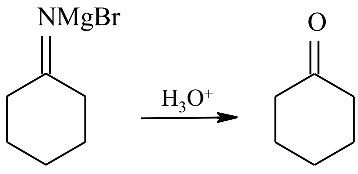
Solutions

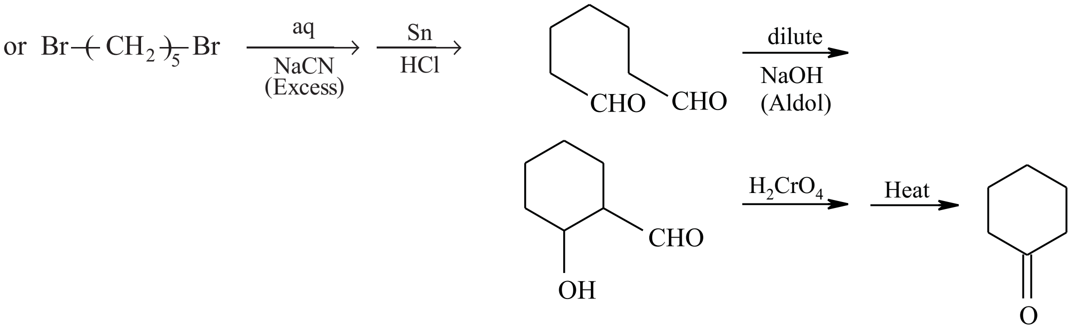
ALDEHYDES AND KETONES

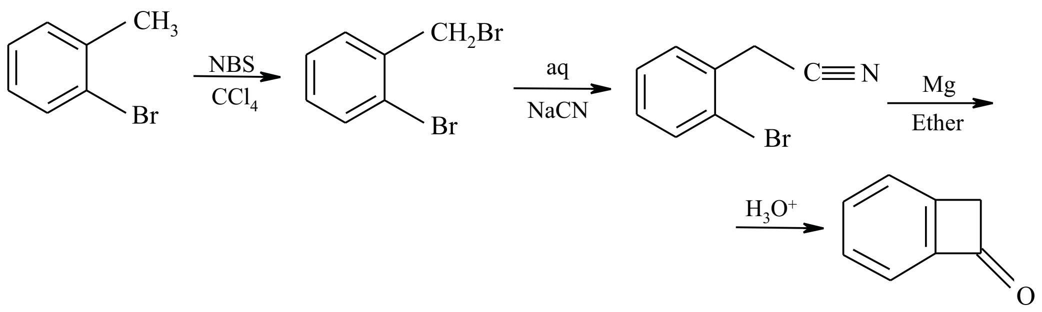
1013.

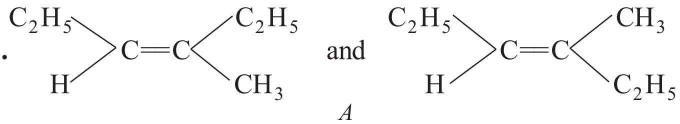
$$\left.\begin{array}{l} C_2H_5Br \xrightarrow[\text{NaCN}]{\text{aq}} C_2H_5CN \\ C_2H_5Br \xrightarrow[\text{ether}]{\text{Mg}} C_2H_5MgBr \end{array}\right] \longrightarrow C_2H_5-\overset{\overset{\text{NMgBr}}{\|}}{C}-C_2H_5 \xrightarrow{H_3O^+} \text{3-pentanone.}$$

1014. (a) $Br\text{-}(CH_2)_5\text{-}Br \xrightarrow[\substack{\text{NaCN} \\ \text{(1.0 equivalent)}}]{\text{aq}} Br\text{-}(CH_2)_5\text{-}CN \xrightarrow[\text{Ether}]{\text{Mg}}$



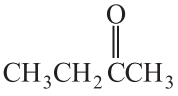


(b)


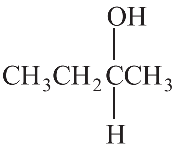
1015.


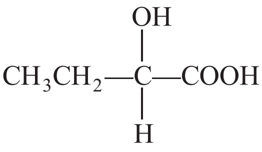
A

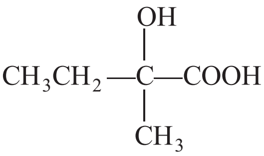
CH_3CH_2CHO
B

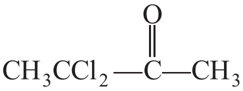

$CH_3CH_2\overset{\overset{O}{\|}}{C}CH_3$
C

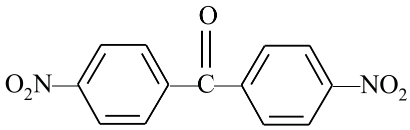
$CH_3CH_2CH_2OH$
D

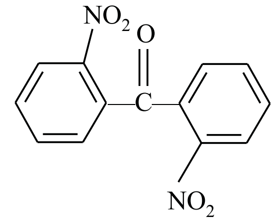

$CH_3CH_2\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}CH_3$
E


$CH_3CH_2—\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}—COOH$
F

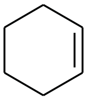

$CH_3CH_2—\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}—COOH$
G

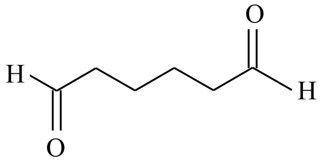
1016. (a) Cl_3CCHO (b)

$CH_3CCl_2—\overset{\overset{O}{\|}}{C}—CH_3$
(c) C_6H_5CHO

(d)


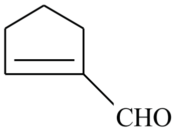
(e)


1017.

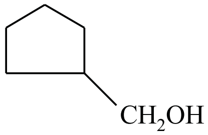

A



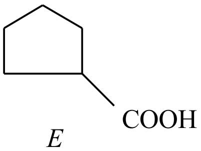
B



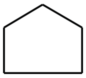
C



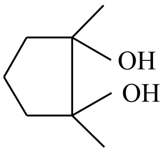
D



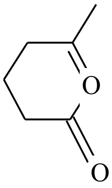
E


F

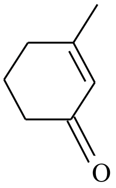
1018. (a)



A

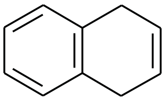


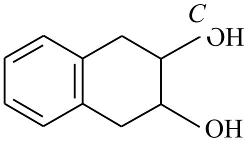
B



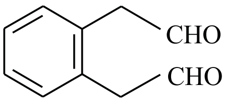
C

(b)


A

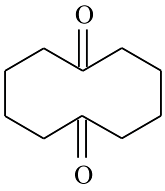


B

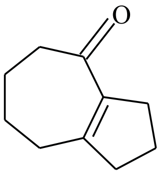


C

(c)

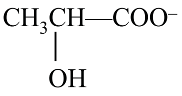


A

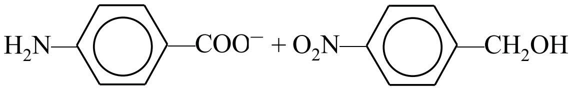


B

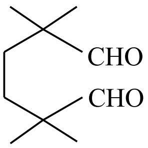
1019. (a)


$$CH_3\underset{\displaystyle OH}{\underset{|}{C}}H—COO^-$$

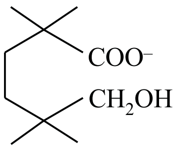
(b)



(c)

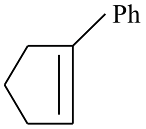


A

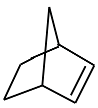


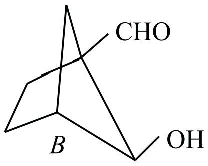
B

1020. (a)



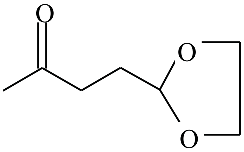
(b)

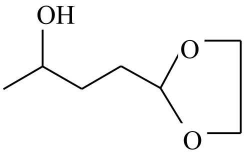

A

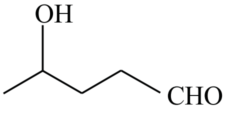


B

1021. (a)

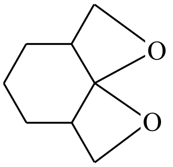




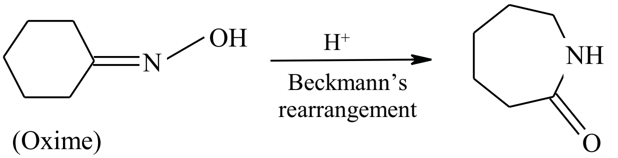


C

(b)



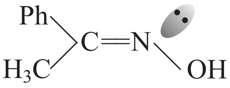
1022. (a)



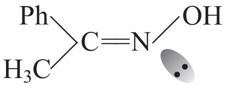
(Oxime)
A

(Caprolactum)
B

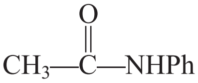
(b)



C



D

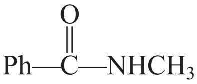


$CH_3-\overset{\overset{O}{\|}}{C}-NHPh$

E

CH_3COO^-

F



$Ph-\overset{\overset{O}{\|}}{C}-NHCH_3$

G

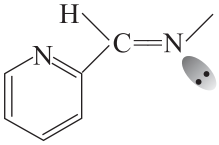
$PhCOO^-$

H

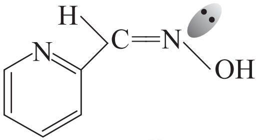
CH_3NH_2

I

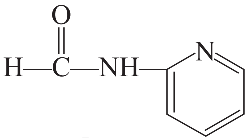
(c)



J



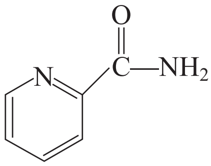
K



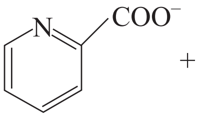
L

$HCOO^-$

M



N

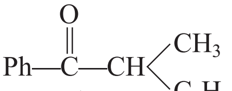


O

$+ NH_3$

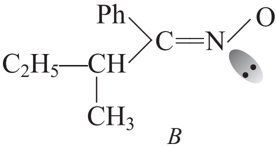
P

1023.

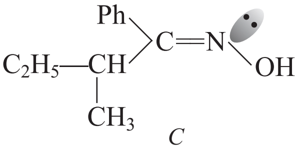


$Ph-\overset{\overset{O}{\|}}{C}-CH{<}^{CH_3}_{C_2H_5}$

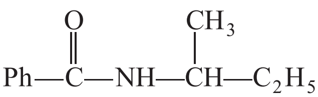
A



B

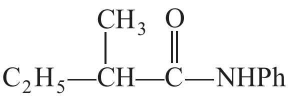


C



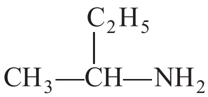
$Ph-\overset{\overset{O}{\|}}{C}-NH-\overset{\overset{CH_3}{|}}{CH}-C_2H_5$

D



$C_2H_5-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-NHPh$

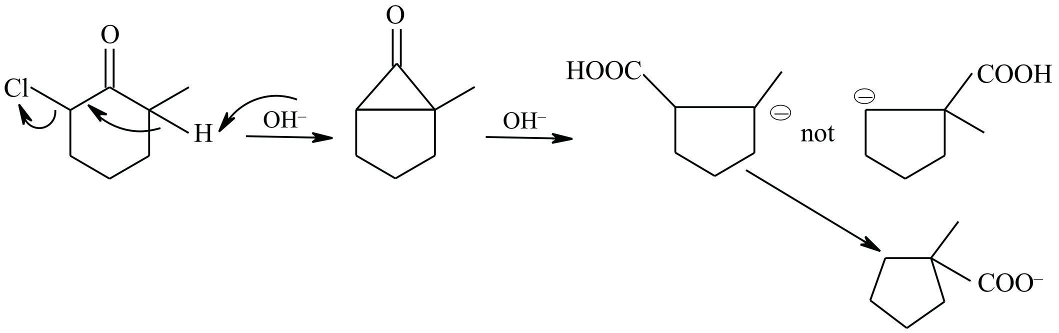
E



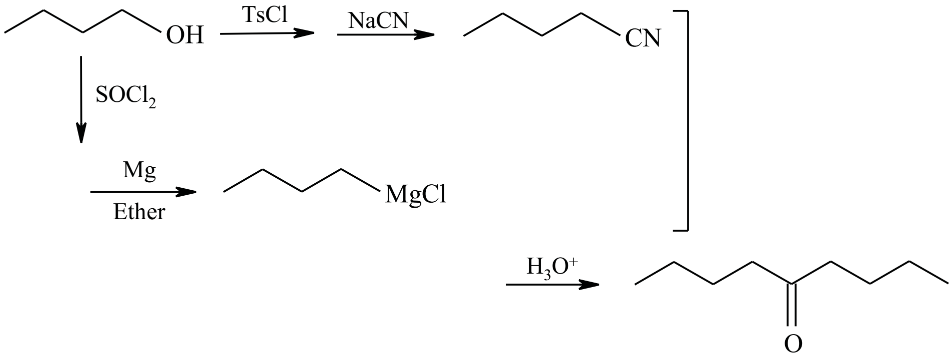
$CH_3-\overset{\overset{C_2H_5}{|}}{CH}-NH_2$

F

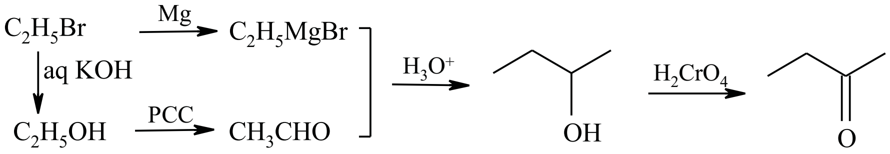
1024.



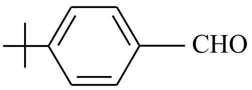
1025. (a)



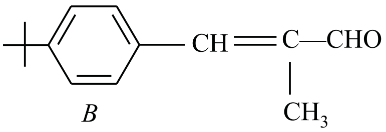
(b)



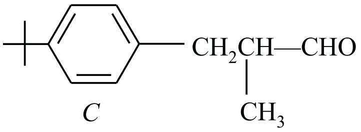
1026.



A

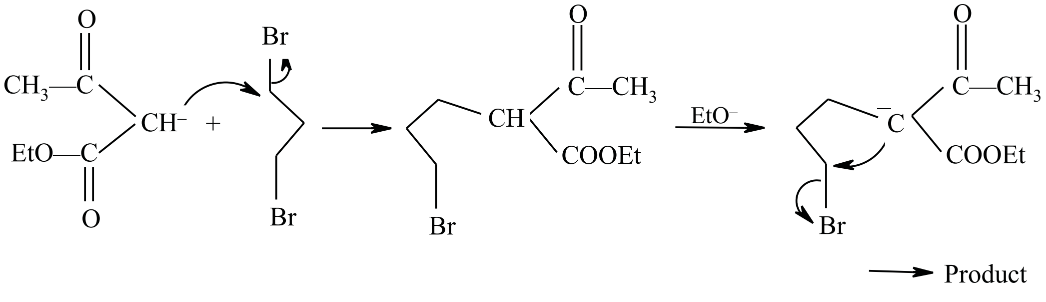


B

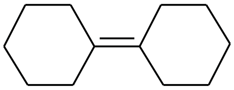


C

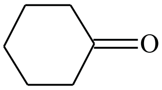
1027.



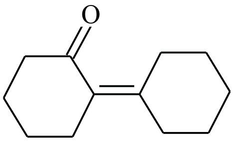
1028.



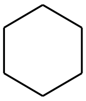
A



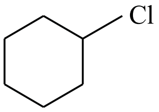
B



C

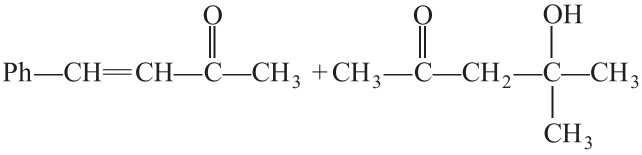


D



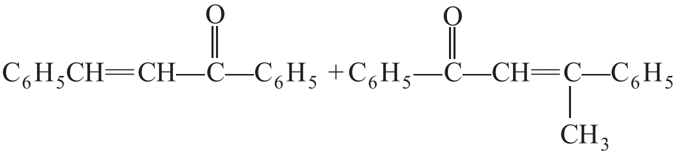
E

1029. (a)



$$\mathrm{Ph{-}CH{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 + CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2{-}\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}{-}CH_3}$$

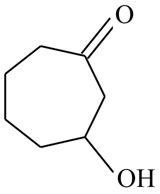
(b)



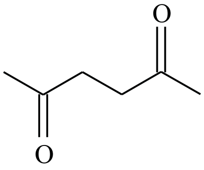
$$\mathrm{C_6H_5CH{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}C_6H_5 + C_6H_5{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH{=}\underset{\underset{\displaystyle CH_3}{|}}{C}{-}C_6H_5}$$

(c) $C_6H_5CH{=}CH{-}NO_2$

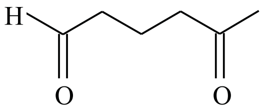
(d)



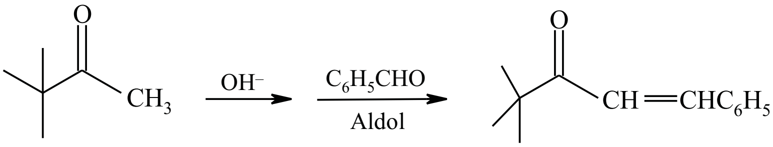
(e)



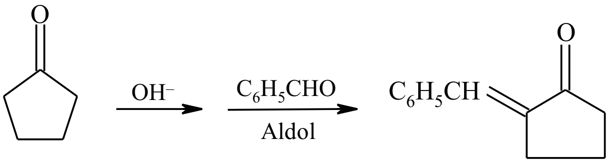
(f)

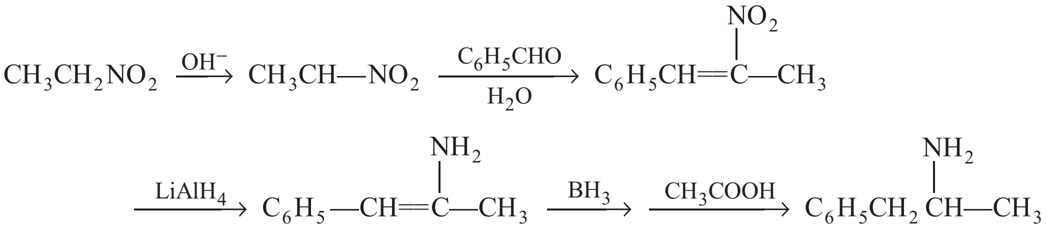


1030. (a)



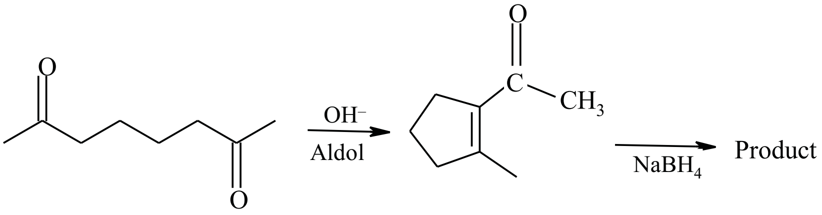
(b)

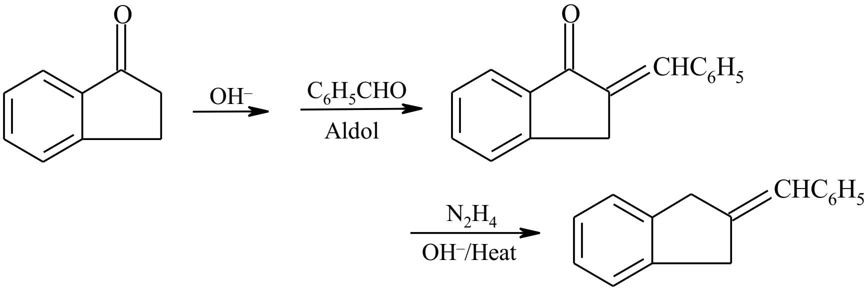


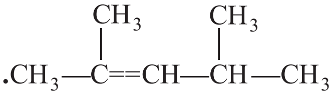
(c) 

$$CH_3CH_2NO_2 \xrightarrow{OH^-} CH_3CH{-}NO_2 \xrightarrow[H_2O]{C_6H_5CHO} C_6H_5CH{=}\overset{NO_2}{\overset{|}{C}}{-}CH_3$$

$$\xrightarrow{LiAlH_4} C_6H_5{-}CH{=}\overset{NH_2}{\overset{|}{C}}{-}CH_3 \xrightarrow{BH_3} \xrightarrow{CH_3COOH} C_6H_5CH_2\,\overset{NH_2}{\overset{|}{C}H}{-}CH_3$$

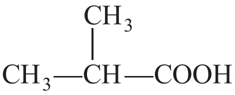
(d) 

(e) 

1031. 

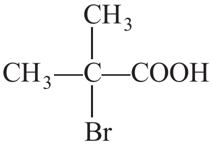
$$CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}\overset{CH_3}{\overset{|}{C}H}{-}CH_3$$

A



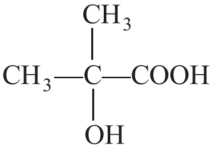
$$CH_3{-}\overset{CH_3}{\overset{|}{C}H}{-}COOH$$

B



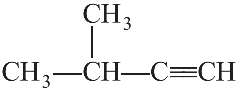
$$CH_3{-}\underset{Br}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}{-}COOH$$

C



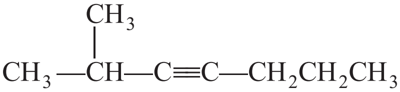
$$CH_3{-}\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}{-}COOH$$

D

1032. 

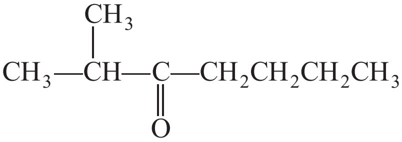
$$CH_3{-}\overset{CH_3}{\overset{|}{C}H}{-}C{\equiv}CH$$

A



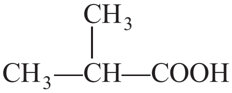
$$CH_3{-}\overset{CH_3}{\overset{|}{C}H}{-}C{\equiv}C{-}CH_2CH_2CH_3$$

B



$$CH_3{-}\overset{CH_3}{\overset{|}{C}H}{-}\underset{O}{\underset{\|}{C}}{-}CH_2CH_2CH_2CH_3$$

C

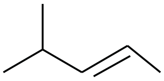


$$CH_3{-}\overset{CH_3}{\overset{|}{C}H}{-}COOH$$

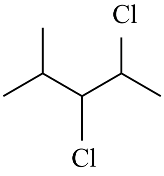
D

$CH_3CH_2CH_2COOH$

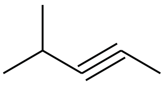
E

1033. 

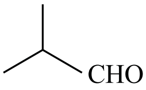
A



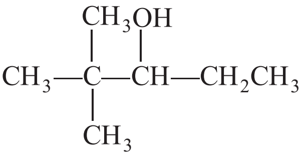
B



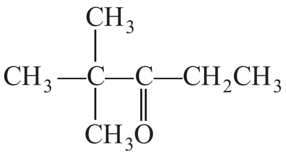
C



D

1034.

$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{OH}{CH}-CH_2CH_3$

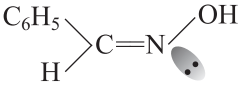
A


$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{O}{\underset{\|}{C}}-CH_2CH_3$

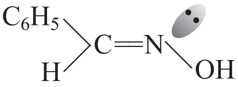
B

1035. C_6H_5CHO

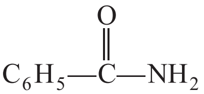
A



B



C

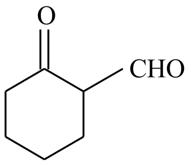

$C_6H_5-\overset{O}{\overset{\|}{C}}-NH_2$

D

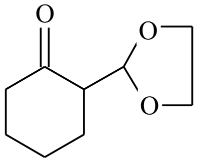

$H-\overset{O}{\overset{\|}{C}}-NHC_6H_5$

E

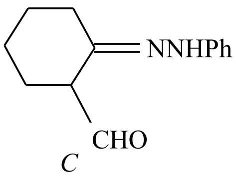
C_6H_5COOH *F* $C_6H_5NH_2$ *G*

1036.


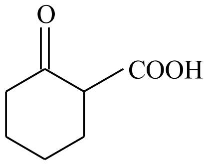
A



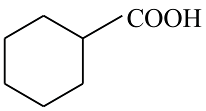
B



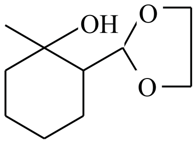
C



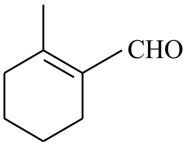
D = *E*



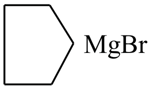
F



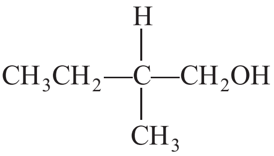
G



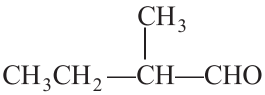
H



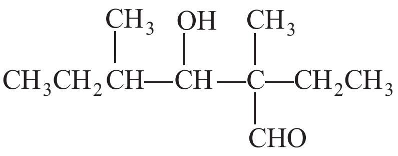
J

1037.

$CH_3CH_2-\underset{CH_3}{\overset{H}{C}}-CH_2OH$

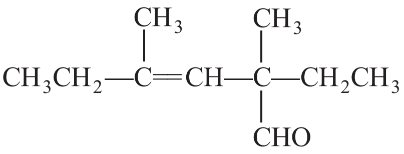
A


$CH_3CH_2-\overset{CH_3}{CH}-CHO$

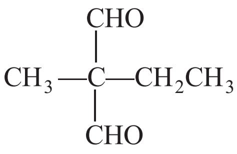
B


$CH_3CH_2\overset{CH_3}{CH}-\overset{OH}{CH}-\underset{CHO}{\overset{CH_3}{C}}-CH_2CH_3$

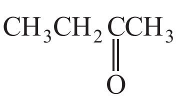
C


$CH_3CH_2-\overset{CH_3}{C}=CH-\underset{CHO}{\overset{CH_3}{C}}-CH_2CH_3$

D


$CH_3-\underset{CHO}{\overset{CHO}{C}}-CH_2CH_3$

E


$CH_3CH_2\underset{O}{\underset{\|}{C}}CH_3$

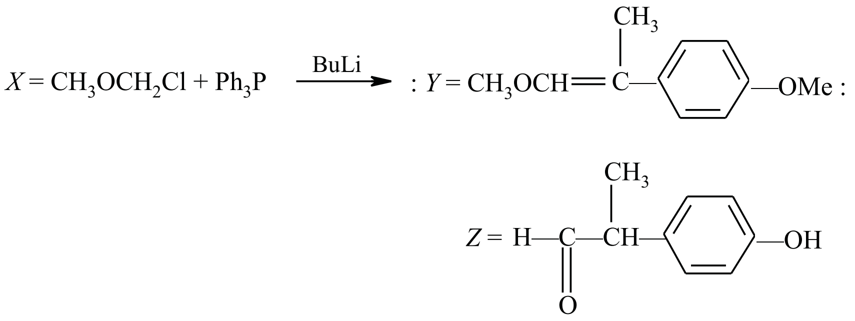
F

1038. (a) $O_3/Zn\text{-}H_2O$ followed by Aldol condensation.

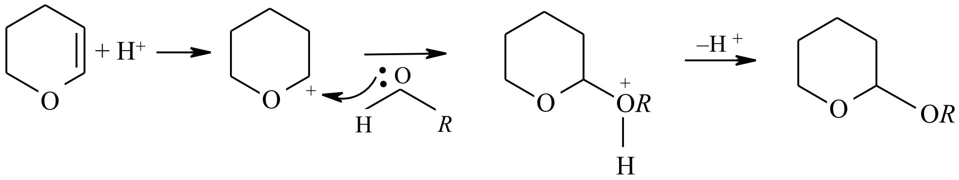
(b) $O_3/Zn\text{-}H_2O$ followed by Aldol condensation.

(c) $X = KMnO_4/NaOH$ (dilute) $Y = HIO_4$, Z = dilute NaOH (Aldol)

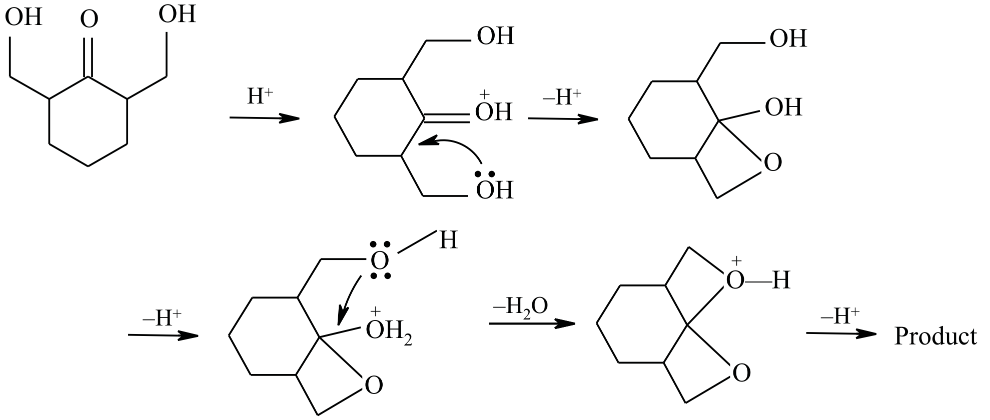
(d)



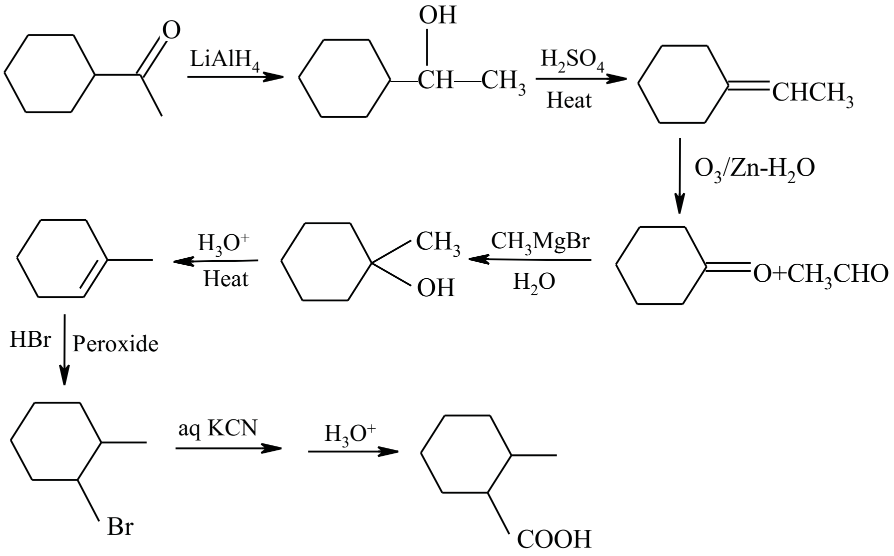
1039. (a)



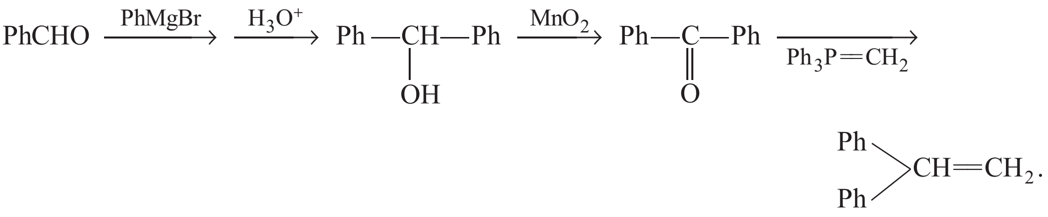
(b)



1040. (a)

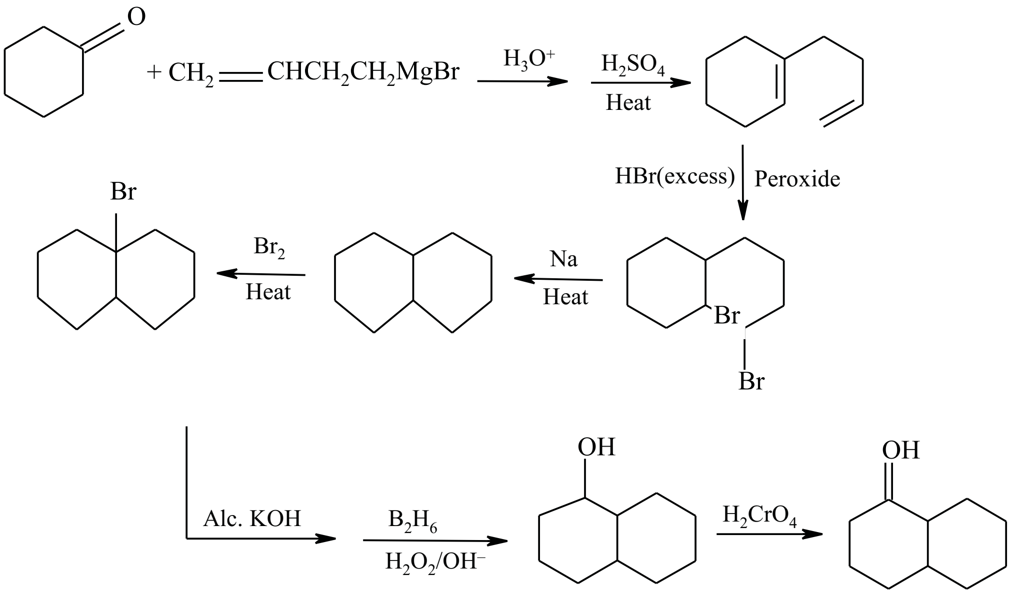


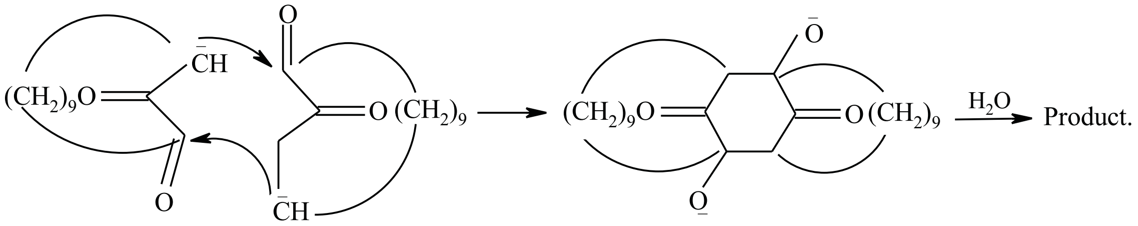
(b)



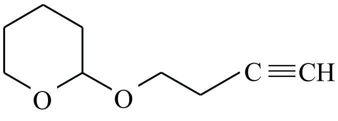
$$PhCHO \xrightarrow{PhMgBr} \xrightarrow{H_3O^+} Ph{-}\underset{OH}{CH}{-}Ph \xrightarrow{MnO_2} Ph{-}\underset{\|O}{C}{-}Ph \xrightarrow[Ph_3P{=}CH_2]{} Ph_2C{=}CH_2.$$

(c)

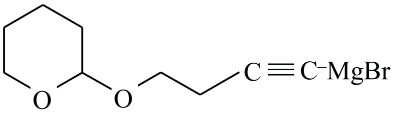




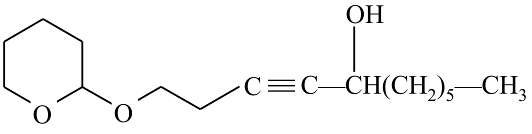
1042. (a)



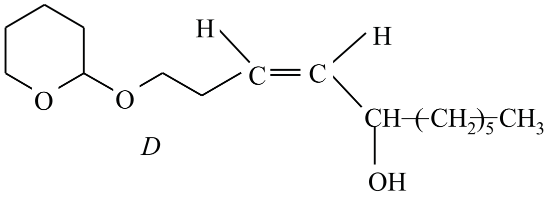
A

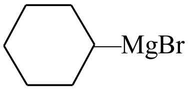


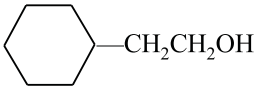
B

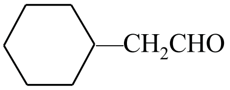


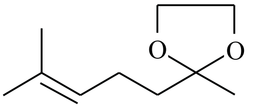
C

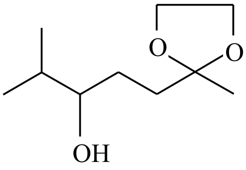

D

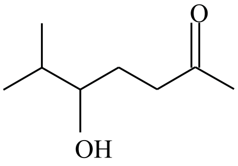
(b) 
E

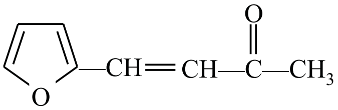

F

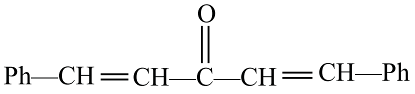

G

(c) 
H


I

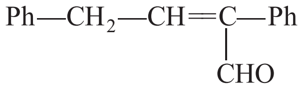

J

1043. (a) 

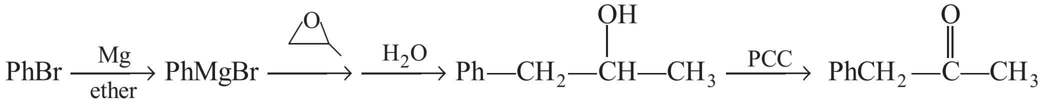
(b) 

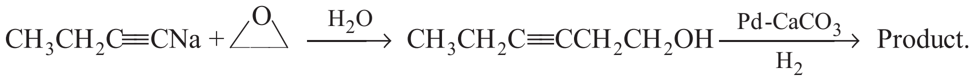
$Ph—CH=CH—\overset{\overset{\displaystyle O}{\|}}{C}—CH=CH—Ph$

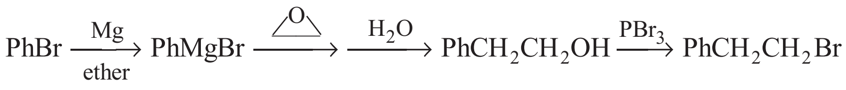
1041. Via aldol condensation :

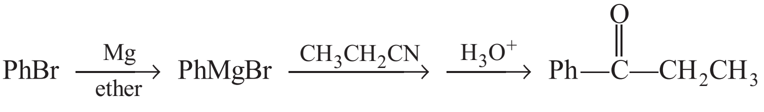
(c) 

$Ph—CH_2—CH=\underset{\underset{\displaystyle CHO}{|}}{C}—Ph$

1044. (a) 

(b) 

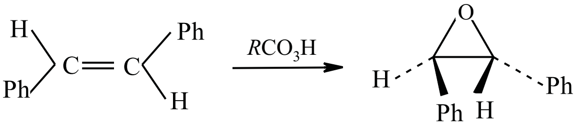
(c) 

(d) 

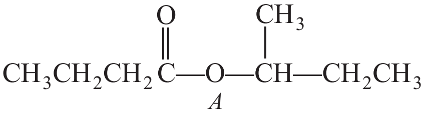
$PhBr \xrightarrow[\text{ether}]{Mg} PhMgBr \xrightarrow{CH_3CH_2CN} \xrightarrow{H_3O^+} Ph—\overset{\overset{\displaystyle O}{\|}}{C}—CH_2CH_3$

(e) Product from (d) $\xrightarrow[\text{Heat}]{N_2H_4/OH^-}$ $PhCH_2CH_2CH_3$

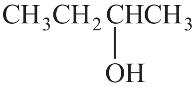
(f) $H{-}C{\equiv}C{-}H \xrightarrow[\text{Heat}]{\text{Na}} \xrightarrow{\text{PhBr}} Ph{-}C{\equiv}C{-}Ph \xrightarrow[\text{liq. NH}_3]{\text{Na}}$



1045.


$CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}{-}CH_2CH_3$

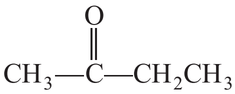
A


$CH_3CH_2\underset{\underset{\displaystyle OH}{|}}{CH}CH_3$

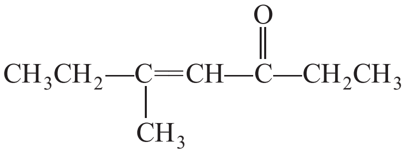
B

$CH_3CH_2CH_2CH_2OH$

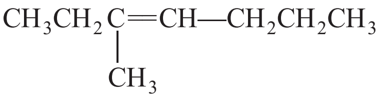
C


$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2CH_3$

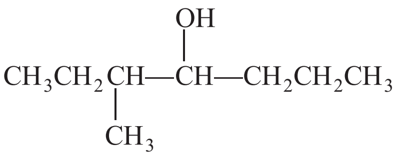
D


$CH_3CH_2{-}\underset{\underset{\displaystyle CH_3}{|}}{C}{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2CH_3$

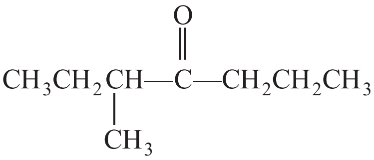
E


$CH_3CH_2\underset{\underset{\displaystyle CH_3}{|}}{C}{=}CH{-}CH_2CH_2CH_3$

F

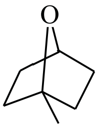

$CH_3CH_2\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}\overset{\overset{\displaystyle OH}{|}}{CH}{-}CH_2CH_2CH_3$

G

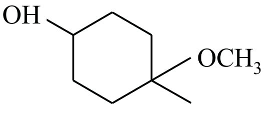

$CH_3CH_2\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2CH_2CH_3 \xrightarrow[\text{Bayer villiger oxidation}]{\text{Mcpba}} A$

H

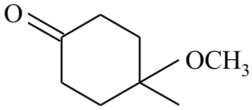
1046.



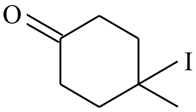
A



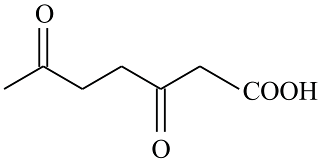
B



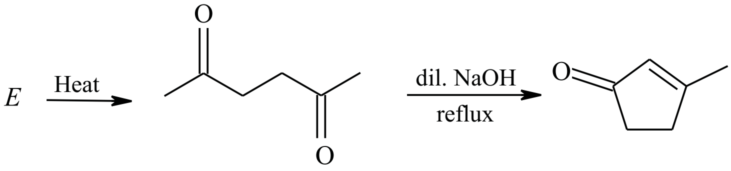
C



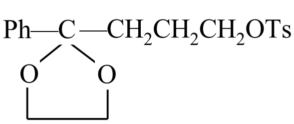
D



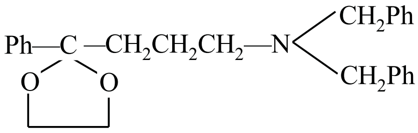
E



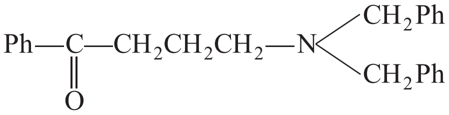
1047. (a)



A

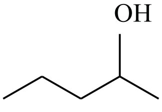


B

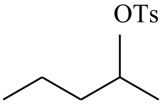


C

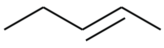
(b)



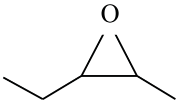
A



B

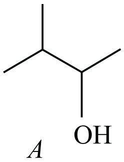


C

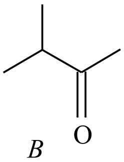


D

(c)

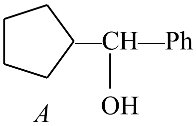


A

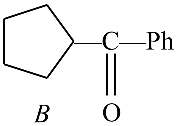


B

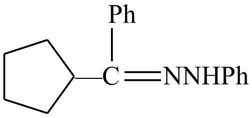
(d)



A



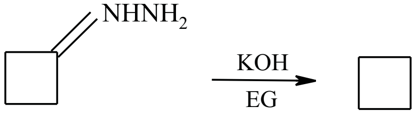
B



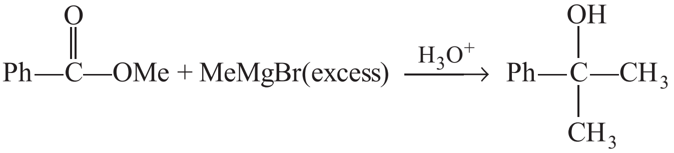
C

(e) $\underset{D}{\mathrm{H{-}C{\equiv}CNa}}$ $\underset{E}{\mathrm{C_6H_5CH_2C{\equiv}CH}}$ $\xrightarrow{C_2H_5MgBr}$ $C_2H_6 + C_6H_5CH_2C{\equiv}CMgBr$

(f)

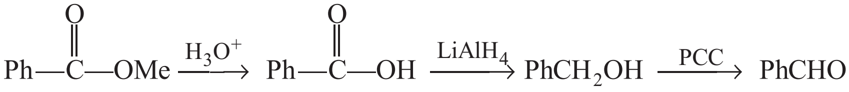


1048. (a)

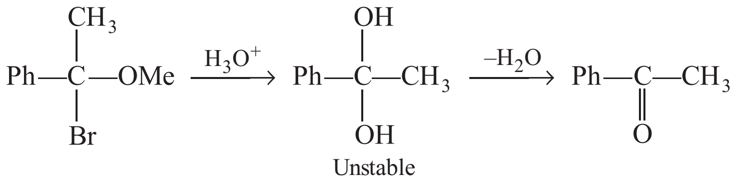


$$\mathrm{Ph{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OMe} + \mathrm{MeMgBr(excess)} \xrightarrow{H_3O^+} \mathrm{Ph{-}\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}{-}CH_3}$$

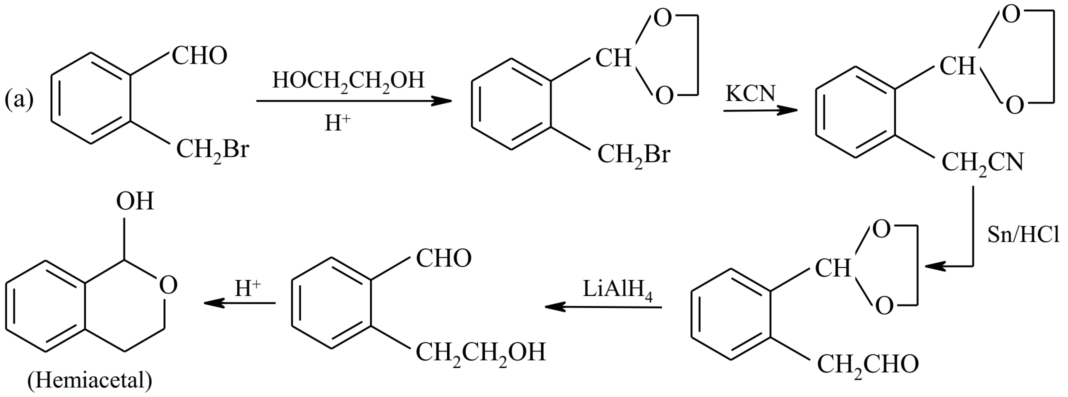
(b)

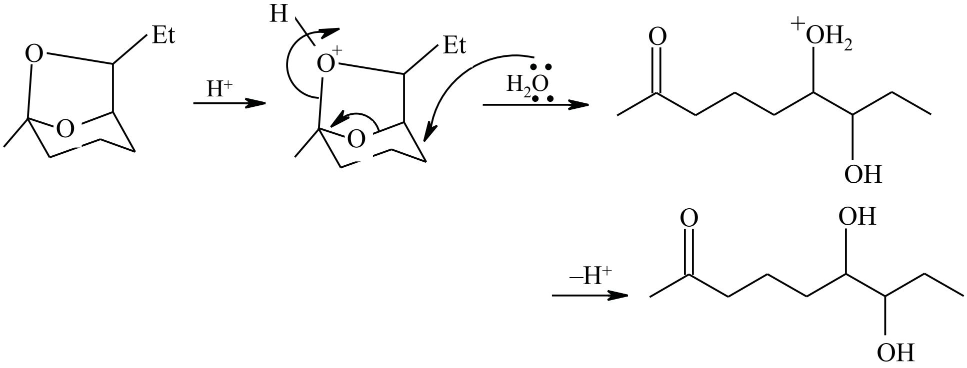


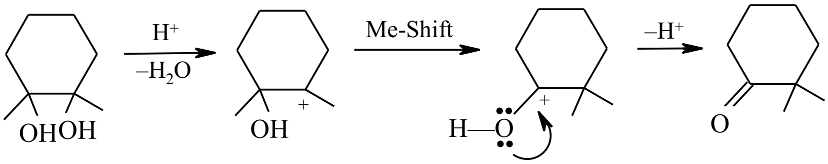
$$\mathrm{Ph{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OMe} \xrightarrow{H_3O^+} \mathrm{Ph{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH} \xrightarrow{LiAlH_4} \mathrm{PhCH_2OH} \xrightarrow{PCC} \mathrm{PhCHO}$$

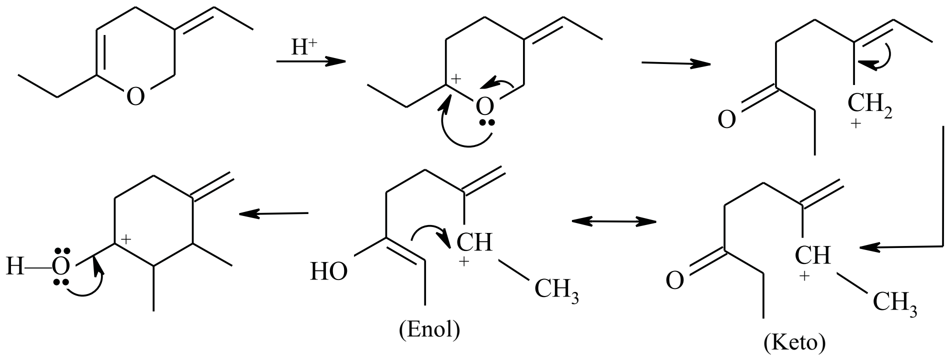
(c) 

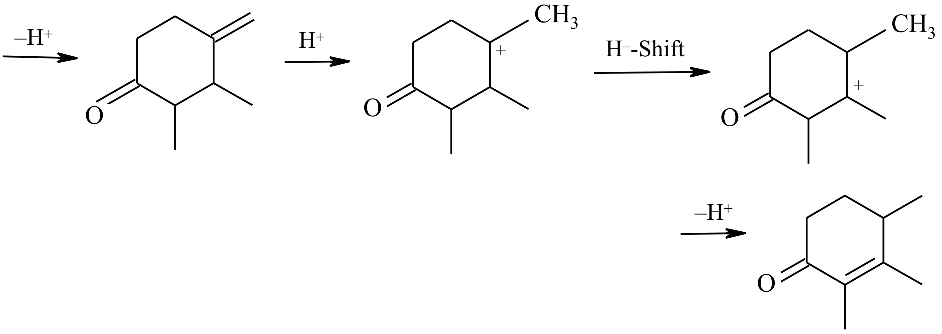
$$\mathrm{Ph{-}\overset{\displaystyle CH_3}{\underset{\displaystyle Br}{C}}{-}OMe} \xrightarrow{H_3O^+} \mathrm{Ph{-}\overset{\displaystyle OH}{\underset{\displaystyle OH}{C}}{-}CH_3} \xrightarrow{-H_2O} \mathrm{Ph{-}\underset{\displaystyle O}{\overset{\|}{C}}{-}CH_3}$$

1049. (a) 

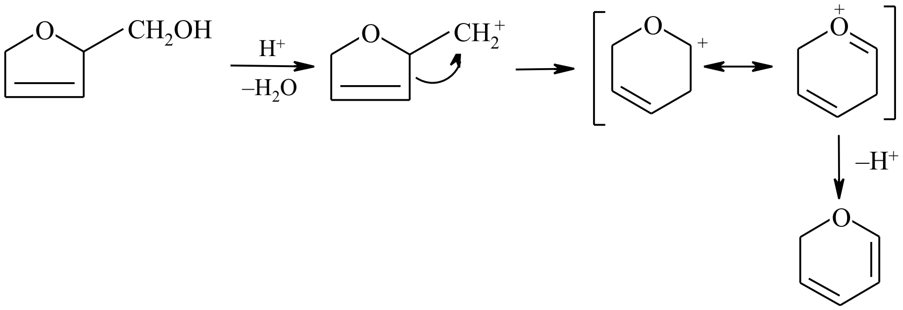
(b) 

1050. (a) 

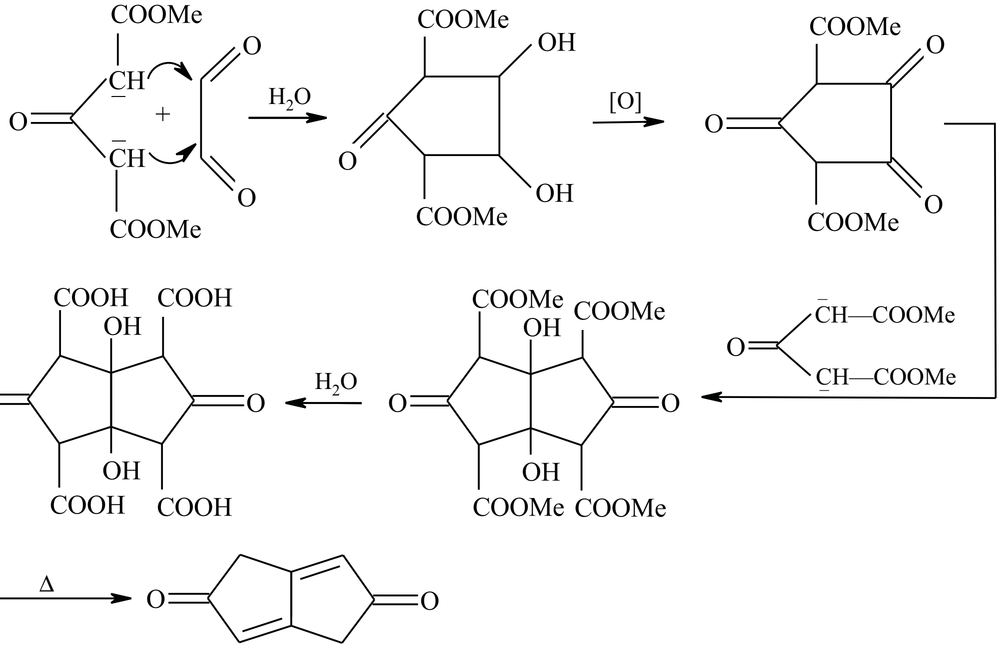
(b) 


–H+
O
H+
CH3
+
O
H–-Shift
CH3
+
O
–H+
O

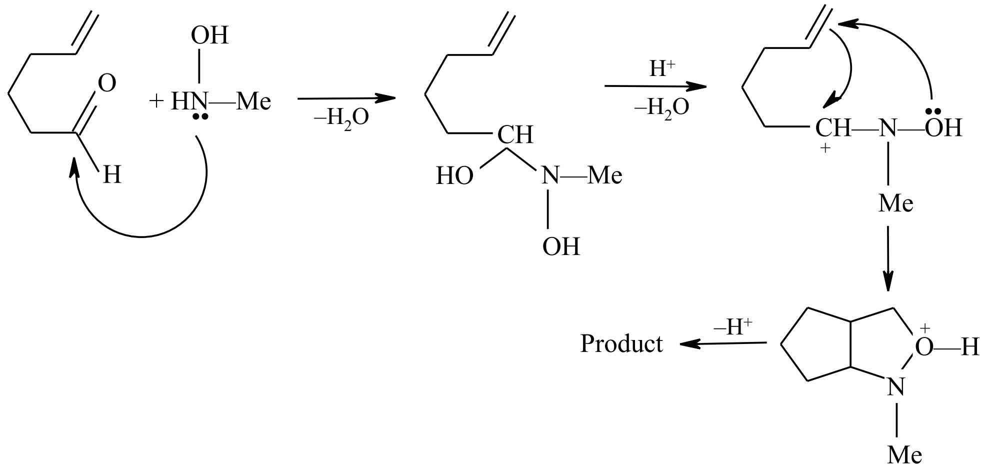
(c)


O
CH2OH
H+
–H2O
O
CH2+
O
+
+
O
–H+
O

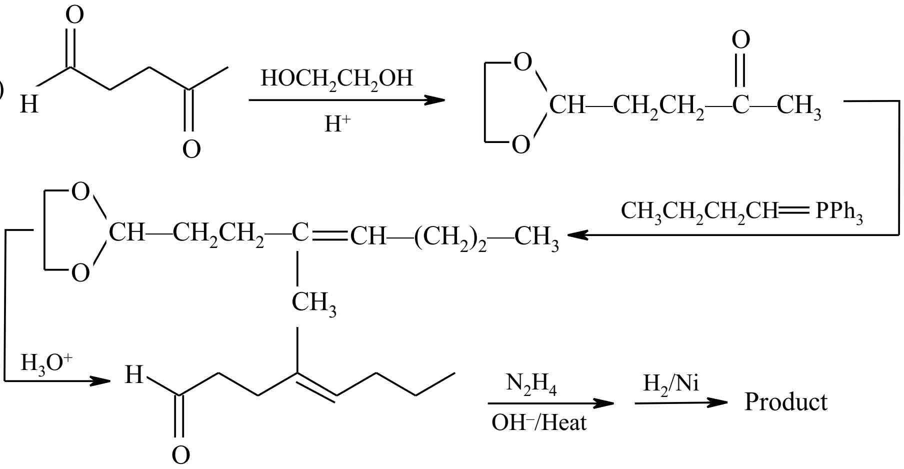
1051. (a)


COOMe
O
CH
+
CH
O
COOMe
O
H2O
COOMe
OH
O
OH
COOMe
[O]
COOMe
O
O
O
COOMe
CH—COOMe
O
CH—COOMe
COOMe
OH
COOMe
O
O
OH
COOMe COOMe
H2O
COOH COOH
OH
O
O
OH
COOH COOH
Δ
O
O

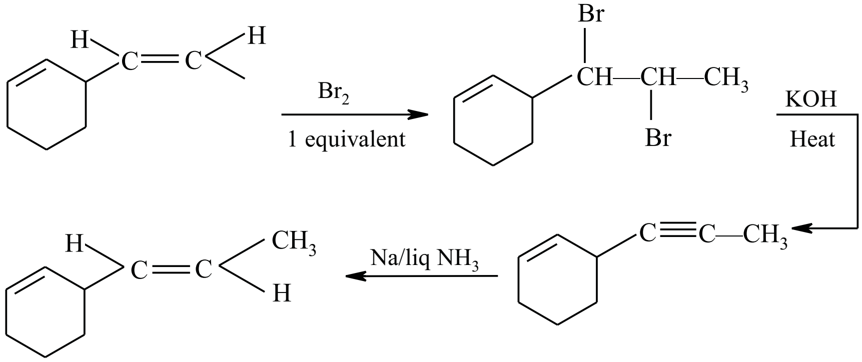
(c)



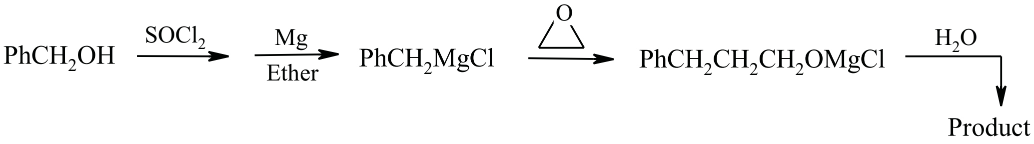
1052. (a)



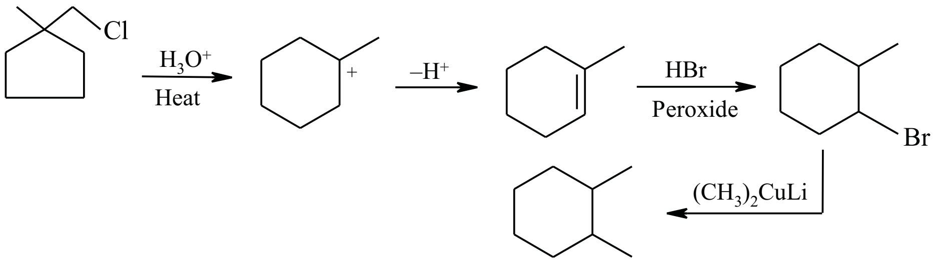
(b)

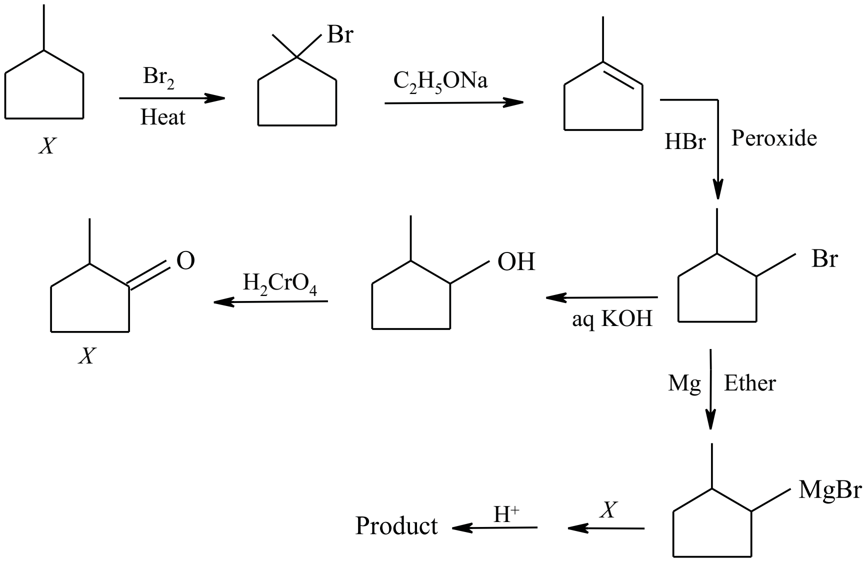


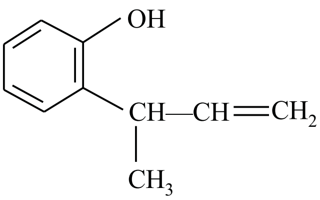
(c)



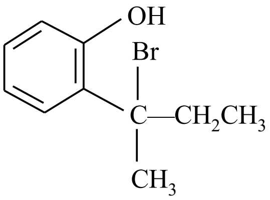
$$\mathrm{PhCH_2OH} \xrightarrow{\mathrm{SOCl_2}} \xrightarrow[\text{Ether}]{\mathrm{Mg}} \mathrm{PhCH_2MgCl} \xrightarrow{\text{oxetane}} \mathrm{PhCH_2CH_2CH_2OMgCl} \xrightarrow{\mathrm{H_2O}} \text{Product}$$

(d) 

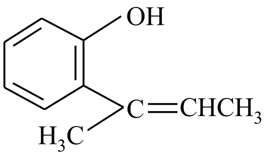
(e) 

1053. 

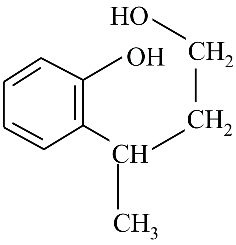
A



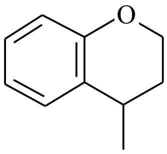
B



C

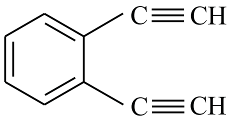


D

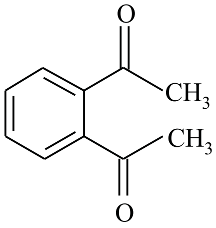


E

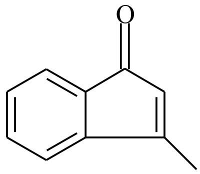
1054.



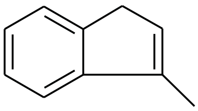
A



B



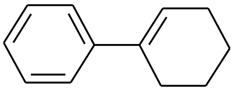
C



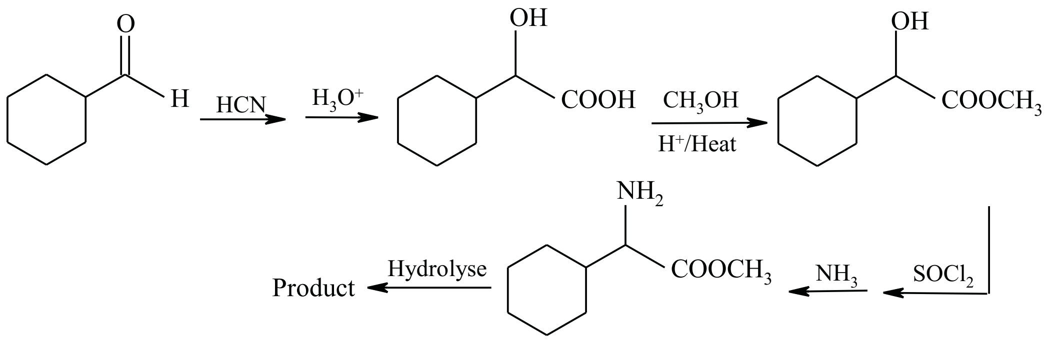
D

1055. (a) N_2H_4/NaOH/Heat (b) $R\text{Li} \longrightarrow \text{CH}_3\text{I} \longrightarrow$ Product.

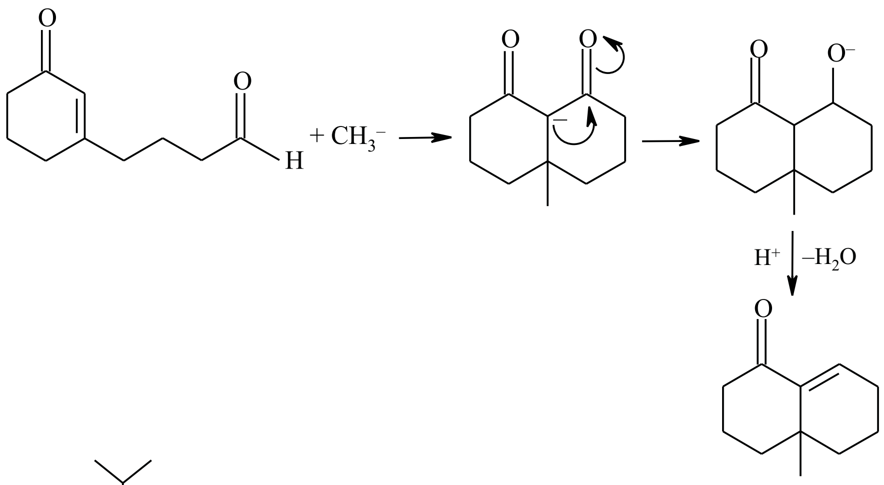
(c)



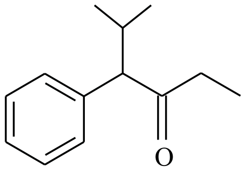
(d)



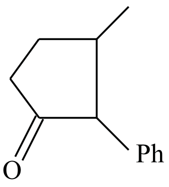
(e)



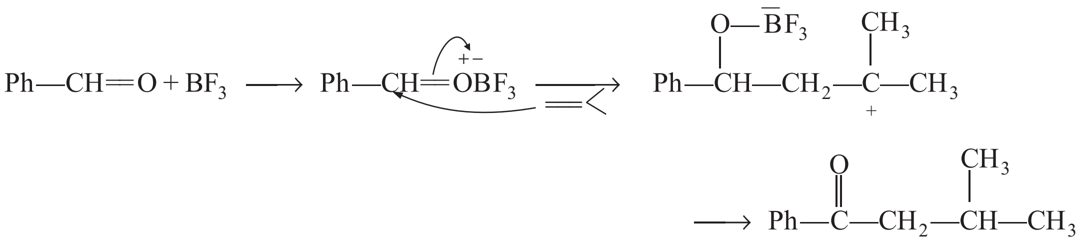
1056. (a)



(b)

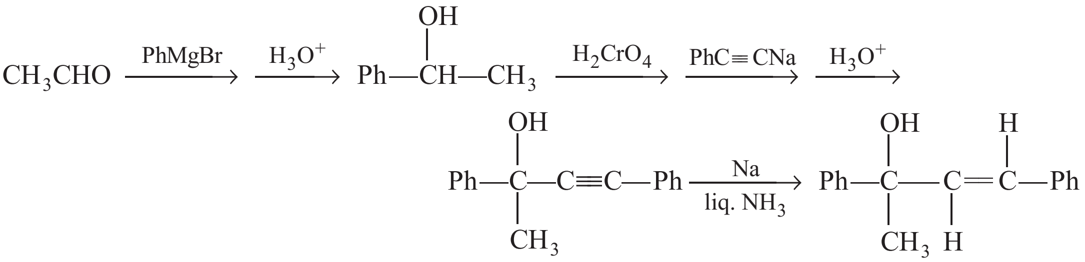


1057.



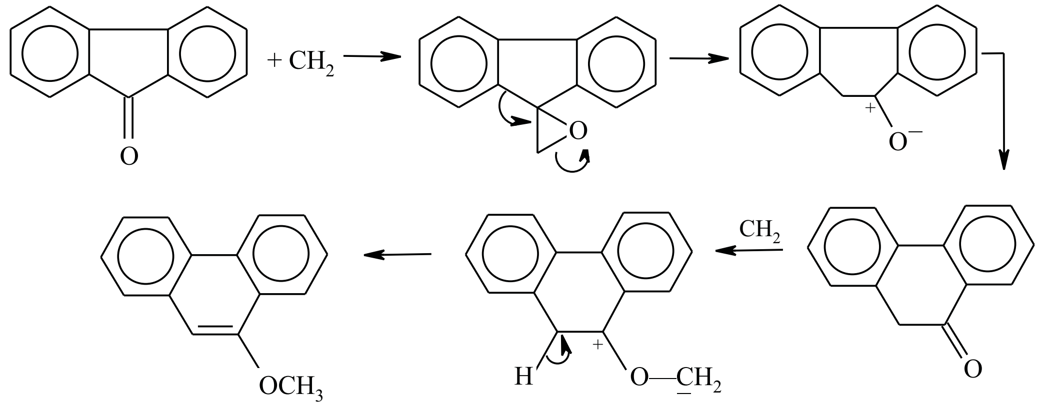
$$Ph{-}CH{=}O + BF_3 \longrightarrow Ph{-}CH{=}\overset{+}{O}\overset{-}{B}F_3 \xrightarrow{=\!<} Ph{-}\underset{}{\overset{O-\overline{B}F_3}{CH}}{-}CH_2{-}\underset{+}{\overset{CH_3}{C}}{-}CH_3 \longrightarrow Ph{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}\overset{CH_3}{CH}{-}CH_3$$

1058.

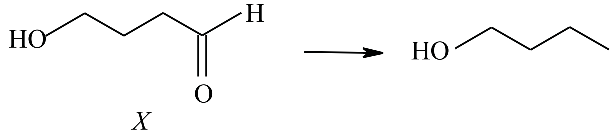


$$CH_3CHO \xrightarrow{PhMgBr} \xrightarrow{H_3O^+} Ph{-}\overset{OH}{CH}{-}CH_3 \xrightarrow{H_2CrO_4} \xrightarrow{PhC\equiv CNa} \xrightarrow{H_3O^+} Ph{-}\underset{CH_3}{\overset{OH}{C}}{-}C{\equiv}C{-}Ph \xrightarrow[\text{liq. }NH_3]{Na} Ph{-}\underset{CH_3}{\overset{OH}{C}}{-}\underset{H}{C}{=}\overset{H}{C}{-}Ph$$

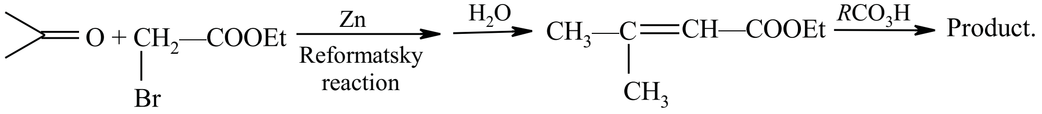
1059. (a)



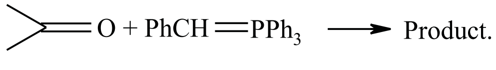
(b)



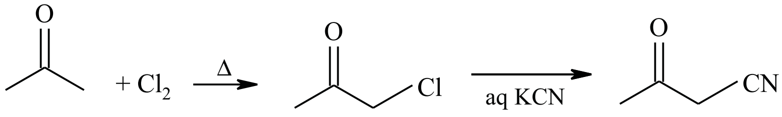
1060. (a)



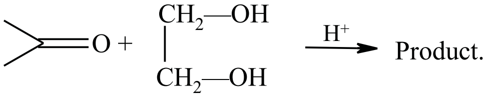
(b)



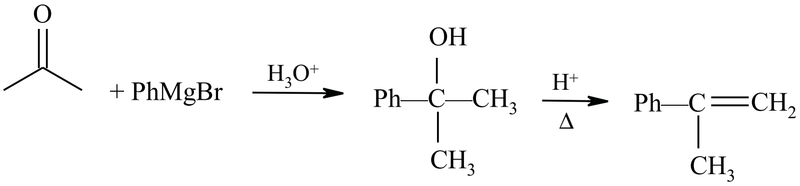
(c)



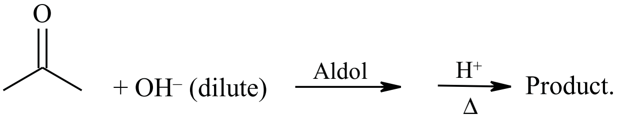
(d)



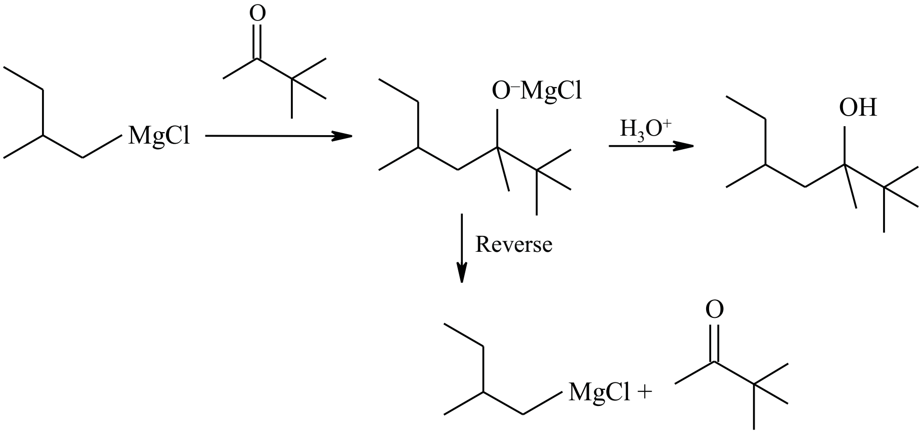
(e)



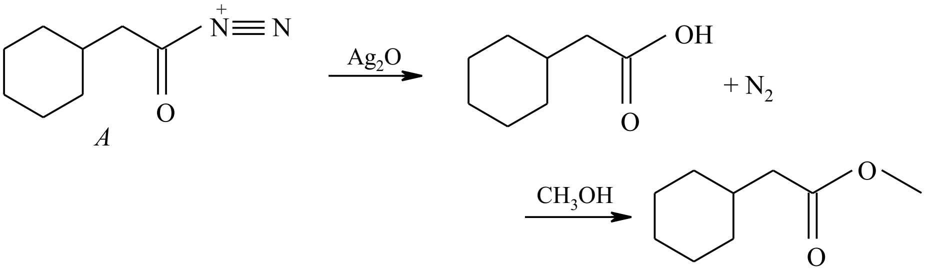
(f)



1061.



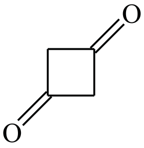
1062. (a)



(b) $H_2C{=}C{=}O$

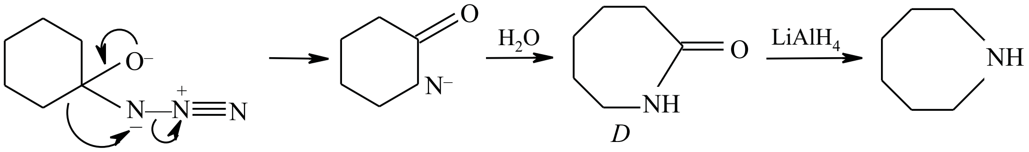
(Ketene)

B

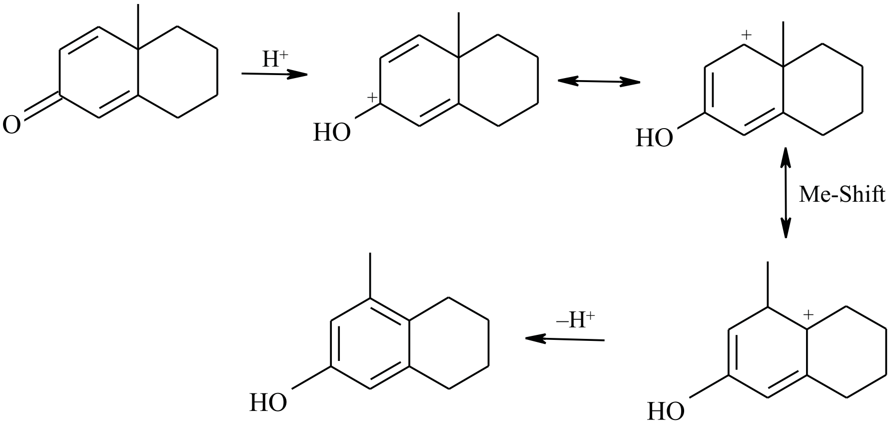


C

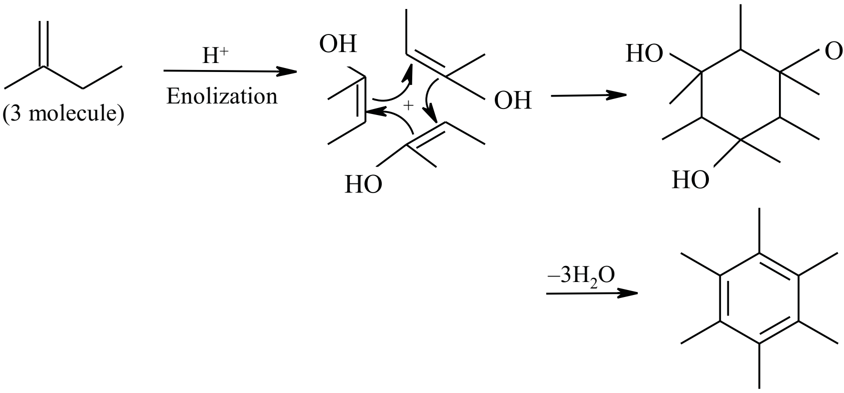
(c)


O⁻
N
N≡N
N⁻
O
H₂O
O
NH
D
LiAlH₄
NH

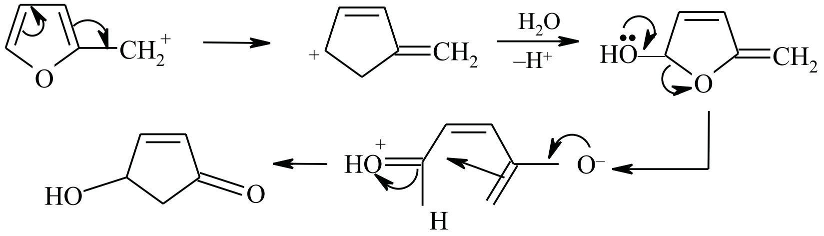
(d)


O
H⁺
HO
HO
Me-Shift
–H⁺
HO
HO

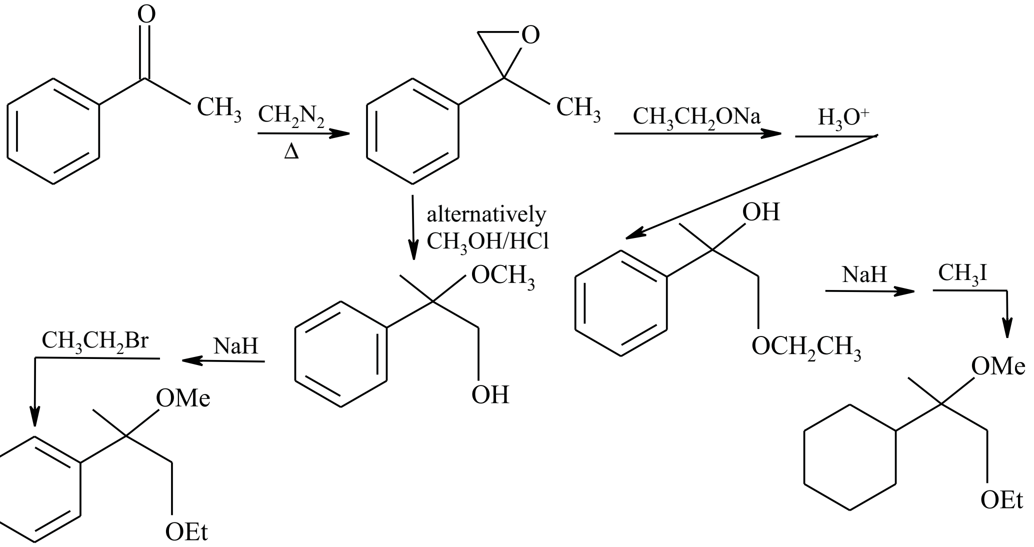
(e)


(3 molecule)
H⁺
Enolization
OH
OH
HO
HO
OH
HO
–3H₂O

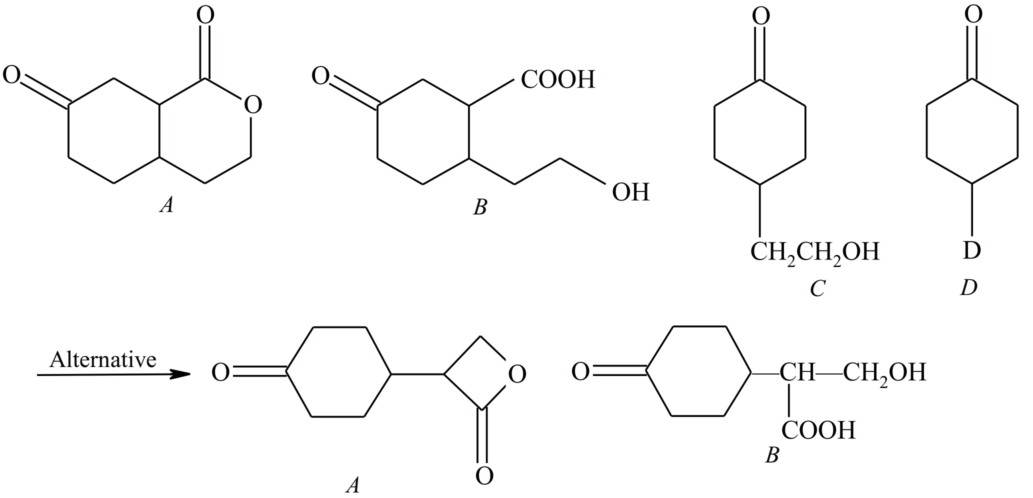
(f)


O
CH₂⁺
CH₂
H₂O
–H⁺
HO
O
CH₂
O⁻
HO
H
HO
O

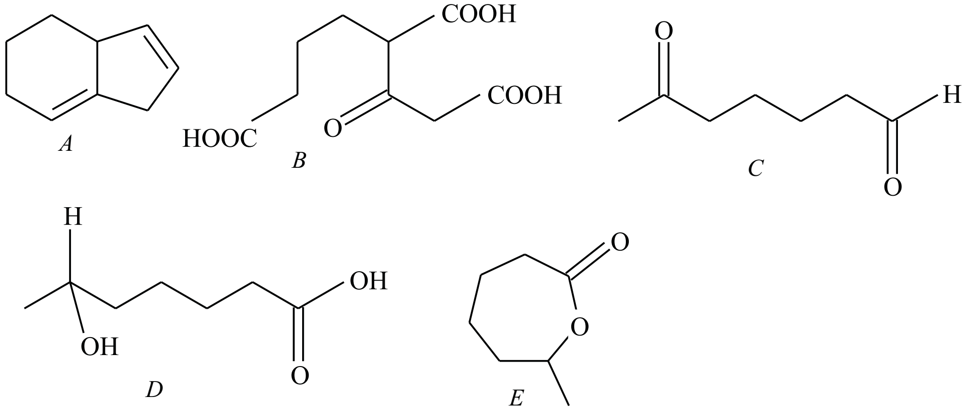
1063.



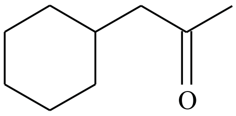
1064.



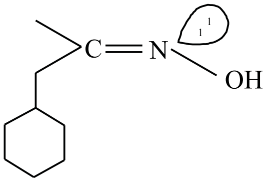
1065.



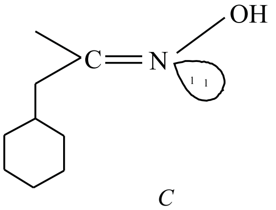
1066.



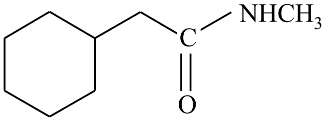
A



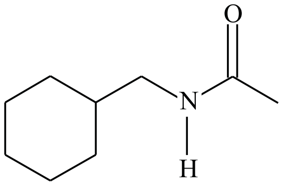
B



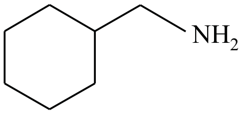
C



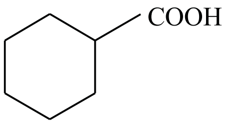
D



E

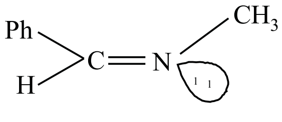


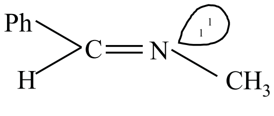
F



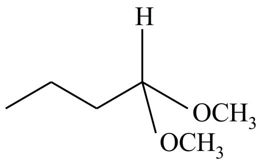
G

1067. (a)

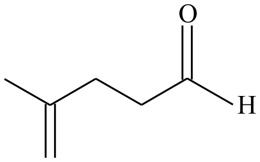




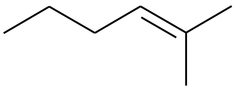
(b)



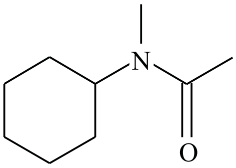
(c)



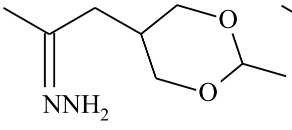
(d)



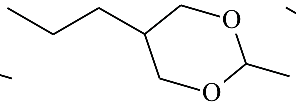
(e)



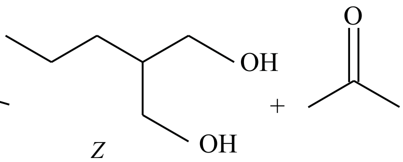
(f)



X



Y



Z

1068. (a) N_2H_4/NaOH/heat, H_3O^+, $Ph_3P{=}CH_2$,

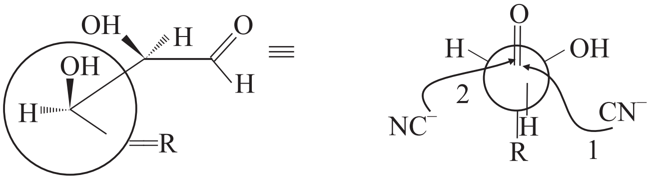
(b) N_2H_4/NaOH/heat, H_3O^+, $HNCH_3/H_2{-}Pd/C$

(c) $Ph_3P{=}CH_2$, $H_2N{-}OCH_3$,

(d) $CH_3Li/HCl/H_2O$, $Ph_3P{=}CH_2$.

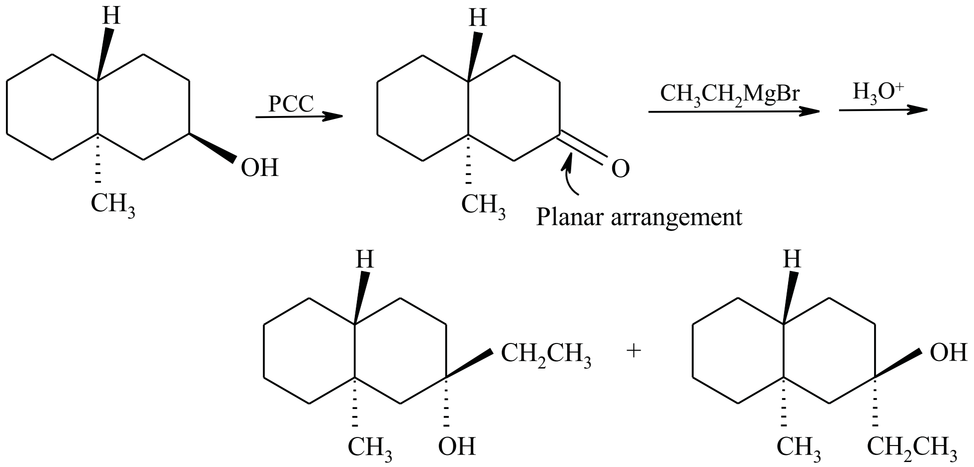
1069. III < II < I.

1070. The nucleophilic addition of cyanide ion will occur at carbonyl carbon. Therefore, the stable conformation at α-carbon will be:



As shown above, attack from side 1 will produce B and attack from side 2 will produce C. Since, attack of CN^- from side 2 will suffer less steric hindrance, C will be formed in greater amount than B.

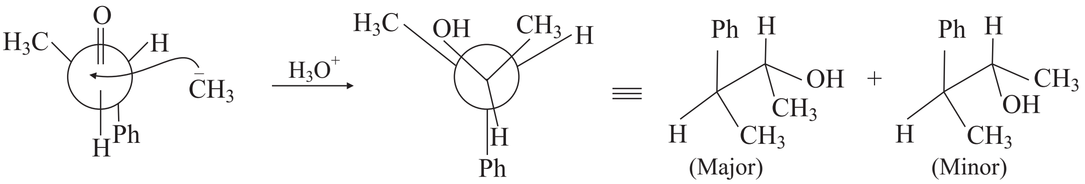
1071. (a)



Major product
(nucleophilic addition of
$CH_3CH_2^-$ occur from side opposite
to —CH_3 group)

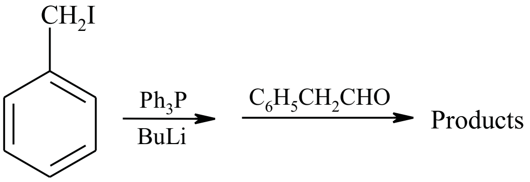
(Minor product)

(b) In the most stable conform shown below:

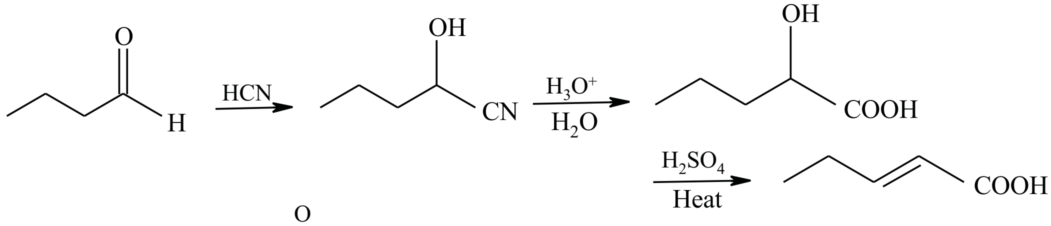


(attack occur from
less-hindered side)

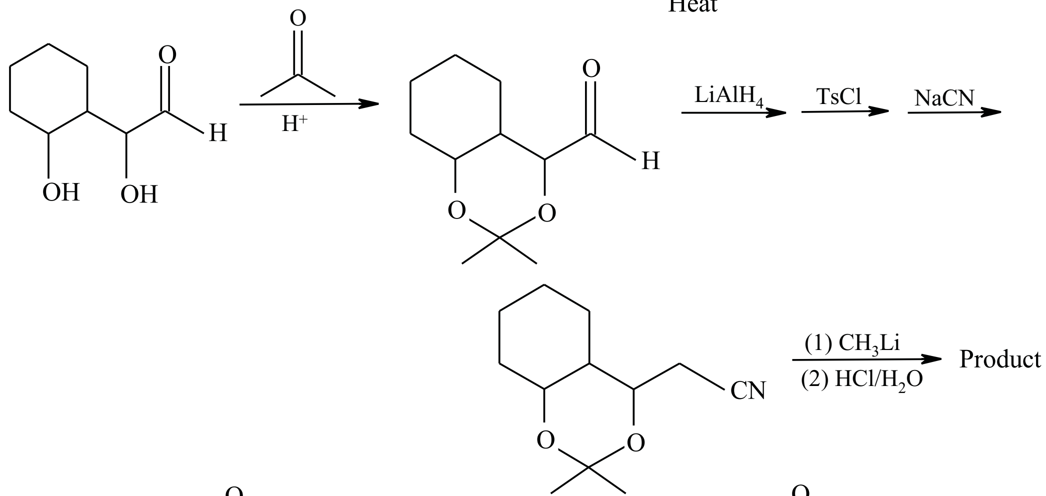
1072.



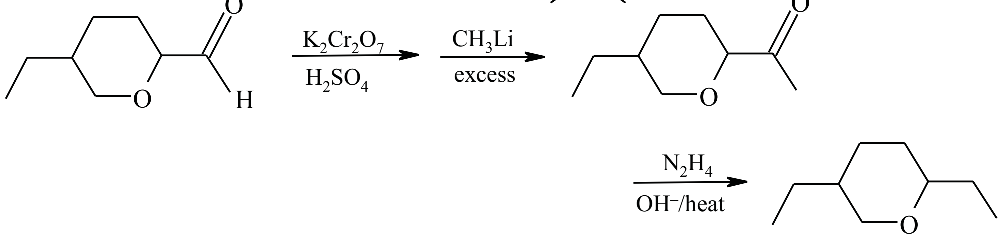
(b)



(c)

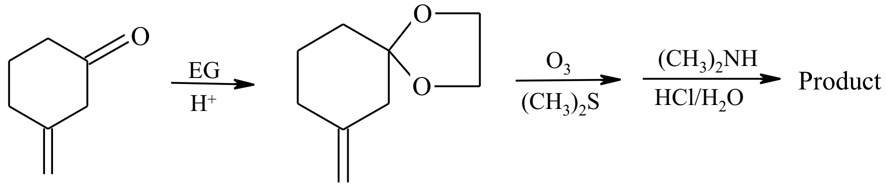


(d)

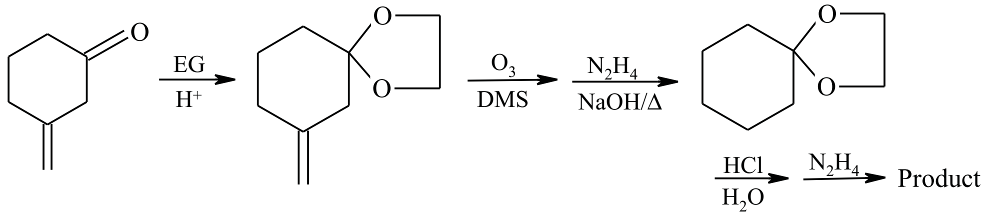


1073. A will proceed more efficiently. The electronegative chlorine, via inductive effect, increases the electrophilicity of the carbonyl carbon, making it more susceptible to attack by cyanide ion.

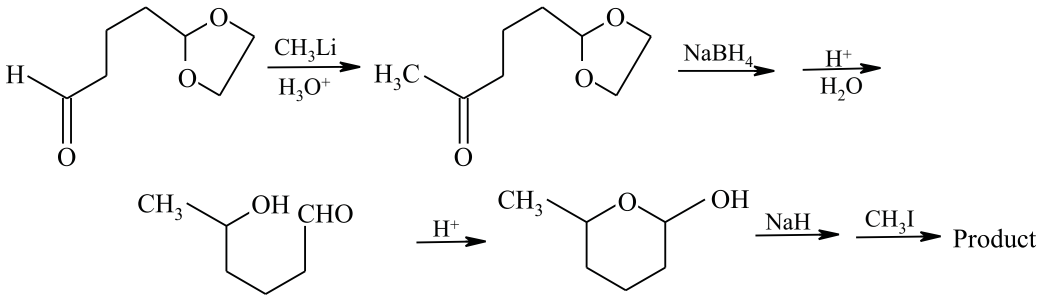
1074. (a)



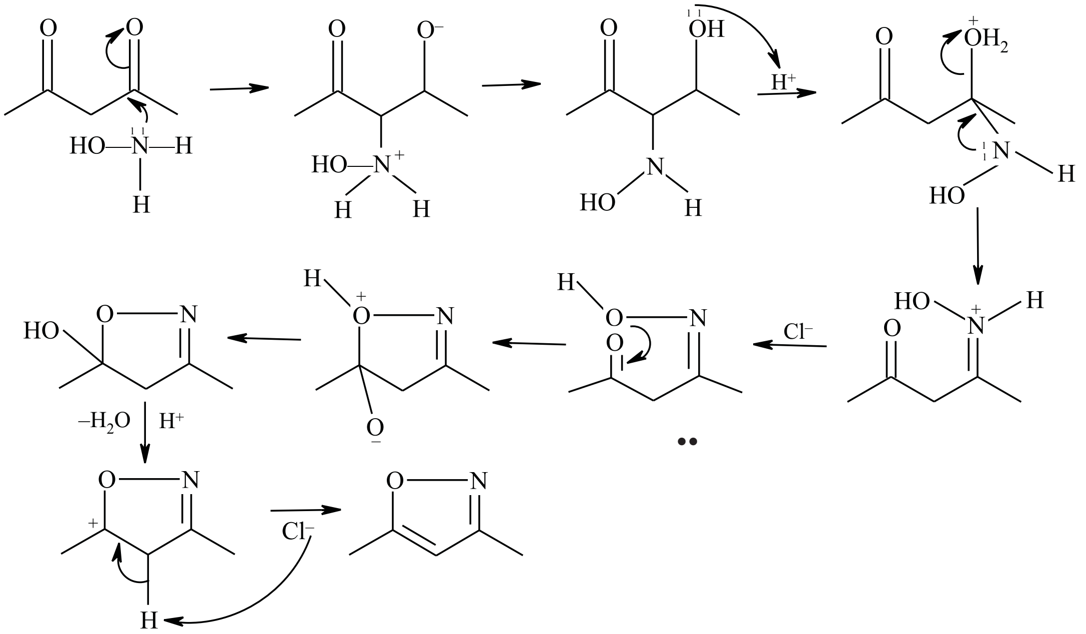
(b)



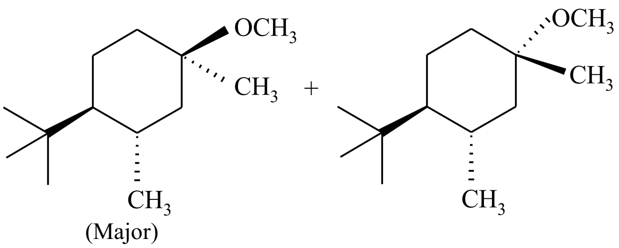
(c)



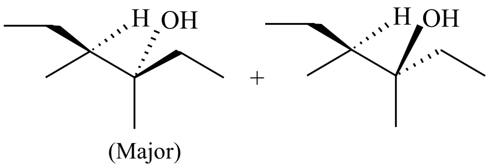
1075.



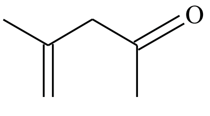
1076. (a)



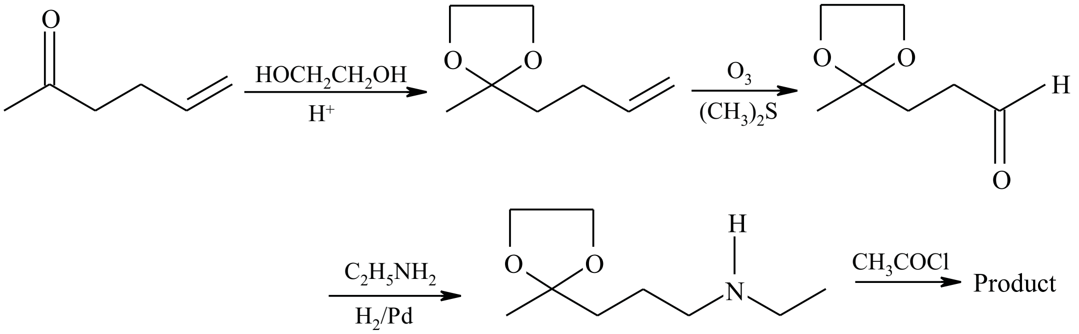
(c)



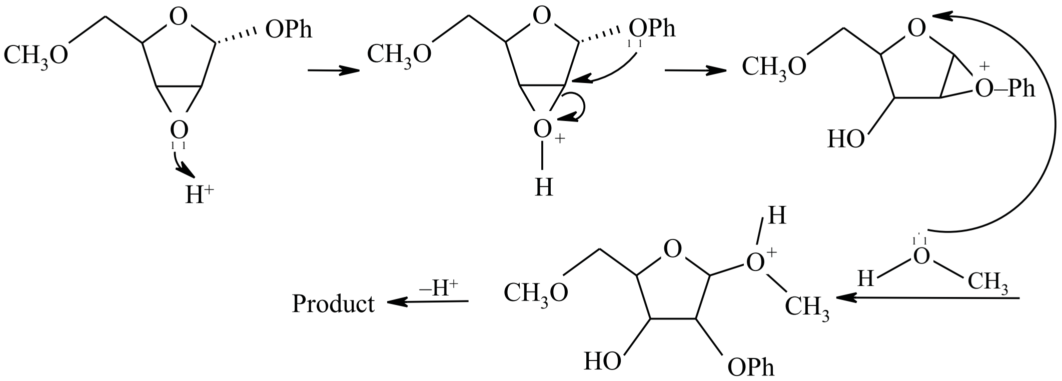
(d)



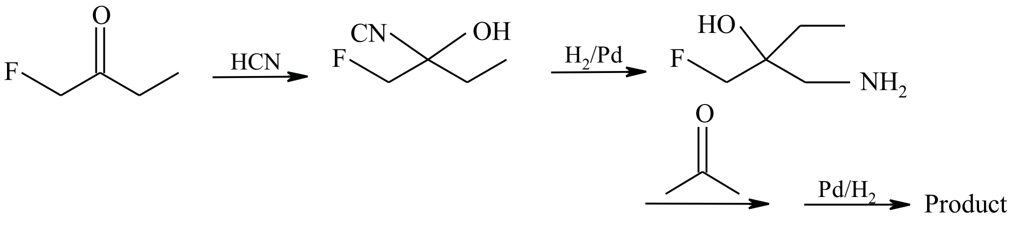
1077.



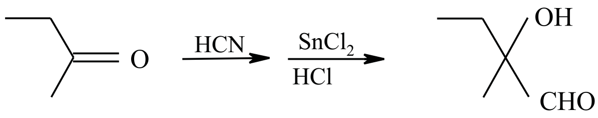
1078.



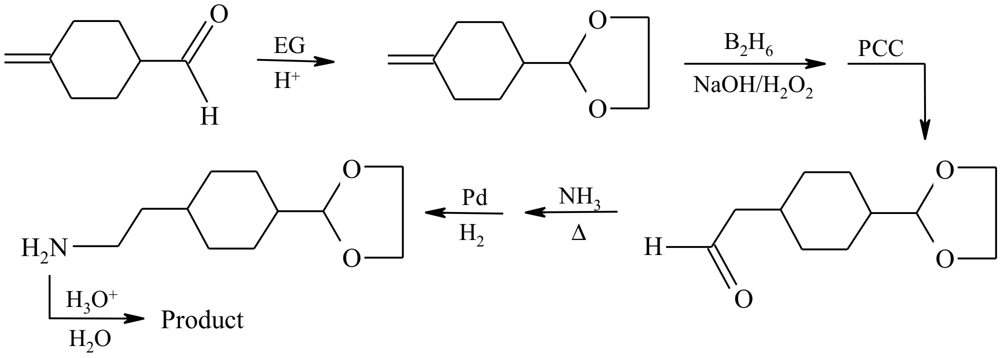
1079. (a)



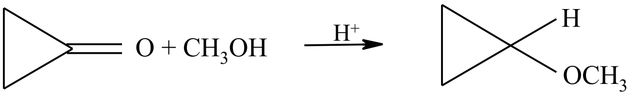
(b)



(c)



1080. The bond angle required at carbonyl carbon is 120°. In the case of cyclohexanone, the six membered ring can accommodate this bond angle easily and thus, the driving force towards hemiacetal formation, where the bond angle is 109° is small. On the other hand, in cyclopropanone, the system is highly strained, and hemiacetal formation enables some of the strain to be alleviated by allowing the carbonyl carbon to be sp^3 hybridized.

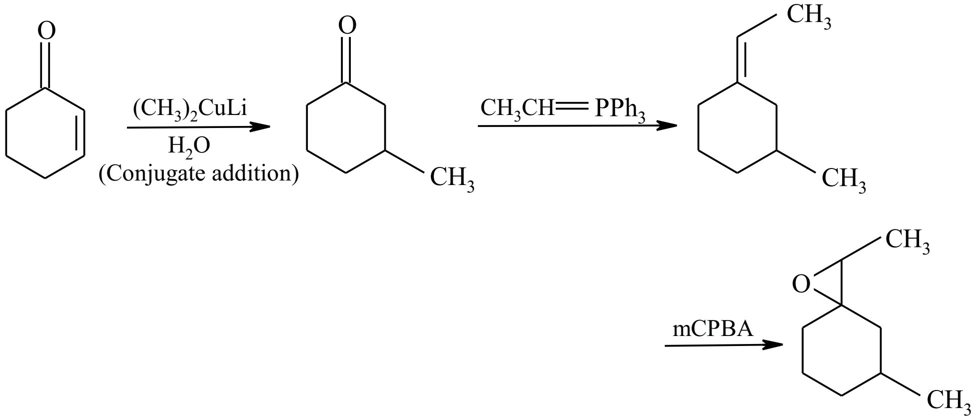


ring is less strained
than cyclopropanone

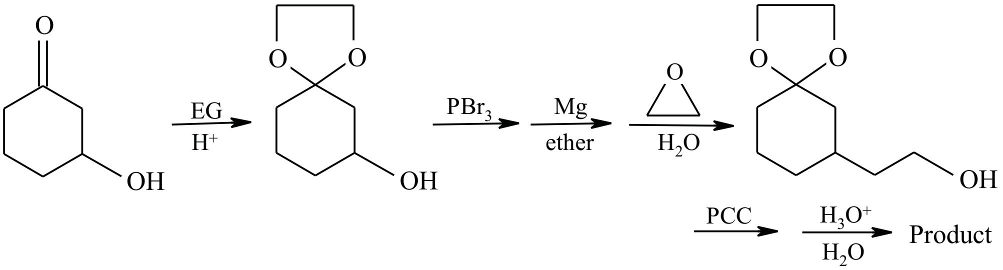
1081. (a) CH_3COCH_2Br, (b) CH_3CHO, (c) CH_3COCF_3, (d) CH_3CHO.

1082. *A* : CH_3ONa/CH_3OH, *B* : $(CH_3)_2NH$, *C* : $CH_3CH{=}CH_2MgBr$; H_3O^+, *D* : CH_3OH/H_2SO_4.

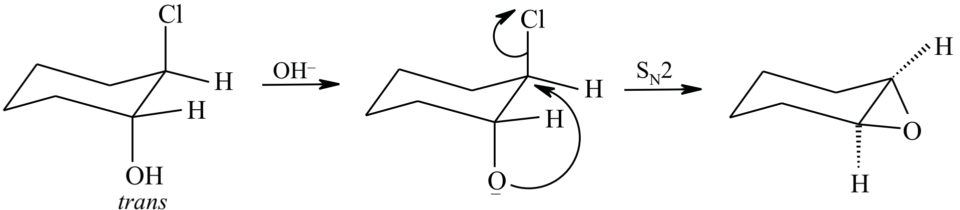
1083. (a)



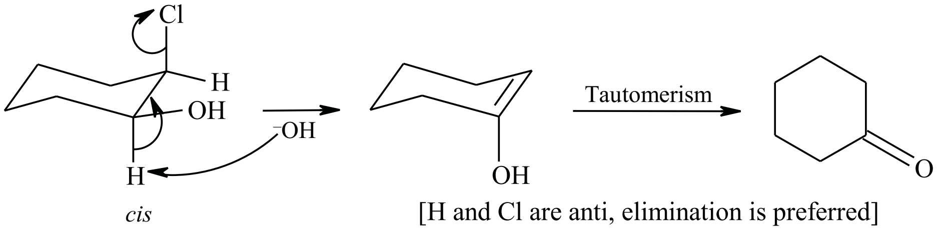
(b)



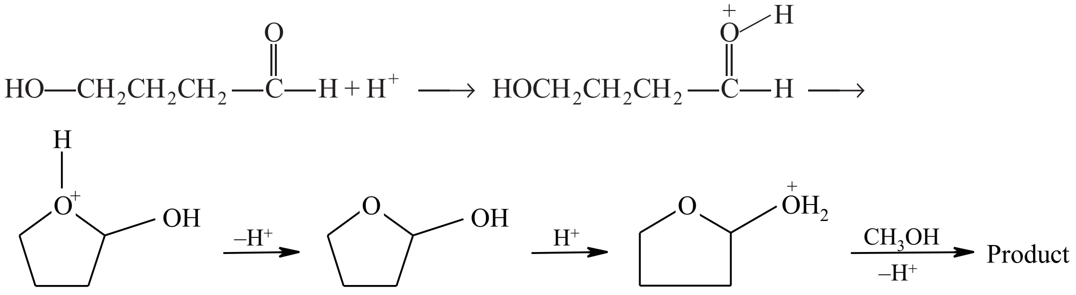
1084.



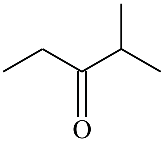
[—O⁻ and Cl are anti, substitution is preferred]

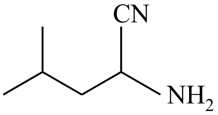


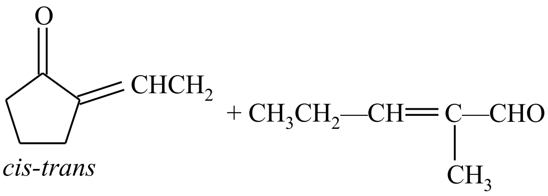
[H and Cl are anti, elimination is preferred]

1085. 

$$\text{HO—CH}_2\text{CH}_2\text{CH}_2\text{—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—H} + \text{H}^+ \longrightarrow \text{HOCH}_2\text{CH}_2\text{CH}_2\text{—}\overset{\overset{+}{\text{O}}\text{—H}}{\overset{\|}{\text{C}}}\text{—H} \longrightarrow$$

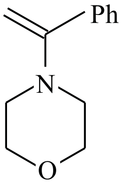
1086. (a) 

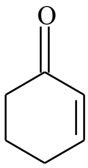
(b) 

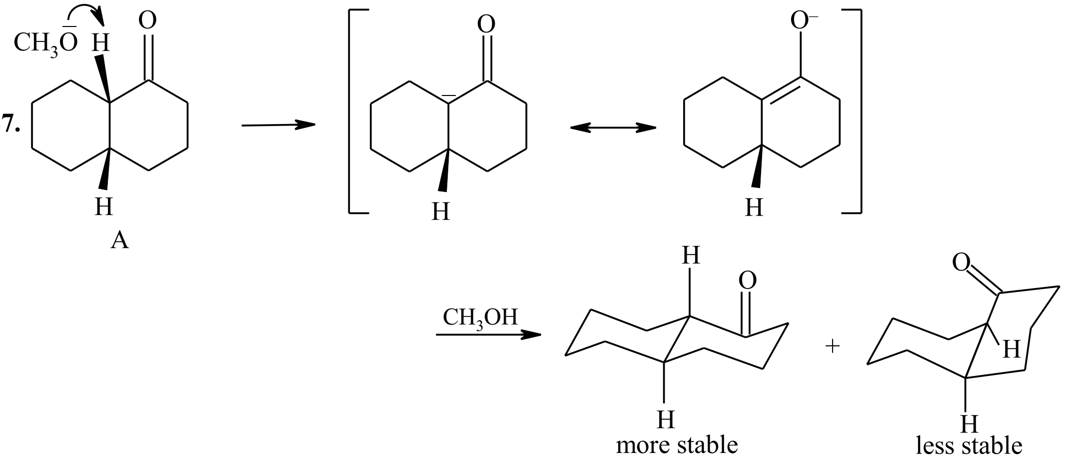
(c) 

$$\text{+ CH}_3\text{CH}_2\text{—CH}{=}\underset{\text{CH}_3}{\underset{|}{\text{C}}}\text{—CHO}$$

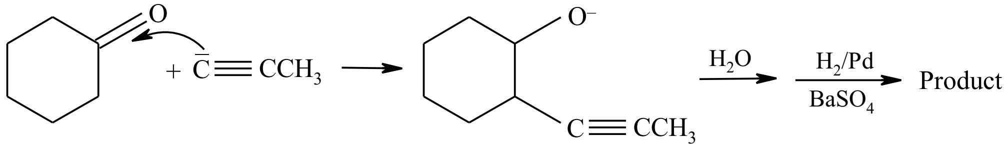
cis-trans

(d) 

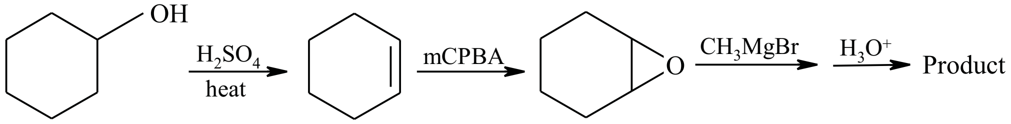
(e) 

1087. 

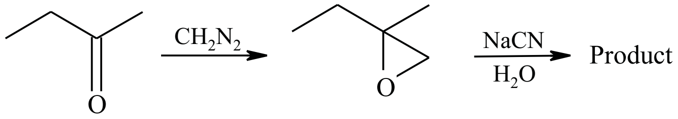
1088. (a)



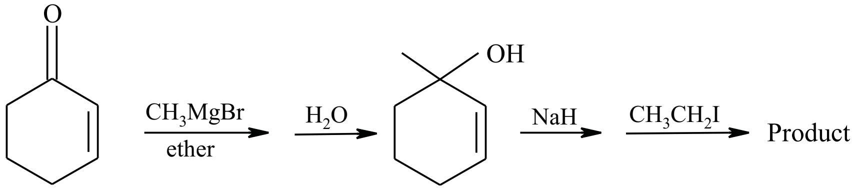
(b)



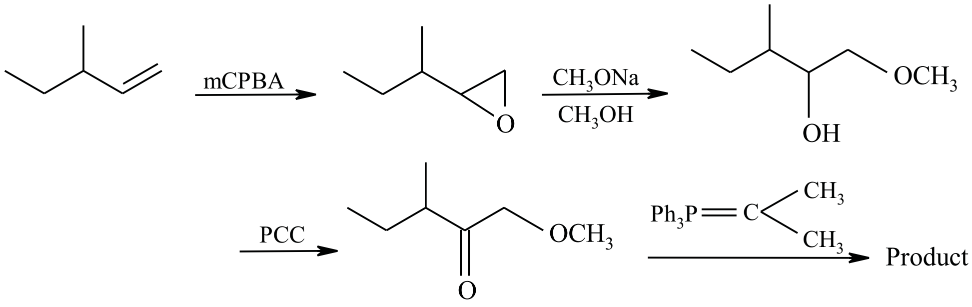
(c)



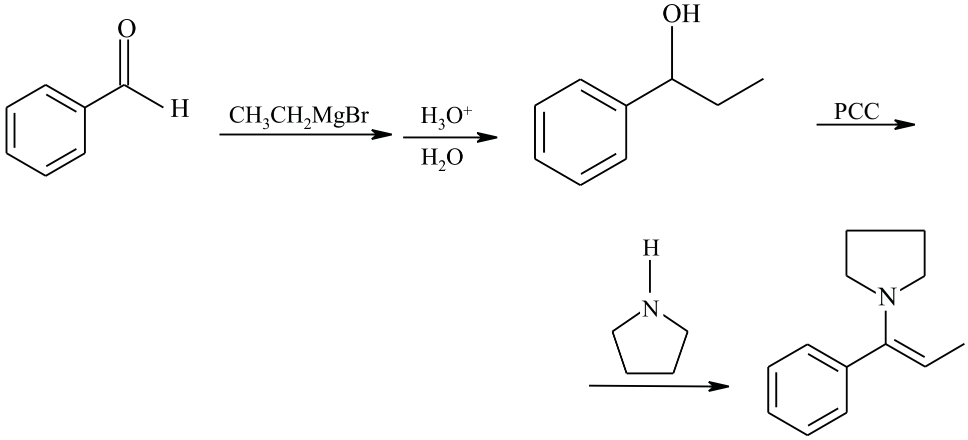
(d)



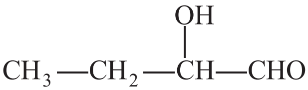
1089. (a)



(b)

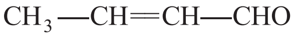


1090.



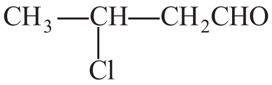
$CH_3-CH_2-\overset{OH}{CH}-CHO$

A



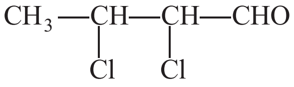
$CH_3-CH=CH-CHO$

B



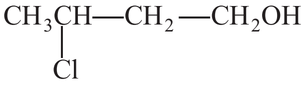
$CH_3-\underset{Cl}{CH}-CH_2CHO$

C



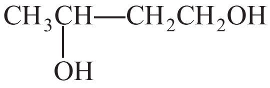
$CH_3-\underset{Cl}{CH}-\underset{Cl}{CH}-CHO$

D



$CH_3\underset{Cl}{CH}-CH_2-CH_2OH$

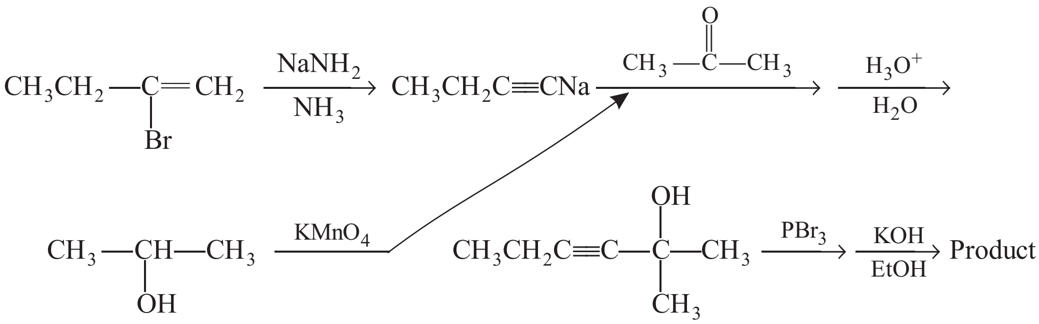
E



$CH_3\underset{OH}{CH}-CH_2CH_2OH$

F

1091. (a)

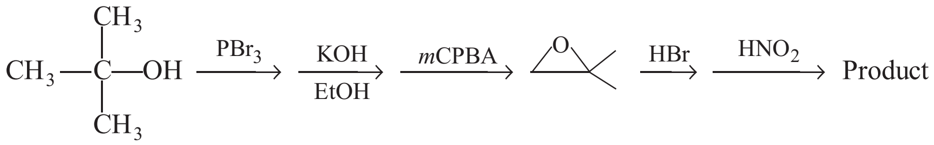


$CH_3CH_2-\underset{Br}{C}=CH_2 \xrightarrow[NH_3]{NaNH_2} CH_3CH_2C\equiv CNa \xrightarrow{CH_3-\overset{O}{\overset{\|}{C}}-CH_3} \xrightarrow[H_2O]{H_3O^+}$

$CH_3-\underset{OH}{CH}-CH_3 \xrightarrow{KMnO_4}$

$CH_3CH_2C\equiv C-\overset{OH}{\underset{CH_3}{C}}-CH_3 \xrightarrow{PBr_3} \xrightarrow[EtOH]{KOH}$ Product

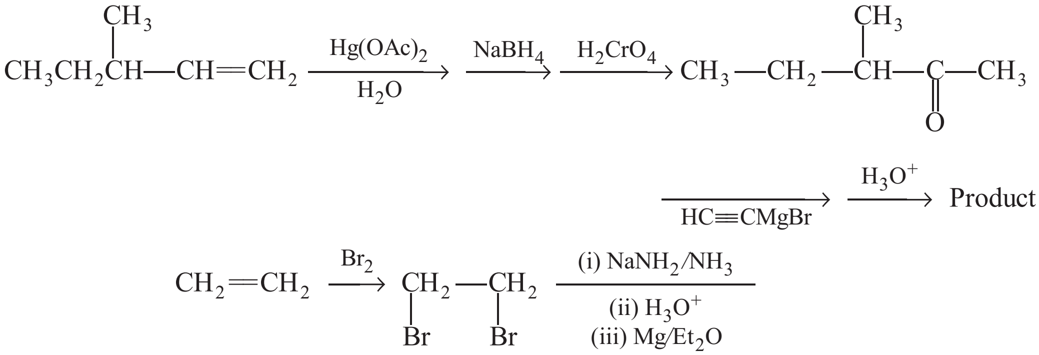
(b)



$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH \xrightarrow{PBr_3} \xrightarrow[EtOH]{KOH} \xrightarrow{mCPBA}$

$\xrightarrow{HBr} \xrightarrow{HNO_2}$ Product

(c)

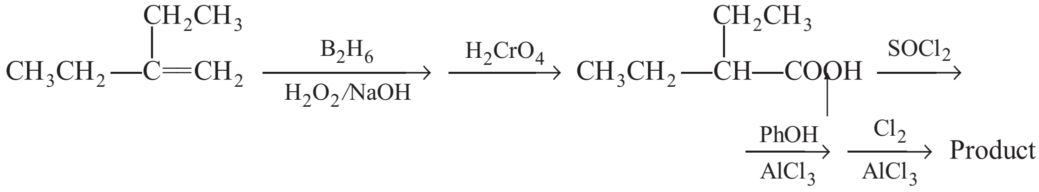


$CH_3CH_2\overset{CH_3}{CH}-CH=CH_2 \xrightarrow[H_2O]{Hg(OAc)_2} \xrightarrow{NaBH_4} \xrightarrow{H_2CrO_4} CH_3-CH_2-\overset{CH_3}{CH}-\underset{O}{\underset{\|}{C}}-CH_3$

$\xrightarrow[HC\equiv CMgBr]{} \xrightarrow{H_3O^+}$ Product

$CH_2=CH_2 \xrightarrow{Br_2} \underset{Br}{CH_2}-\underset{Br}{CH_2} \xrightarrow[\text{(ii) } H_3O^+ \text{ (iii) } Mg/Et_2O]{\text{(i) } NaNH_2/NH_3}$

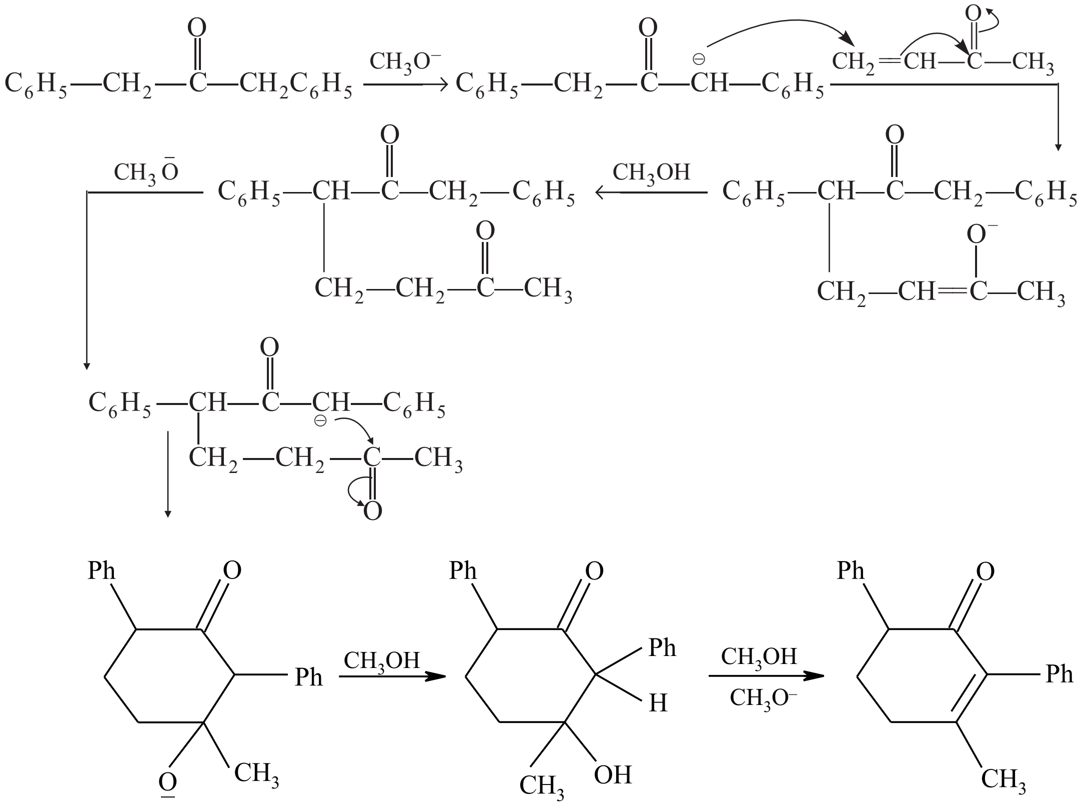
(d)



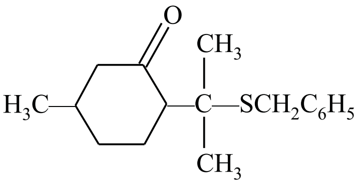
$CH_3CH_2-\overset{CH_2CH_3}{C}=CH_2 \xrightarrow[H_2O_2/NaOH]{B_2H_6} \xrightarrow{H_2CrO_4} CH_3CH_2-\overset{CH_2CH_3}{CH}-COOH \xrightarrow{SOCl_2}$

$\xrightarrow[AlCl_3]{PhOH} \xrightarrow[AlCl_3]{Cl_2}$ Product

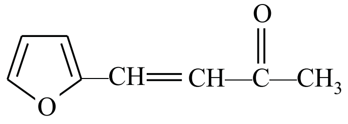
1092.



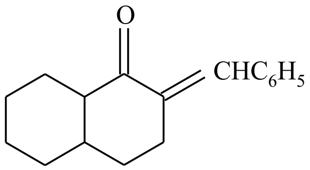
1093. (a)



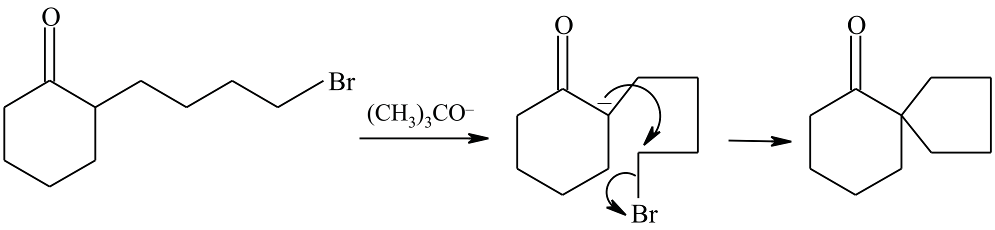
(b)



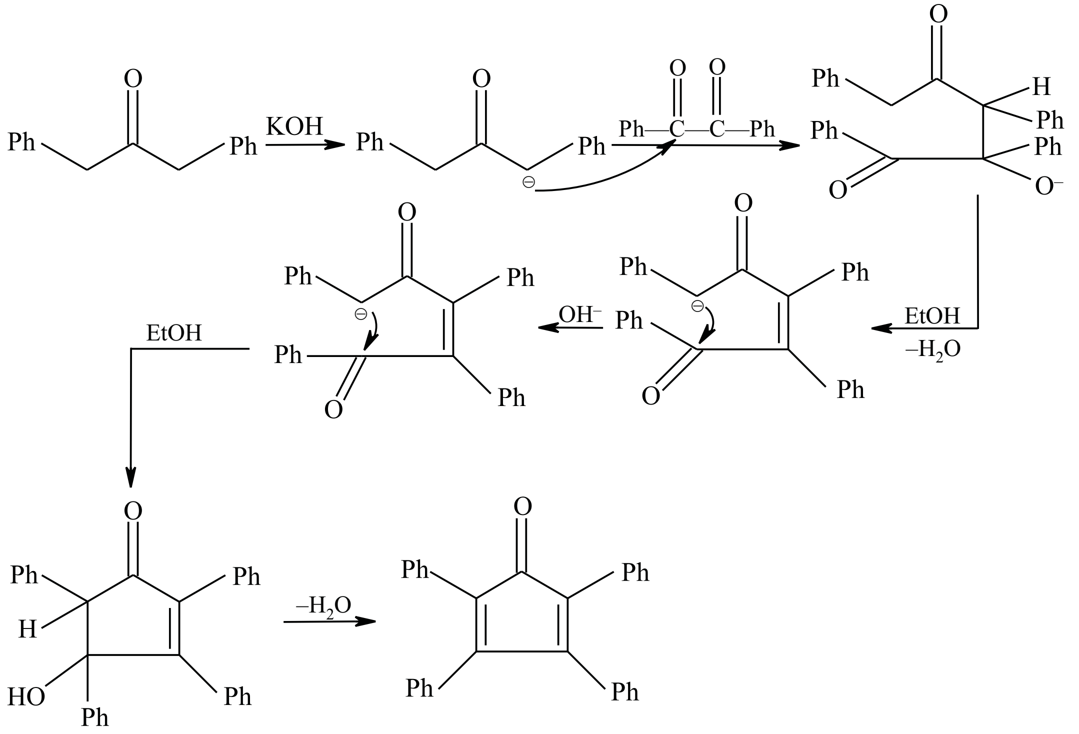
(c)



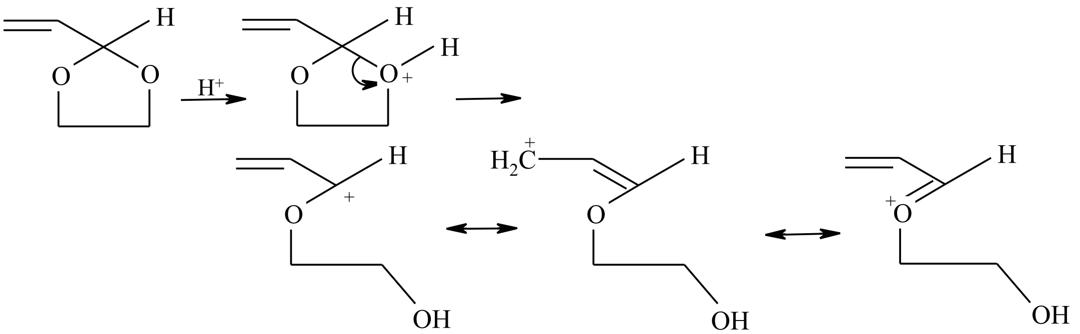
1094. (a)



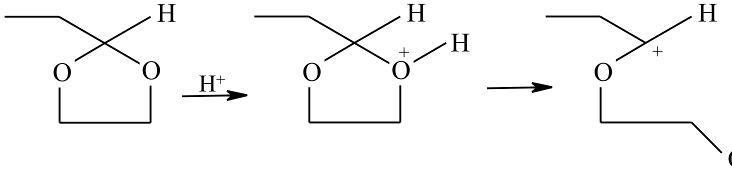
(b)



1095. Difference in reactivity towards hydrolysis reaction lies in the stability of carbocation intermediate as:

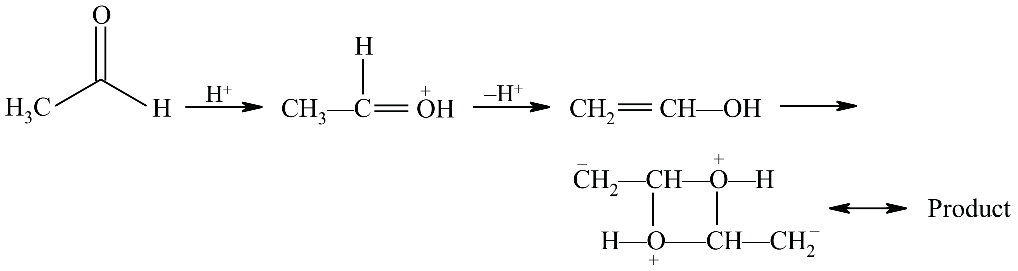


Allylic group provide extrastability due to resonance



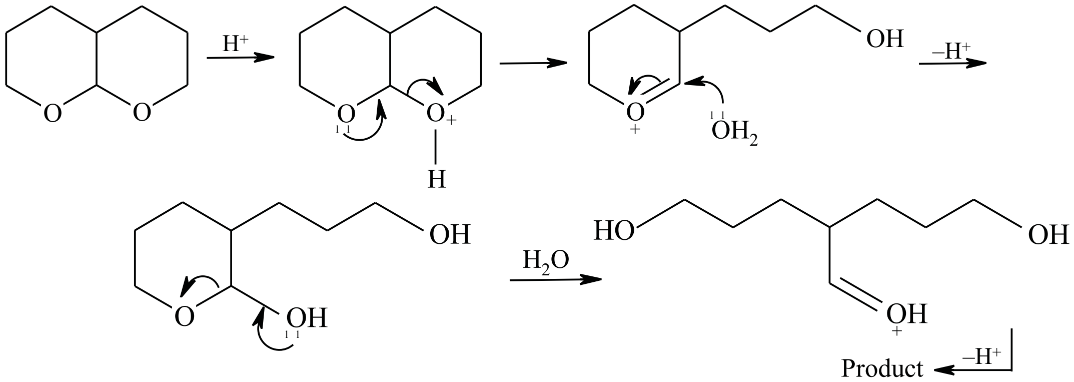
not stabilized by allylic resonance

1096.

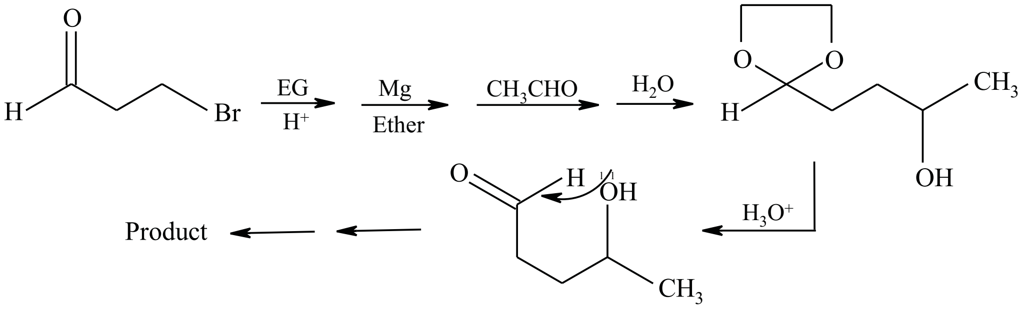


1097. II < III < I.

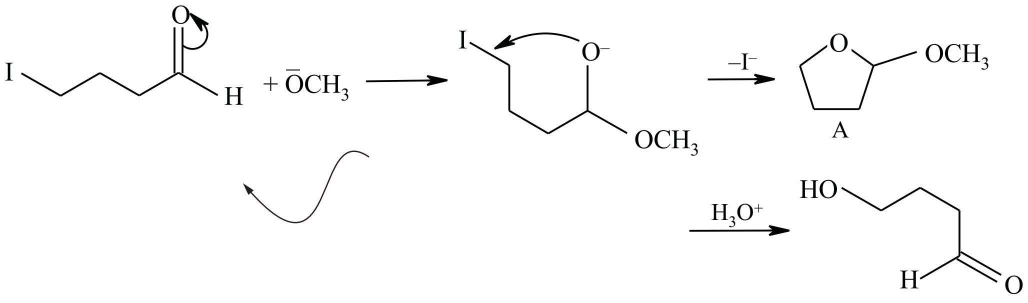
1098.



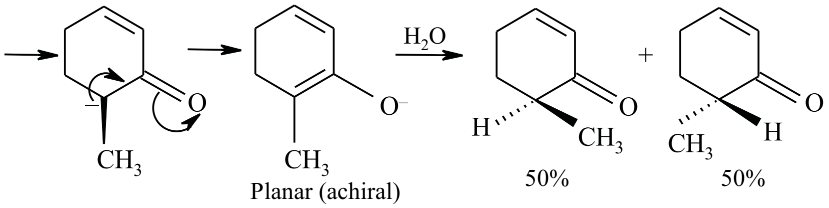
1099.



1100.

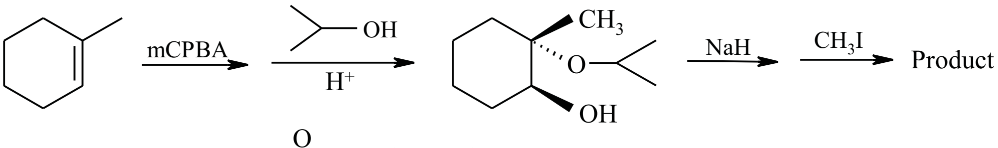


1101. Compound + EtO$^-$

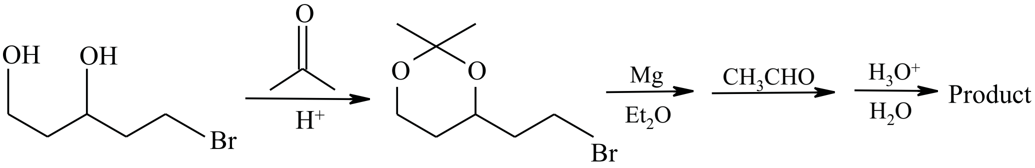


1102. (a) $PhCHO \xrightarrow{MeMgBr} \xrightarrow{H_3O^+} \xrightarrow[CH_2Cl_2]{PCC}$ Product

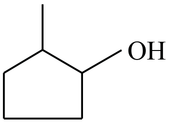
(b)

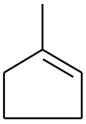


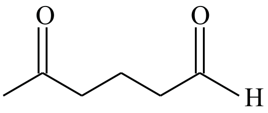
(c)

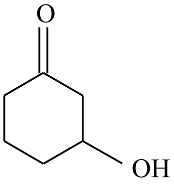


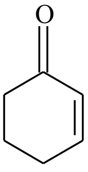
1103.

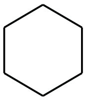

A


B

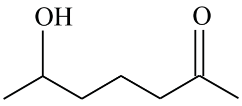

C

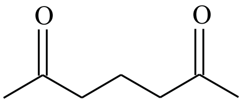

D

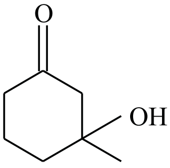

E

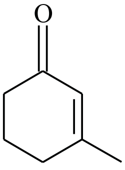

F

1104.

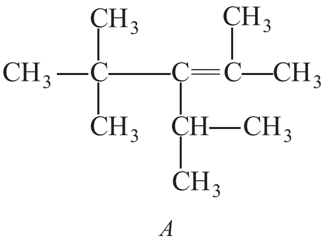

A


B

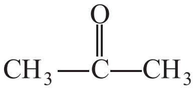

C


D

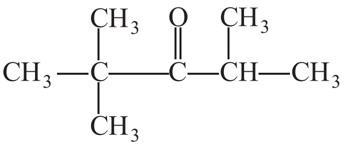
1105.


$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-\underset{\displaystyle \underset{\displaystyle CH_3}{CH}-CH_3}{C}=\overset{\displaystyle CH_3}{C}-CH_3$

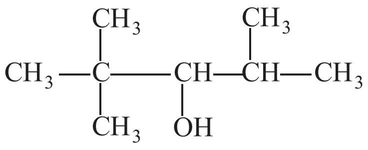
A


$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$

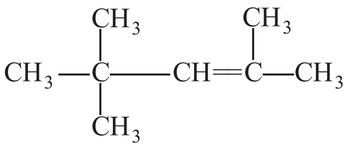
B


$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-\overset{\displaystyle CH_3}{CH}-CH_3$

C

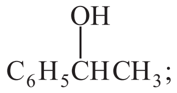
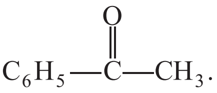

$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{OH}{CH}-\overset{CH_3}{CH}-CH_3$

D


$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=\overset{CH_3}{C}-CH_3$

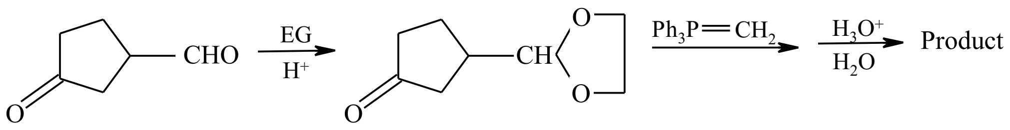
E

1106. *A*: $C_6H_5CH_2CH_3$; *B*:  $C_6H_5\overset{Br}{C}HCH_3$; *C*: $C_6H_5CH=CH_2$;

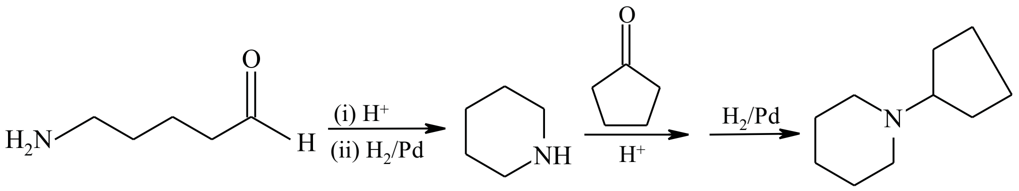
D: C_6H_5CHO; *E*:  $C_6H_5\overset{OH}{C}HCH_3$; *F*:  $C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3$.

1107. $ClCH_2- > H > (CH_3)_2CH- > Ph$

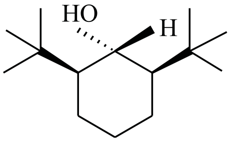
1108. (a)



(b)

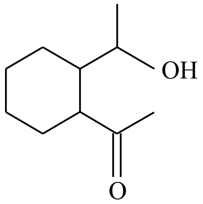


1109. (a)

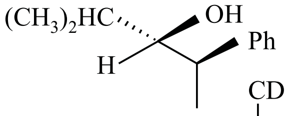


(Racemic)

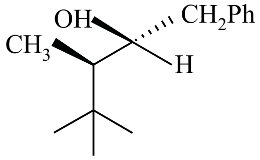
(b)



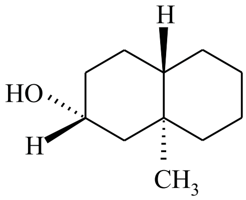
(c)



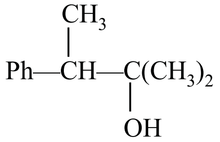
(d)



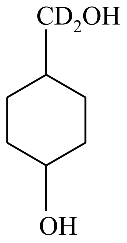
(e)



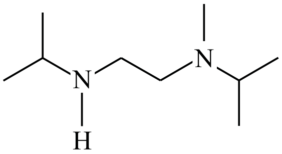
(f)


$Ph-\overset{CH_3}{CH}-\underset{OH}{C}(CH_3)_2$

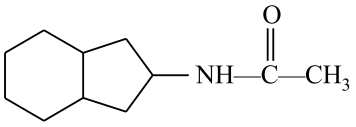
(g)



1110. (a)

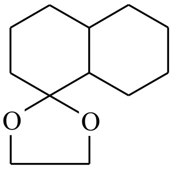


(b)

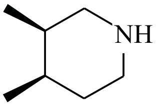


(c) $PhCH_2MgBr/Et_2O$, H_3O^+, PCC/CH_2Cl_2

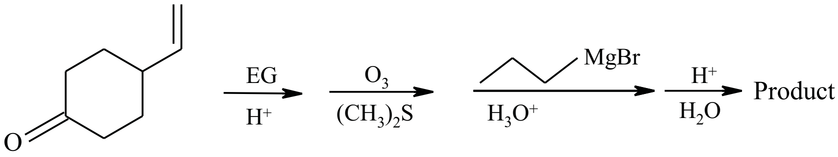
(d)



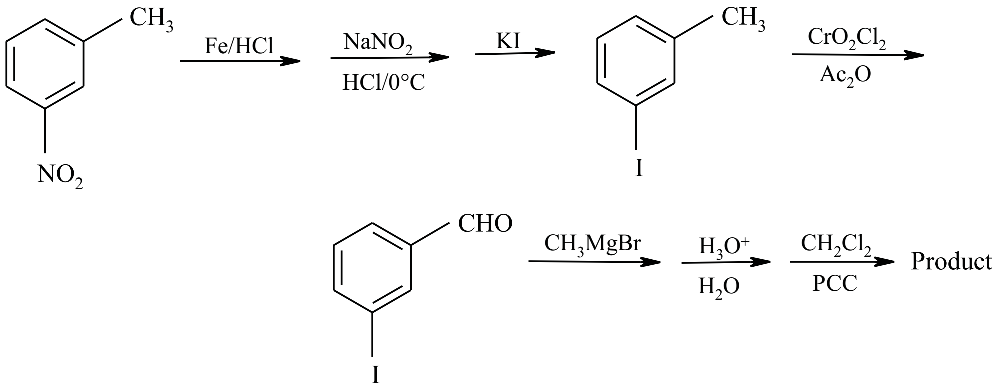
(e)



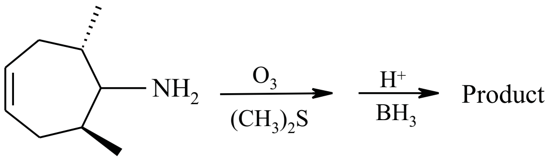
1111. (a)



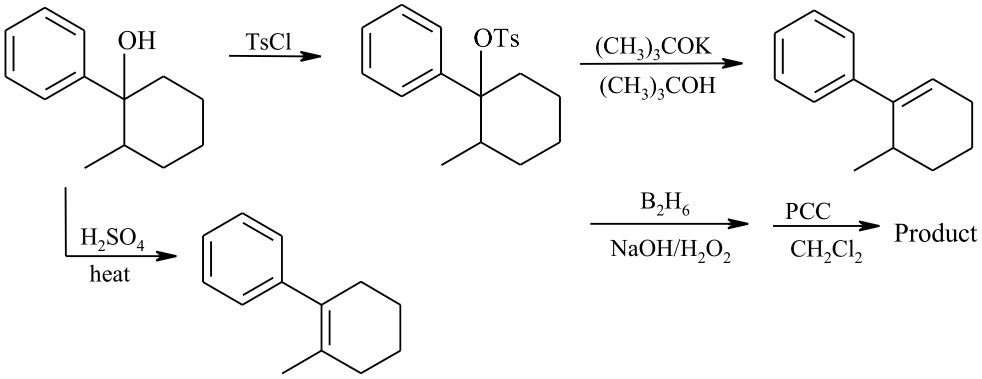
(b)



(c)

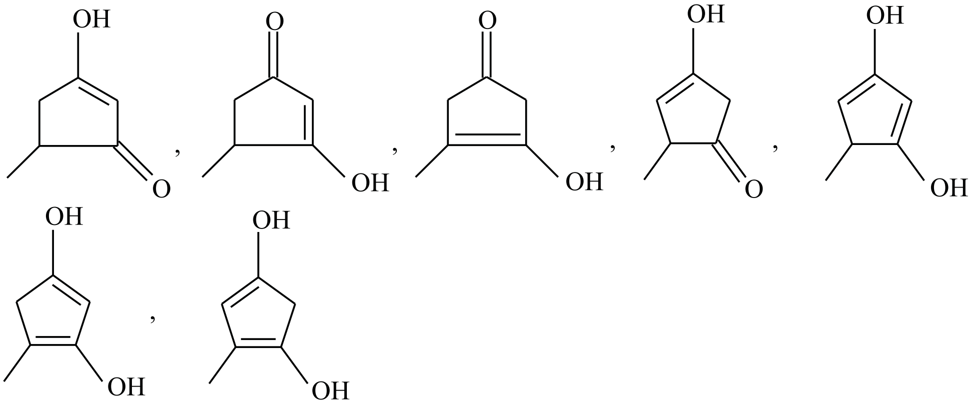


1112.

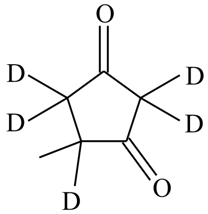


Major product
(not required)

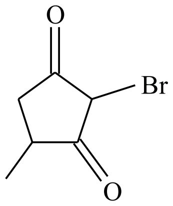
1113. (a)



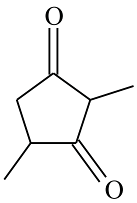
(b) (i)



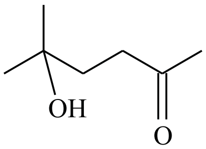
(ii)



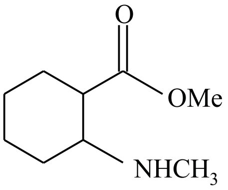
(iii)



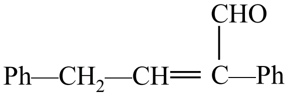
1114. (a)



(b)

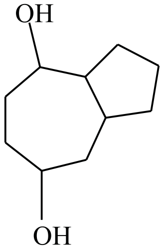


(c)

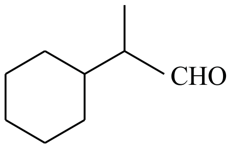


$\text{Ph—CH}_2\text{—CH}{=}\overset{\text{CHO}}{\overset{|}{\text{C}}}\text{—Ph}$

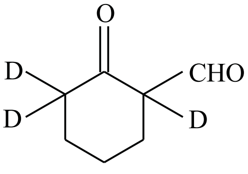
(d)



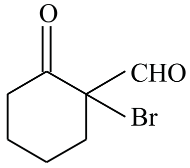
(e)



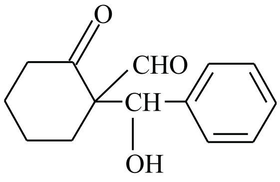
1115. (a)



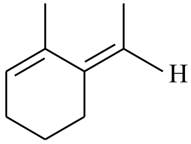
(b)



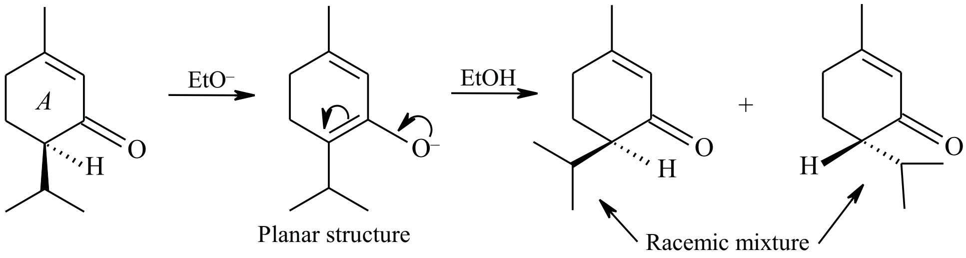
(c)



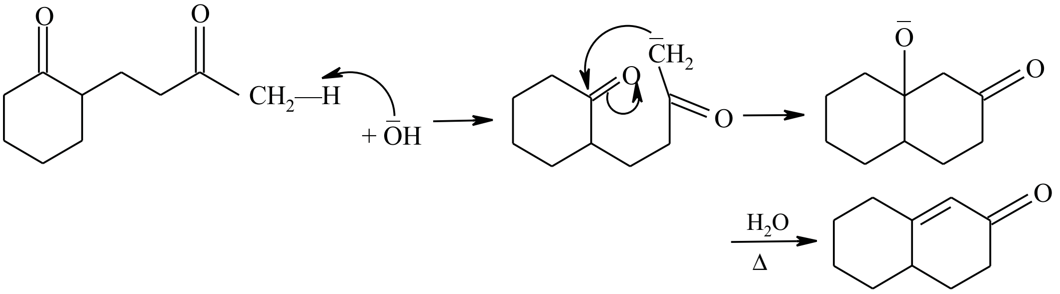
(d)



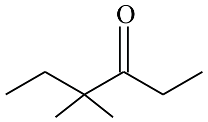
1116. A has enolizable hydrogen bonded to chiral carbon, therefore, it acquire planarity at chiral carbon when converted to its enol form. Due to planarity at chiral carbon in the enol form, it forms both enantiomers in equal amount when converted back to keto form. No such enolization is possible with *B* since it has no α – H at chiral carbon and hence, its optical activity is retained even in aqueous alkaline solution.



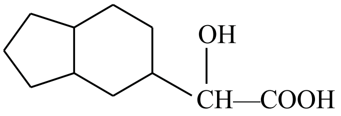
1117.



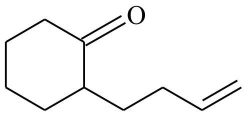
1118. (a)



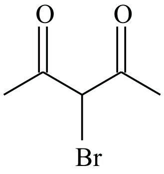
(b)



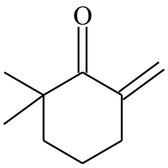
(c)



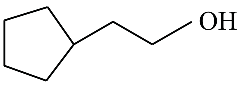
(d)



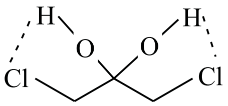
(e)



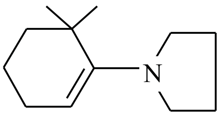
(f)



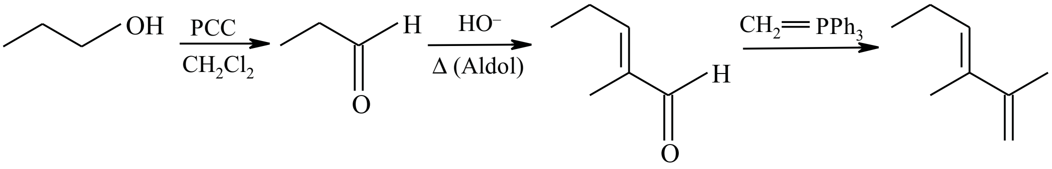
(g)



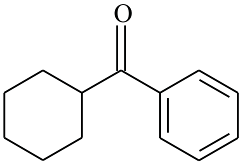
(h)



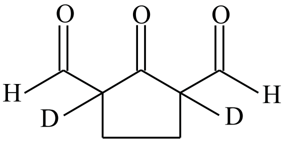
1119.



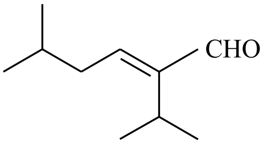
1120. (a)



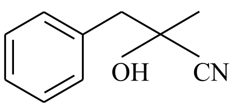
(b)



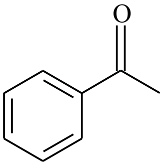
(c)



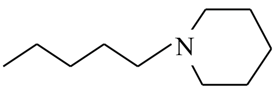
(d)



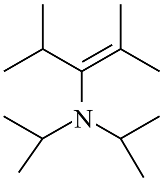
(e)



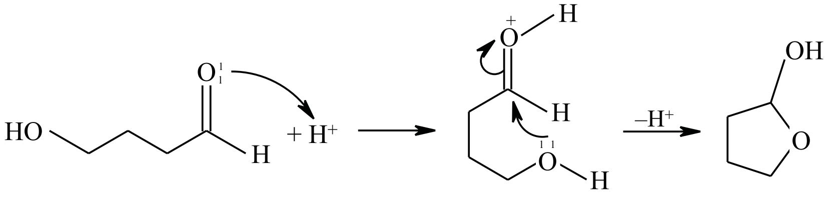
(f)

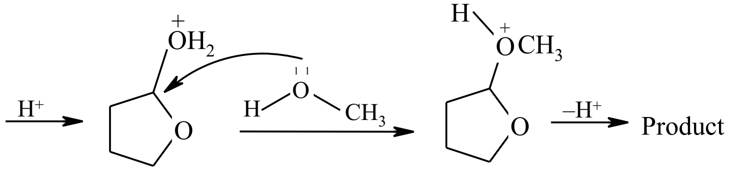


(g)

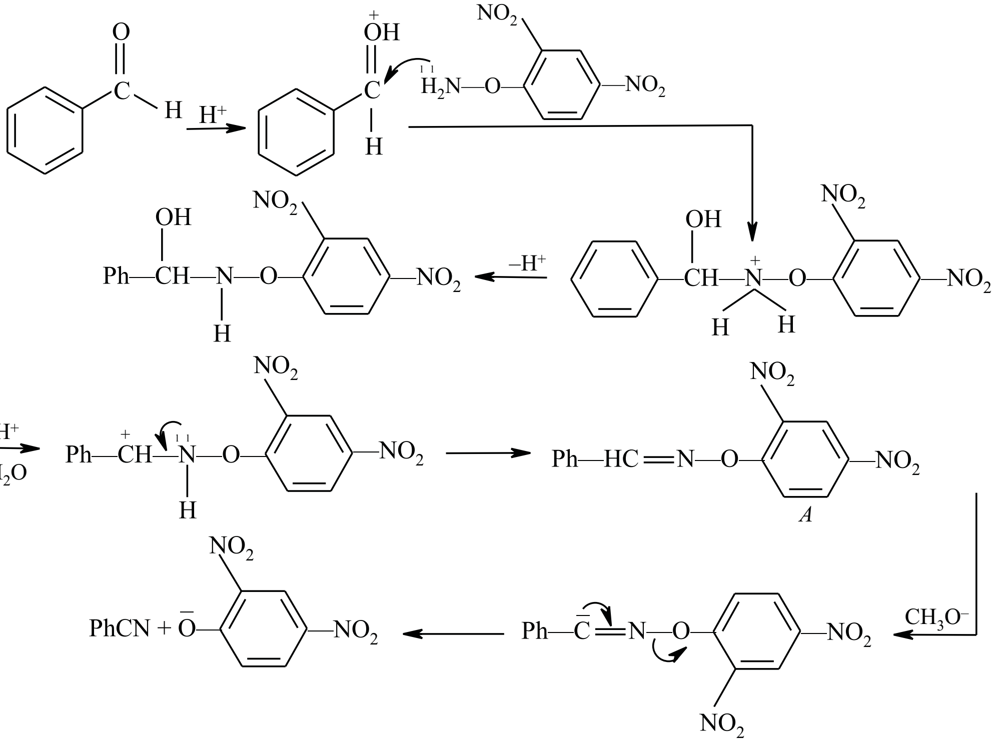


1121. (a)





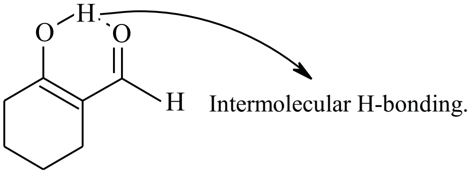
(c)



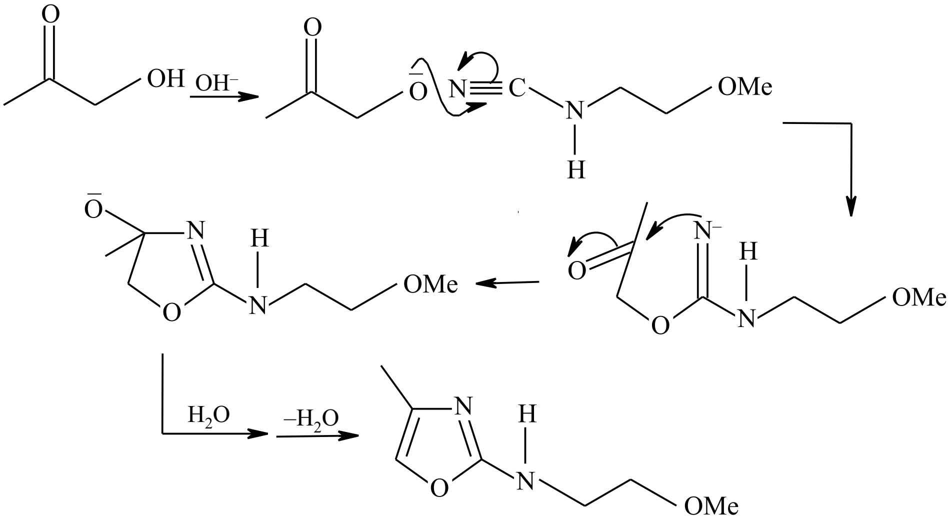
1122. High proportion of enol in the equilibrium mixture of compound II can be rationalized by two factors:

(a) It is conjugated system.

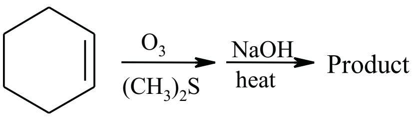
(b) It forms a six membered cyclic ring via intermolecular H-bonding as:



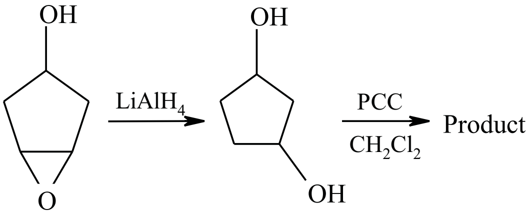
1123.



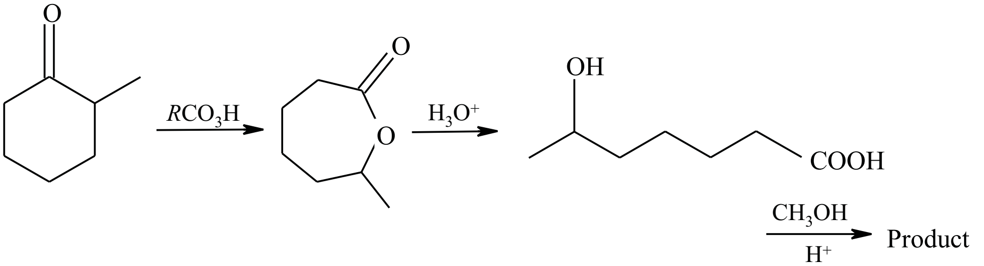
1124. (a)



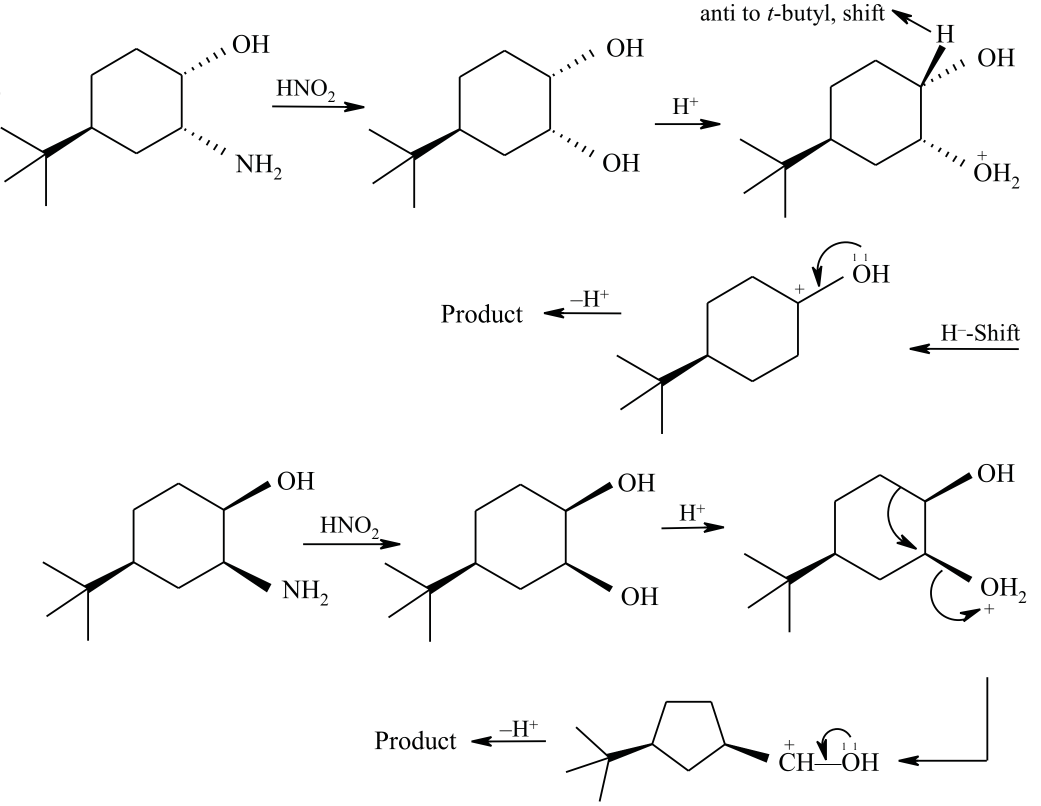
(b)



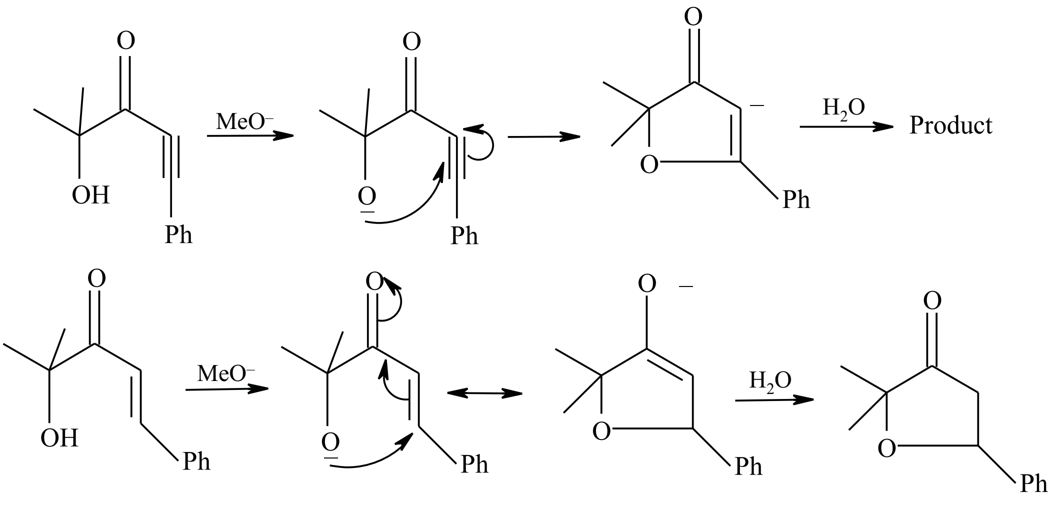
(c)



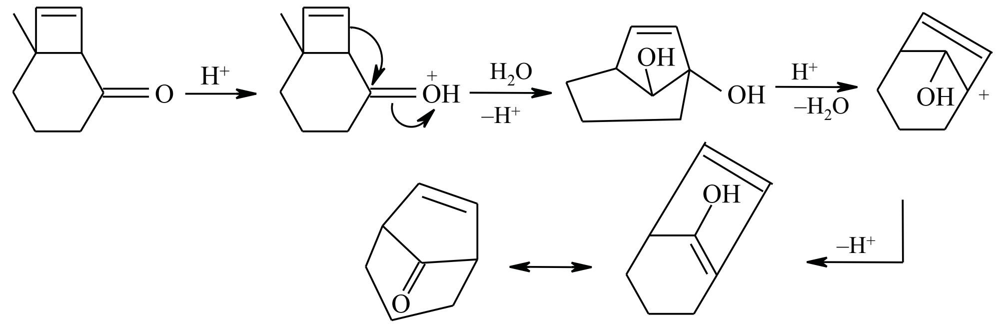
1125. (a)


anti to *t*-butyl, shift
H
OH
NH$_2$
HNO$_2$
H$^+$
$\overset{+}{O}H_2$
H$^-$-Shift
Product
–H$^+$
$\overset{+}{C}H$—OH

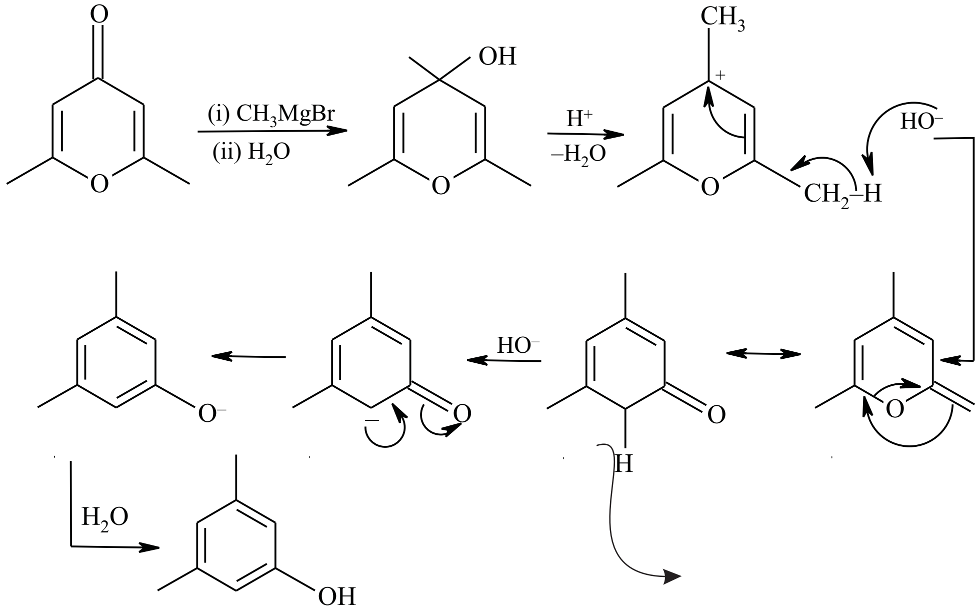
(b)


O
OH
Ph
MeO$^-$
H$_2$O
Product
–

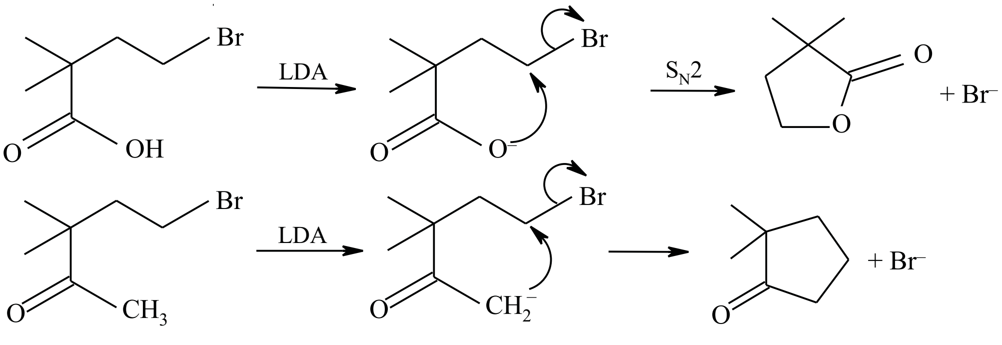
1126. (a)


O
H+
+
OH
H2O
–H+
OH
OH
H+
–H2O
OH
+
–H+
OH
O

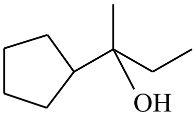
(b)


O
O
(i) CH3MgBr
(ii) H2O
OH
O
H+
–H2O
CH3
+
O
CH2–H
HO–
O
O
H
O
HO–
–
O
O–
H2O
OH

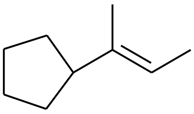
1127.


Br
O
OH
LDA
Br
O
O–
SN2
O
O
+ Br–
Br
O
CH3
LDA
Br
O
CH2–
O
+ Br–

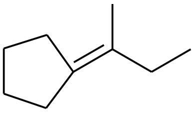
1128.



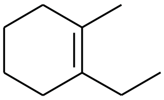
A



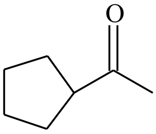
B



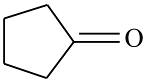
C



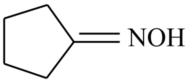
D



E

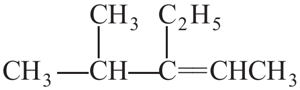


F



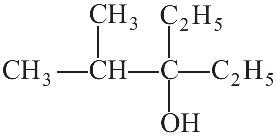
G

1129.



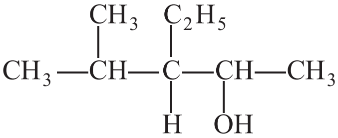
$CH_3-CH(CH_3)-C(C_2H_5)=CHCH_3$

A



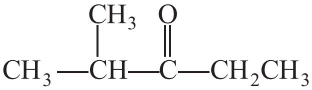
$CH_3-CH(CH_3)-C(C_2H_5)(OH)-C_2H_5$

B



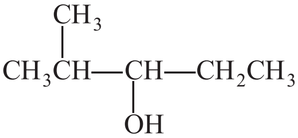
$CH_3-CH(CH_3)-CH(C_2H_5)-CH(OH)-CH_3$

C



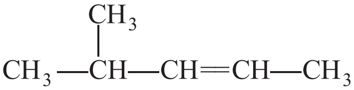
$CH_3-CH(CH_3)-C(=O)-CH_2CH_3$

D



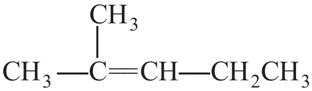
$CH_3CH(CH_3)-CH(OH)-CH_2CH_3$

E



$CH_3-CH(CH_3)-CH=CH-CH_3$

F



$CH_3-C(CH_3)=CH-CH_2CH_3$

G