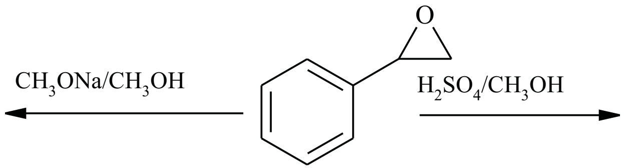
ALCOHOLS AND ETHERS

PROBLEM 908 Why does ethylene oxide react readily with nucleophiles such as ammonia, whereas THF is inert to nucleophilic attack by ammonia?

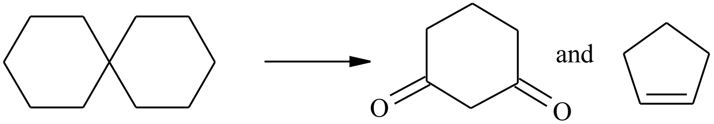
PROBLEM 909 Give the products and mechanism of each of the reaction shown below:



PROBLEM 910 Bring about the following conversion from the indicated starting materials:

(a)

(b)



PROBLEM 911 An optically inactive organic compound *A*($C_7H_{11}Br$) is treated with Mg in ether to give *B*($C_7H_{11}MgBr$), which react violently with D_2O to give methylcyclohexene with deuterium atom on the methyl group (*C*). Reaction of *B* with acetone followed by hydrolysis gives *D*($C_{10}H_{18}O$). Heating *D* with concentrated sulphuric acid gives *E*($C_{10}H_{16}$). Determine structure of *A* to *E*.

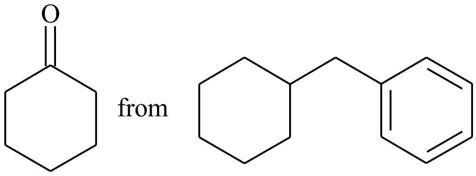
PROBLEM 912 When ethanol is heated with conc. H_2SO_4 at 140°C, diethyl ether is obtained, whereas at 180°C ethylene is the major product. Suggest reason.

PROBLEM 913 Compound *A* is an optically active alcohol. Treatment with chromic acid convert *A* into a ketone *B*. In a separate reaction, *A* is treated with PBr_3, converting it into *C*. *C* on reaction with Mg is added to *B* to yield *D*, which after hydrolysis gives 3,4-dimethyl-3-hexanol. Identify *A* to *D*.

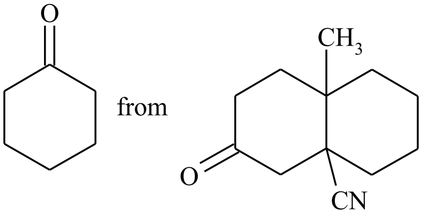
PROBLEM 914 A compound '*A*' $C_{10}H_{14}O$ exist in diastereomeric form, liberates a gas on reaction with CH_3MgBr. Treatment of *A* with aqueous HBr gives *B*($C_{10}H_{13}Br$), which exist in enantiomeric forms. *B* on treatment with alcoholic solution of KOH gives a compound *C*. Ozonolysis of *C* followed by work-up with H_2O_2 gives a compound *D* and acetophenone. Identify *A* to *D*.

PROBLEM 915 Synthesize the followings from the indicated starting materials:

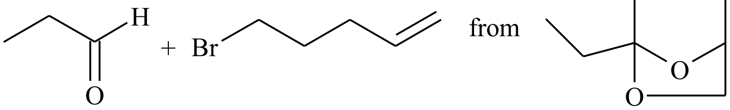
(a)

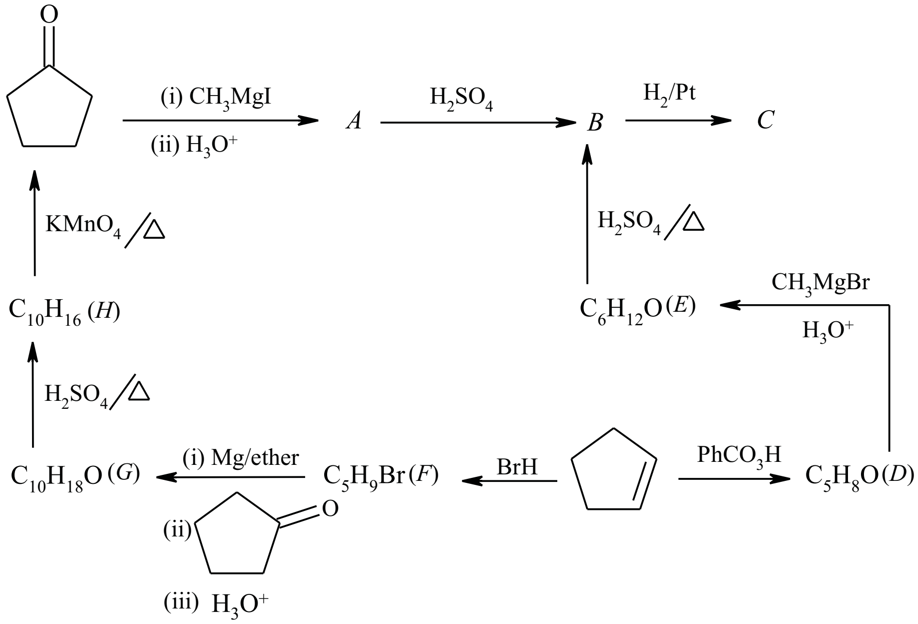


(b)

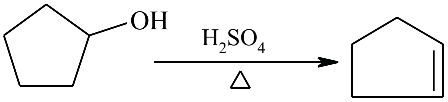


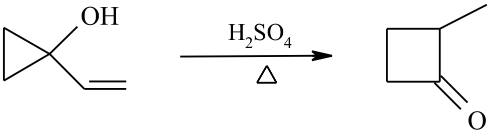
(c)

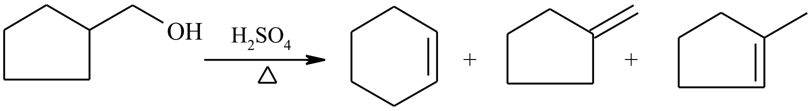


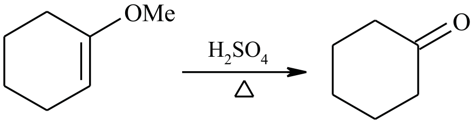


Problem 916 Determine the structure of compound *A* through *H*

(a)


(b)


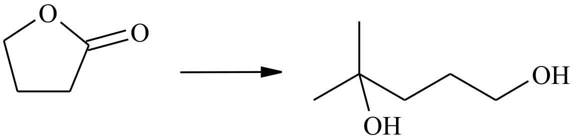
(c)


(d)


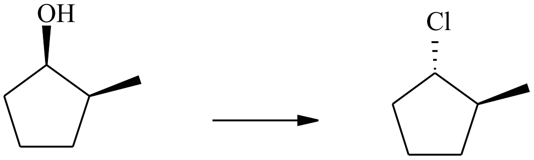
Problem 917 Propose mechanism of the following reactions:

Problem 918 Convert: (a) 2-methyl-2-butene to $(CH_3)_2C(OH)CHDCH_3$

(b) Synthesize 2,5-dimethyl-3-hexanone using alcohol containing not more than four carbon.

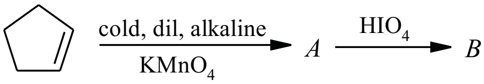
(d)


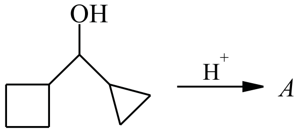
(c) C_6H_5Br to $(C_6H_5)_2C(OH)CH_3$ using any additional compound containing not more than three carbon.



Problem 919 (a) Convert:

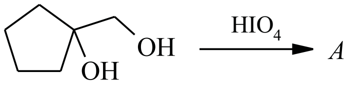
(b) Cyclohexyl bromide when treated with potassium ethoxide, the major product is a cyclohexene whereas when ethyl bromide is treated with potassium salt of hexanol, the major product is ethyl-cyclohexyl ether. Explain the difference.

(a)


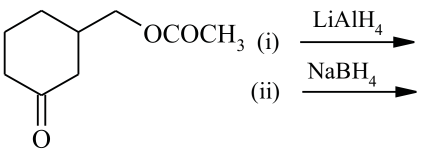
(b)


PROBLEM 920 Predict major product:

(c)



(d)



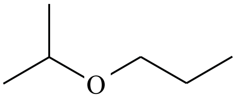
PROBLEM 921 An optically active compound $A(C_{10}H_{17}Br)$ when treated with alcoholic solution of KOH yield two compound *B* and *C* of molecular formula $C_{10}H_{16}$ of which '*B*' is optically active. Ozonolysis of *A* followed by treatment with Zn-H_2O gives acetone as one of the product. Hydrogenation of either *B* or *C* yield 4-isopropyl-1-methyl cyclohexane, identify *A,B* and *C*.

PROBLEM 922 When *cis*-2,3-dimethyl oxirane is treated with water containing a trace of $HClO_4$, a racemic mixture of 2,3-butandiol is formed, trans-2,3-dimethyl oxirane give meso-2,3-butandiol under identical conditions. Write mechanism for these reactions.

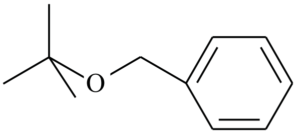
PROBLEM 923 When 3-methyl-2-pentanol is treated with $ZnCl_2$ in concentrated solution of HCl, a mixture of chloroalkanes forms, including chiefly 2-chloro-3-methylpentane, and 3-chloro-3-methyl pentane. When 3-methyl-2-pentanol is treated with thionyl chloride in pyridine, only 2-chloro-3-methyl pentane is formed. Write detailed mechanism that accounts for the observation.

PROBLEM 924 Synthesize the following by Williamson's method, choosing alkoxide anion and alkyl halide that will give the best yield:

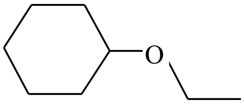
(a)



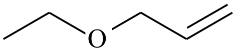
(b)



(c)



(d)



PROBLEM 925 Treatment of 3-methyl-2-butanol with HCl, only a trace of 2-chloro-3-methyl butane is formed. An isomeric product was isolated in 97% yield. Suggest a reasonable structure of this product.

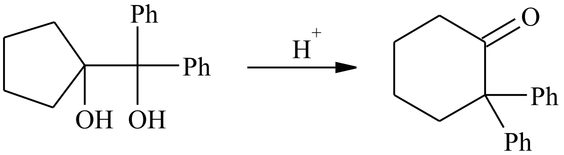
PROBLEM 926 Suggest reasonable explanation for the following observations:

(a) The first order rate constant for the solvolysis of $(CH_3)_2C{=}CHCH_2Cl$ in ethanol is 600 times greater than that of allylchloride.

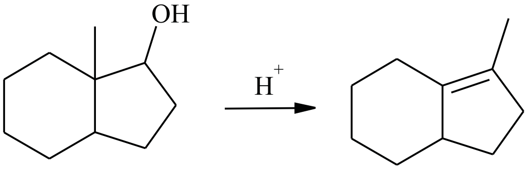
(b) After a solution of 3-buten-2-ol in aqueous H_2SO_4 be allowed to stand for a week, it was found to contain both 3-bute-2-ol and 2-buten-1-ol.

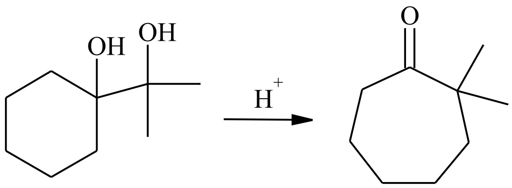
PROBLEM 927 Propose mechanism of the following reactions:

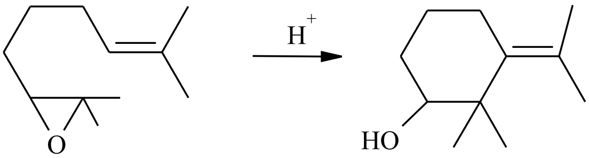
(a)



(b)

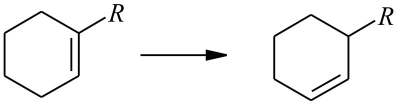


(c) 

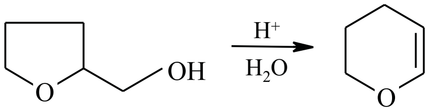
(d) 

Problem 928 A compound $X(C_{14}H_{14}O)$ on mild oxidation yields $C_{14}H_{12}O(Y)$. If *X* is treated with a dehydrating agent, it loses a molecule of water and resulting product on vigorous oxidation yields two molecules of benzoic acid. Give structure of *X* and *Y*.

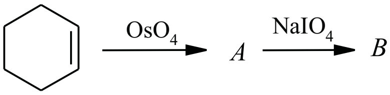
Problem 929 Convert:

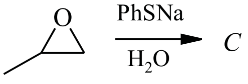
(a) 

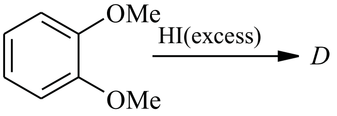
(b) Propose mechanism:

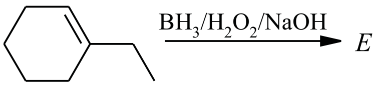


(c) Write products:

(i) 

(ii) 

(iii) 

(iv) 

Problem 930 Two optically active compounds *A* and *B* have same molecular formula $C_9H_{12}O$ and do not decolourise bromine water solution. Both *A* and *B* are oxidised by $KMnO_4$ to give benzoic acid and react with Na to give a colourless, odourless gas. Compound *A* gives yellow precipitate with I_2/OH^- whereas *B* does not. Also *A* loses optical activity on treatment with PCC while *B* retain optical activity on similar treatment. Deduce the structure of *A* and *B*.

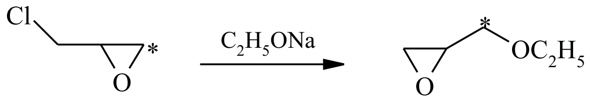
Problem 931 Compounds *A, B* and *C* are isomeric alcohols with formula $C_5H_{12}O$. *A* and *B* reacts with chromic acid solution, *B* giving an acid *D*. The three isomeric alcohol reacts with HBr with decreasing relative rates $C > A >> B$, all giving same $C_5H_{11}Br$(*E*). in varying yields. *A* alone can be oxidised by I_2/OH^- to *F*. Write structure of *A* to *F*.

Problem 932 C_7H_{14} (*A*) decolourises Br_2 in CCl_4 and reacts with $Hg(OAc)_2$ in THF-H_2O followed by reduction with $NaBH_4$ to produce a resolvable compound *B*. *A* undergoes reductive ozonolysis to give the same compound *C* as obtained by oxidation of 3-hexanol with $KMnO_4$. Identify *A*, *B* and *C*.

Problem 933 An organic compound *A* (C_7H_{14}) reacts with BH_3-THF and then with H_2O_2/OH^- to give a chiral *B*. Oxidation of *B* with $KMnO_4$ affords a chiral carboxylic acid *C*. Ozonolysis of *A* followed by work-up with $(CH_3)_2S$ produces $C_6H_{12}O$(*D*) as one product. *D* on treatment with $LiAlH_4$ produces another compound *E*($C_6H_{14}O$) which is optically active. *E* on heating with conc.H_2SO_4 produces *F*(C_6H_{12}) as major product. *F* on ozonolysis followed by work-up with DMS produces acetone as one product. Identify *A* to *F*.

Problem 934 Treating 3,3-dimethyl-1-butene with dilute sulphuric acid is largely unsuccessful as a method of preparation of 3,3-dimethyl-2-butanol because an isomeric compound is major product. What is the isomeric product and how it is formed?

Problem 935 When C_2H_5ONa reacts with 1-(chloromethyl) oxirane, labelled with ^{14}C as shown by astric in (*) I, the major product is an epoxide bearing the labelled carbon as shown in II. Provide mechanism to explain this fact.

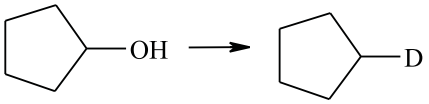


I II

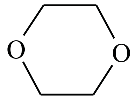
Problem 936 An unknown organic compound *A*($C_4H_{10}O_2$) reacts with sodium metal to liberate one mole of hydrogen gas per mole of *A*. Although *A* is inert towards periodic acid, it does reacts with CrO_3 to form *B*($C_4H_6O_3$). Identify *A* and *B*.

Problem 937 Convert:

(a)



(b) $CH_2{=}CH_2 \longrightarrow$



Problem 938 Synthesize the following compounds starting with isobutane:

- (a) *ter*-butyl bromide
- (b) 2-methyl propene
- (c) *iso* -butyl bromide
- (d) *iso* butyl methyl ether
- (e) $(CH_3)_2CHCH_2OCOCH_3$
- (f) $(CH_3)_2CHCH_2CN$

Problem 939 A neutral compound *A* has molecular formula $C_{10}H_{16}O_2$. *A* does not decolourise aqueous solution of Br_2 and evolve no gas on treatment with Na. *A* on acidic hydrolysis produces two compounds *B*(C_4H_8O) and *C*($C_6H_{10}O_2$). *B* on treatment with $SOCl_2$ gives *D*(C_4H_7Cl) which on further treatment with aqueous solution of KCN followed by hydrolysis of product yielded *E*($C_5H_8O_2$). *E* on reducing with $LiAlH_4$ gives *F*($C_5H_{10}O$) which on heating with concentrated sulphuric acid solution yields *G*(C_5H_8). *G* on treatment with HCl yields *H*(C_5H_9Cl). *C* on heating with soda lime gives *I*(C_5H_{10}). *I* on monochlorination with $Cl_2/h\nu$ give H as sole product. Identify *A* to *I* describing mechanism of their formation in each step.

PROBLEM 940 An organic compound *A* has molecular formula $C_6H_{10}O$ and known to decolourise aqueous solution of bromine. *A* is also resolvable and on catalytic hydrogenation with H_2/Pt yields *B*($C_6H_{12}O$) which is optically inactive. Also *B* does not change the orange colour of an acidic solution of dichromate ion. *B* on heating with concentrated sulphuric acid solution yields *C*(C_6H_{10}) which on reductive ozonolysis gives the following compound:

$$H-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

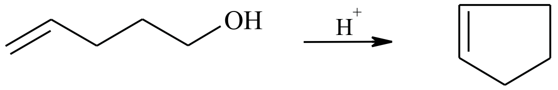
Deduce structures of *A*, *B* and *C*.

PROBLEM 941 An organic compound *A*($C_5H_8O_2$) does not decolourise aqueous solution of bromine and evolve no gas on treatment with CH_3MgBr. *A* on reaction with concentrated solution of HI produced methylene iodide and an another compound *B*($C_4H_6I_2$). *B* on heating with sodium metal produced *C*(C_4H_8) which on monochlorination gave a single isomeric product C_4H_7Cl. Deduce structures of *A*, *B* and *C*.

PROBLEM 942 Starting with 2-methyl propene and using any other needed reagents, synthesize the following compounds:

(a) $(CH_3)_2CHCH_2OH$
(b) $(CH_3)_2CDCH_2T$
(c) $(CH_3)_2CHCH_2T$
(d) $(CH_3)_2CHCH_2OCH_2CH_3$

PROBLEM 943 Propose mechanism:



PROBLEM 944 Coniferyl alcohol(*X*) is not soluble in water or $NaHCO_3$, has molecular formula $C_{10}H_{12}O_3$. A solution of Br_2 in CCl_4 is decolourised by *X* forming $C_{10}H_{12}O_3Br_2$(*A*). Upon reductive ozonolysis of *X*, 4-hydroxy-3-methoxy benzaldehyde and *B*($C_2H_4O_2$) are produced. *X* reacts with benzoylchloride C_6H_5COCl in presence of a base to form *C*($C_{24}H_{20}O_5$). This product rapidly decolourises aqueous solution of $KMnO_4$ and is insoluble in NaOH. *X* reacts with cold HBr to form *D*($C_{10}H_{11}O_2Br$). *X* reacts with HI to produce *E*($C_9H_9O_2I$) and CH_3I. In aqueous base, CH_3I and *X* forms *F*($C_{11}H_{14}O_3$), which is not soluble in strong base but decolourises aqueous solution of Br_2. Deduce structures of *X* and *A* to *F*.

PROBLEM 945 An optically active organic compound *A* has molecular formula $C_7H_{12}O_2$ and does not decolourise cold, dilute and alkaline solution of potassium permanganate. *A* on treatment with concentrated HCl gives CH_2Cl_2 and *B*($C_6H_{10}Cl_2$). *B* on treatment with aqueous solution of KI gives *C*(C_6H_{10}) which decolourise bromine water. *C* on treatment with acidic solution of $KMnO_4$ gives 2-methyl pentan-1,5-dioic acid. Deduce structures of *A* to *C*.

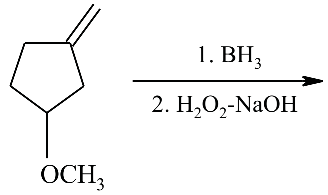
PROBLEM 946 An optically active organic compound *A* has molecular formula $C_9H_{18}O$ which neither change colour of Bayer's reagent nor of acidic dichromate solution, but evolve a colourless gas on heating with Na-metal. *A* on dehydration with conc.H_2SO_4 produces *B*(C_9H_{16}) which exist in two stereomeric forms. Ozonolysis of *B* followed by work-up with Zn-H_2O produced ethanal and

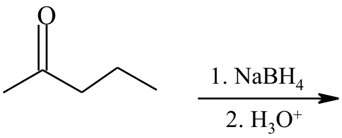
C($C_7H_{12}O$). *C* on treatment with $LiAlH_4$ produced *D*($C_7H_{14}O$) which is enantiomeric and change the colour of acidic dichromate solution from orange to blue-green. *D* on dehydration produced E(C_7H_{12}) which on ozonolysis followed by hydrolysis of product in presence of Zn produced cyclopentanone. Deduce structures of *A* to *E* showing stereochemical structures of *B*.

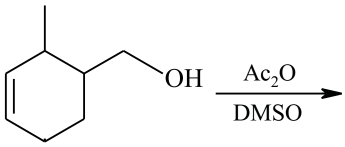
PROBLEM 947 An organic compound *A*($C_{11}H_{22}$) when ozonolyzed yields *B*($C_6H_{12}O$) and *C*($C_5H_{10}O$). Mild oxidation of *C* yields *D*($C_5H_{10}O_2$). Compound *B* reacts with NaOCl to yield chloroform and sodium salt of *D*. Reduction of *B* with $LiAlH_4$ yields *E*($C_6H_{14}O$). Dehydration of *E* gives *F*(C_6H_{12}). Ozonolysis of *F* yields *G*(C_2H_4O) and *H*(C_4H_8O). Compound *H* does not react with Tollen's reagent or Fehling solution but does form an oxime and semicarbazide. Write structures of *A* to *H* describing the reaction involved.

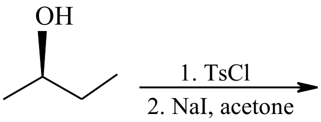
PROBLEM 948 An optically active organic compound *A*($C_8H_{16}O$) does not decolourise the brown colour of bromine-water but turns orange colour of acidic dichromate solution to blue green converting itself into another optically active compound *B*. *A* on heating with conc.H_2SO_4 produced *C*(C_8H_{14}) as major product which does not show stereomerism. *C* on reductive ozonolysis produced *D*(C_5H_8O) as one of the product which does not change the colour of acidic dichromate solution. *D* on reduction with $LiAlH_4$ produced *E*($C_5H_{10}O$) which on dehydration followed by reductive ozonolysis of product yields a non-resolvable *F*($C_5H_8O_2$). *F* gives positive Fehling's solution test but negative haloform test. Deduce structural formula of *A* to *F*.

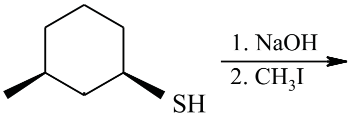
PROLBEM 949 Predict products in the following reactions showing stereochemistry where applicable:

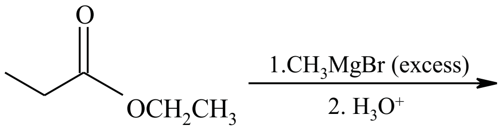
(a) 

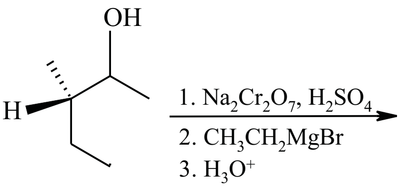
(b) 

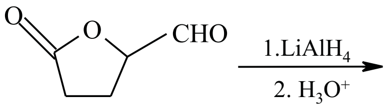
(c) 

(d) 

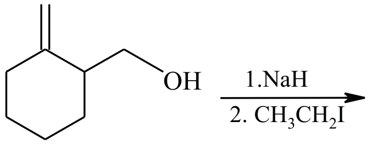
(e) 

(f) 

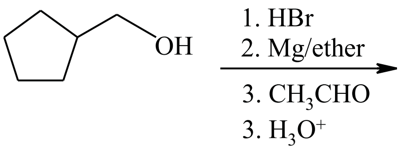
(g) 

(h) 

(i)

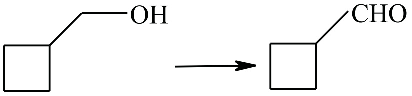


(j)

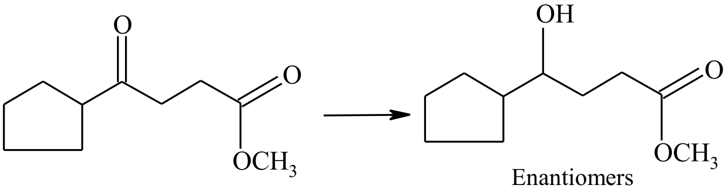


PROBLEM 950 Provide reagents that will effect the following transformations (more than one steps may be required):

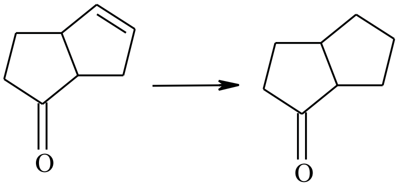
(a)



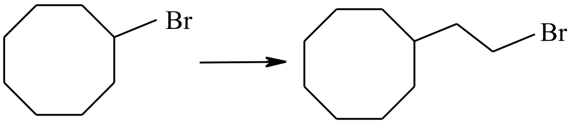
(b)



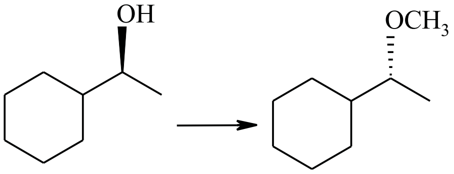
(c)



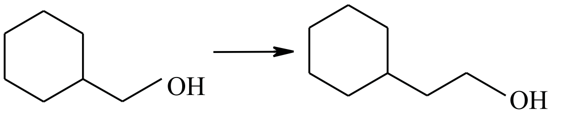
(d)



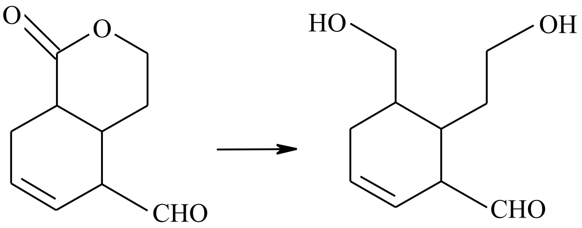
(e)



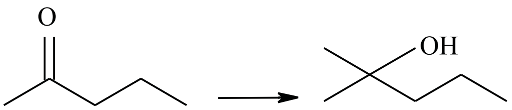
(f)



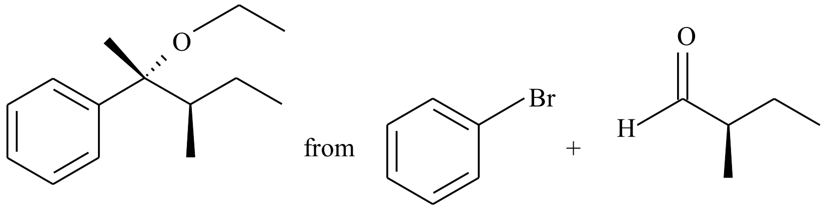
(g)



(h)

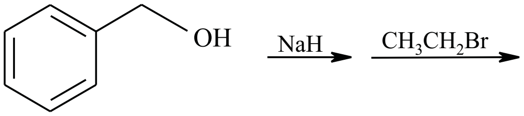


Problem 951 Devise synthesis of the following compound starting from the indicated starting materials and any other reagents you need.

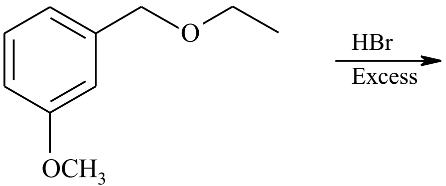


Problem 952 Predict all products of the following reactions and show stereochemistry where applicable:

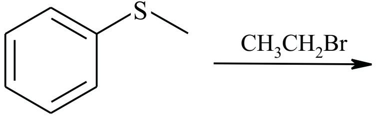
(a)



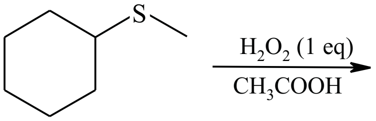
(b)



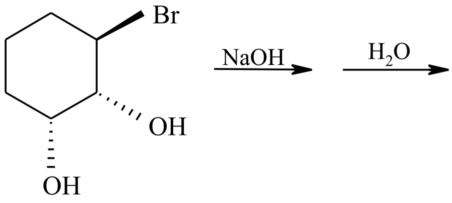
(c)



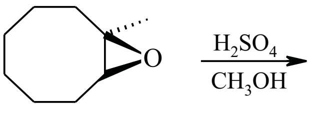
(d)



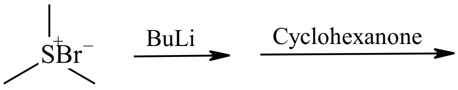
(e)

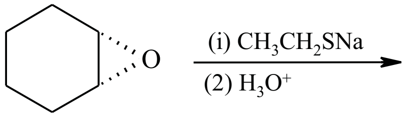


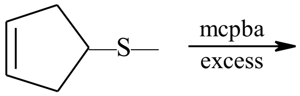
(f)

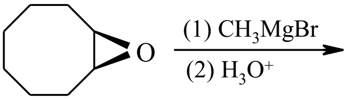


(g)

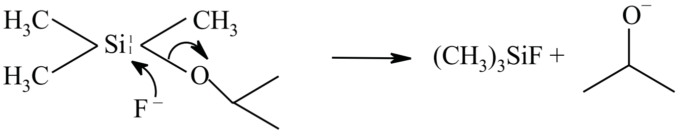


(h) 

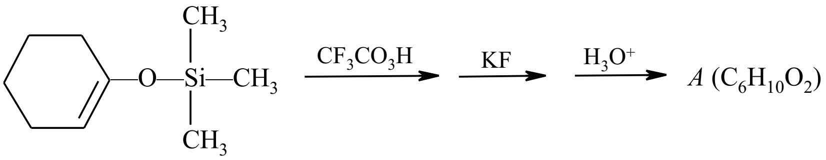
(i) 

(j) 

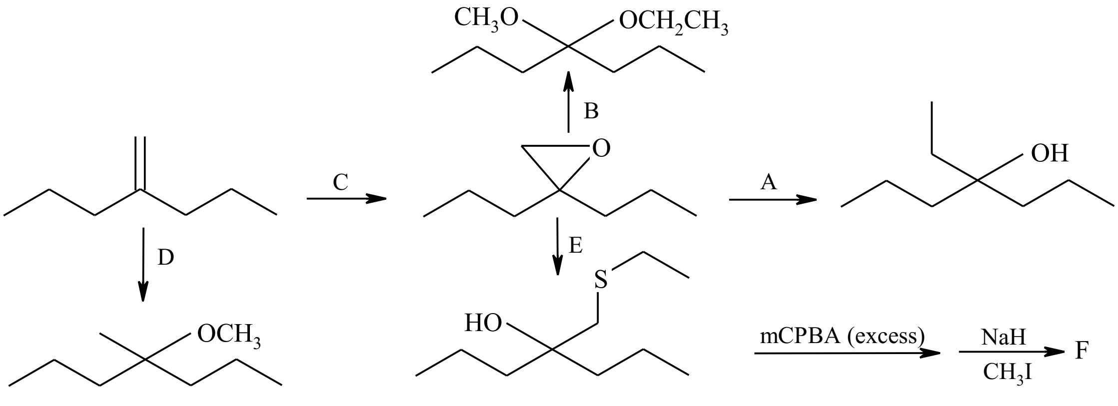
Problem 953 Silicon-oxygen bonds are easily cleaved by fluoride ions as:



Based on the above information, provide a structure of *A*($C_6H_{10}O_2$). Provide mechanism of formation of *A*.

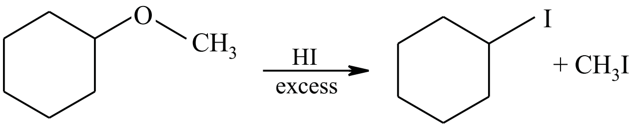


Problem 954 Provide reagents that will effect the following transformations:

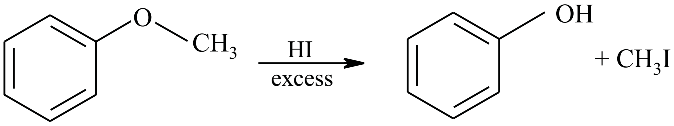


Problem 955 The reaction of a dialkyl ether with excess of HI provides two alkyl iodides. However, under the similar reaction conditions, aryl-alkyl ethers affords an alkyl iodide and a phenol. Explain the observations with the help of following reactions.

(1)

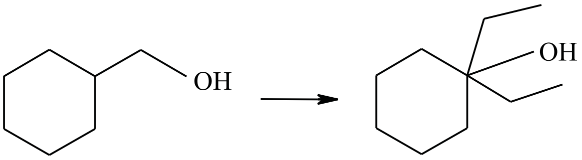


(2)

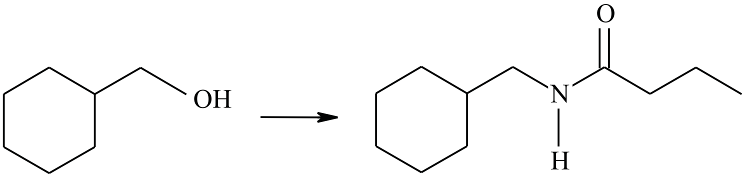


PROBLEM 956 Bring about the following transformations:

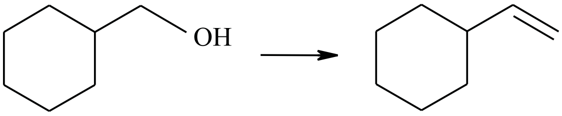
(a)



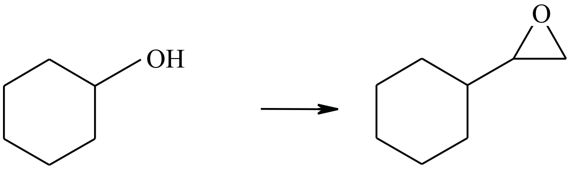
(b)



(c)

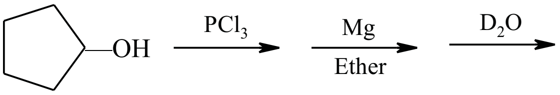


(d)

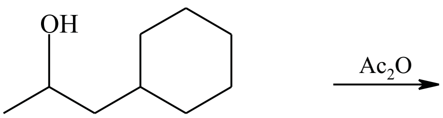


PROBLEM 957 Predict products of the following reactions. Show stereochemistry where important. In case where more than one stereoisomers are formed, draw both the products and indicate which one will be the major product.

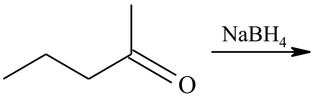
(a)



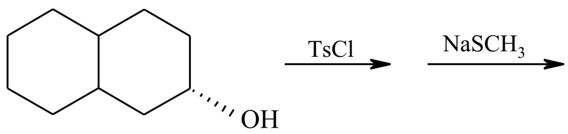
(b)



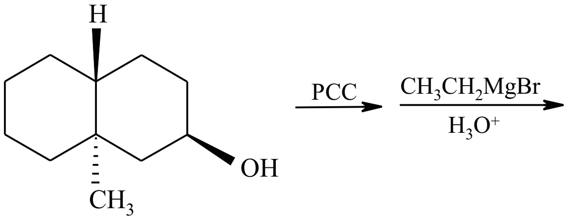
(c)



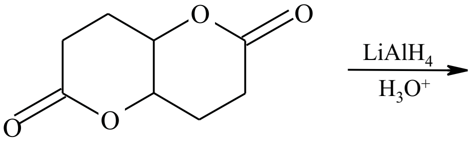
(d)



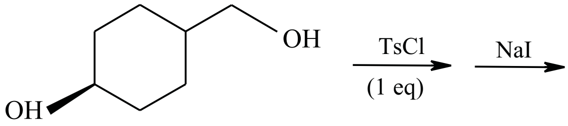
(e)



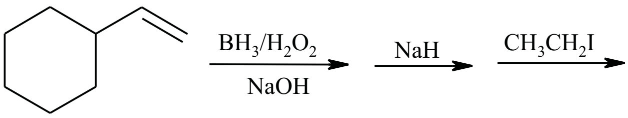
(f)



(g)

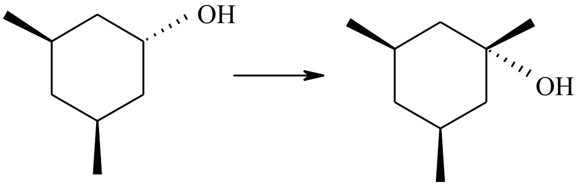


(h)

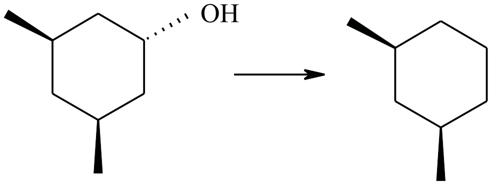


PROBLEM 958 Provide reagents that will bring about the following transformations:

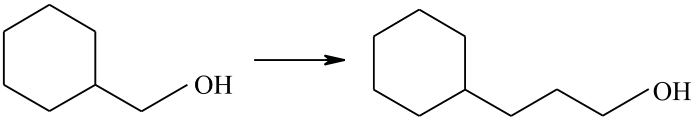
(a)



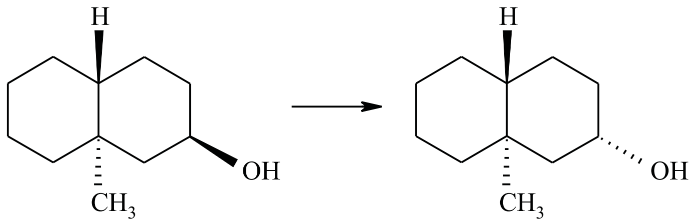
(b)



(c)

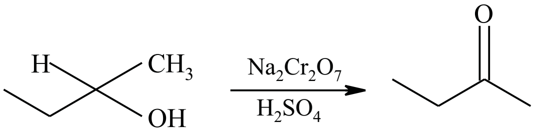


(d)

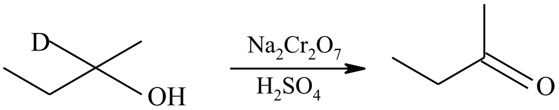


Problem 959 Reaction *A* proceeds more quickly than *B*. Explain why this is so. On the basis of your explanation of first part, what product would you expect from reaction *C*?

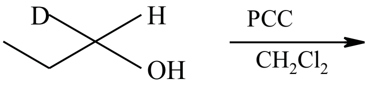
A :



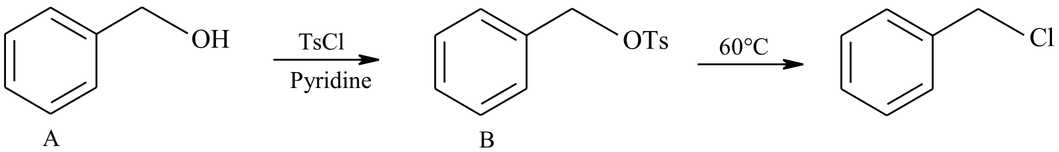
B :



C :

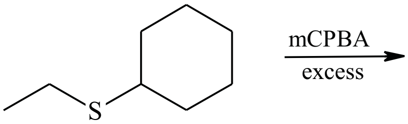


Problem 960 When benzyl alcohol (A) is treated with TsCl and pyridine at room temperature, the tosylate (B) is formed. However, when the same reaction is carried out at 60°C, the chloride (C) is produced. Draw a mechanism of formation of C from B and explain the effect of temperature on reaction.

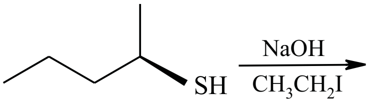


Problem 961 Predict products in the following reactions : (Provide structures of stereoisomers where appropriate):

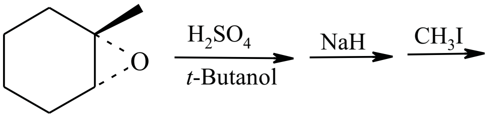
(a)



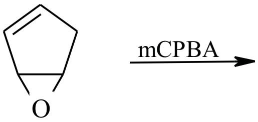
(b)



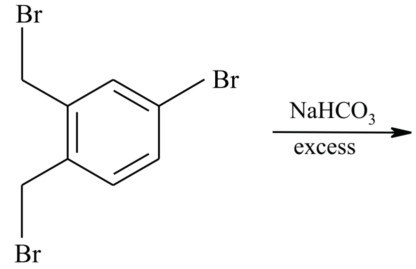
(c)



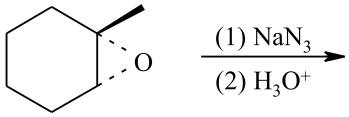
(d)



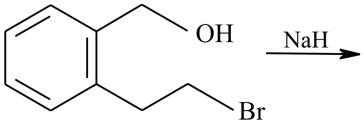
(e)



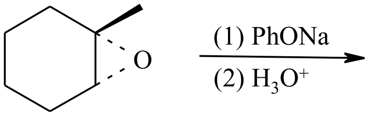
(f)



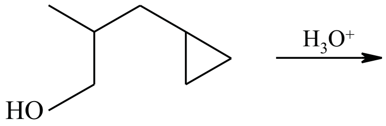
(g)



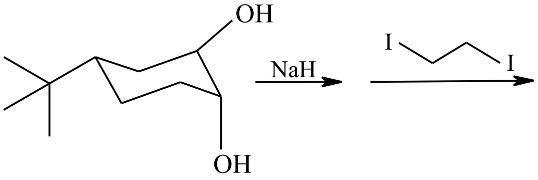
(h)



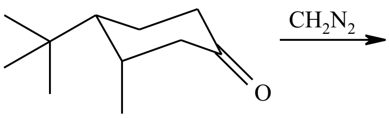
(i)



(j)

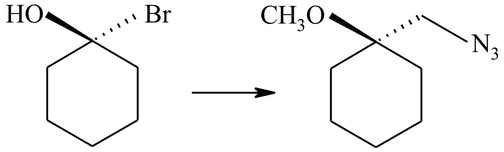


(k)

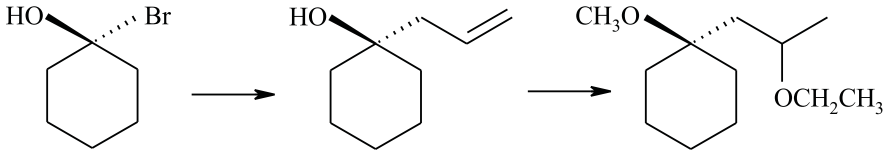


PROBLEM 962 Provide the reagents that will effect the following transformations:

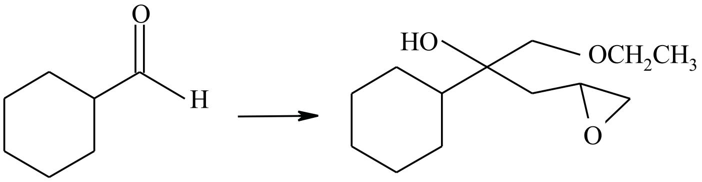
(a)



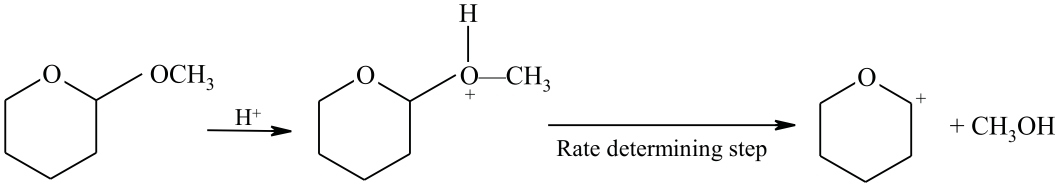
(b)



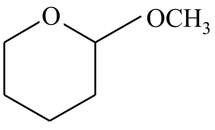
PROBLEM 963 Bring about the following transformations:

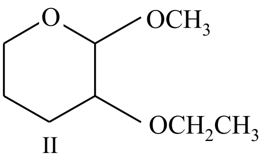


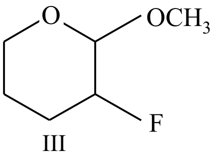
PROBLEM 964 Hydrolysis of ether proceed via carbocation intermediate as shown below:

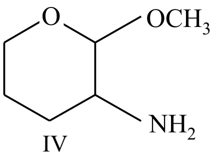


Based on the above information, rationalize the relative rate of hydrolysis of compounds A to D below:

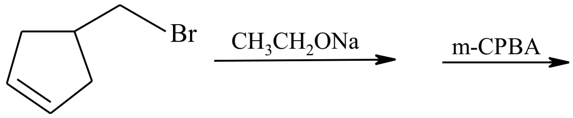

I

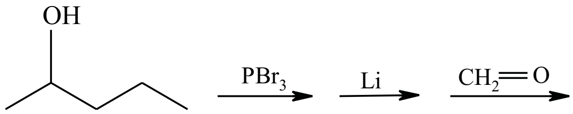

II

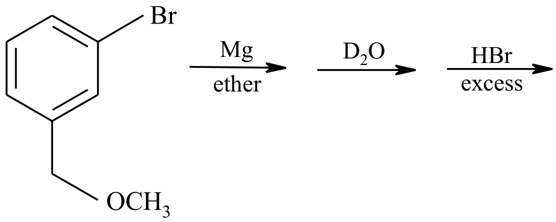

III

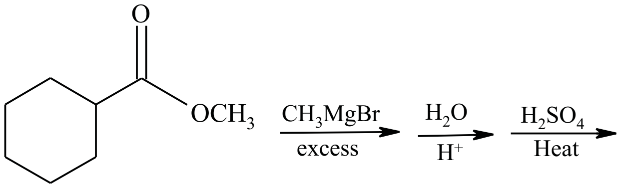

IV

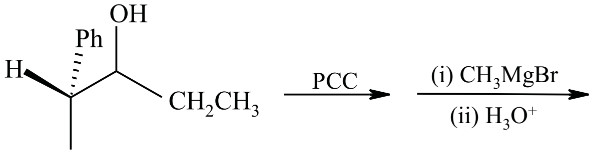
PROBLEM 965 Write products in the following reactions. Provide structures of stereo-isomers where appropriate:

(a)


(b)


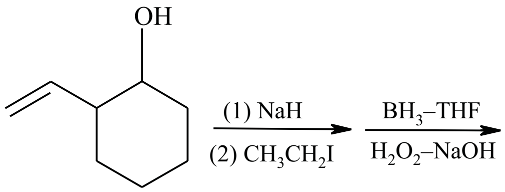
(c)


(d)


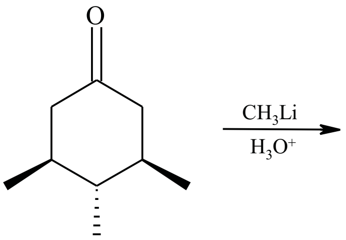
(e)


PROBLEM 966 Provide products in the following reactions:

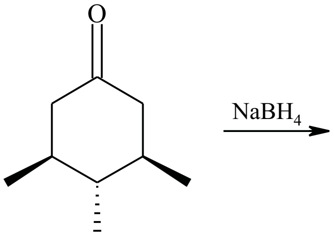
(a)



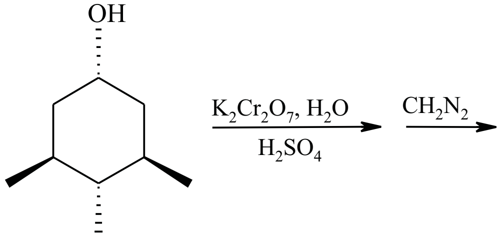
(b)



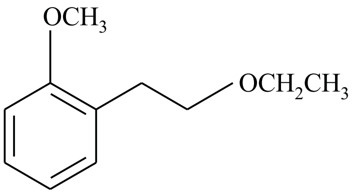
(c)



(d)

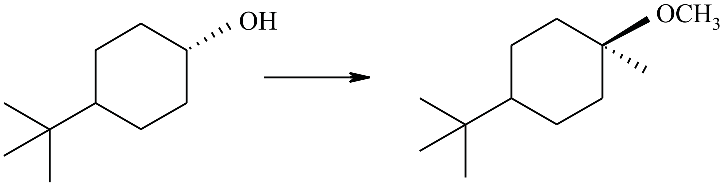


(e)

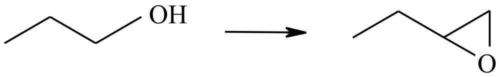


PROBLEM 967 Bring about the following transformations:

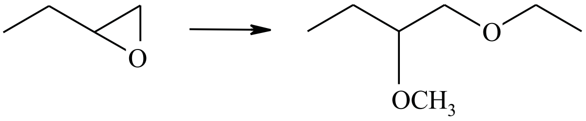
(a)



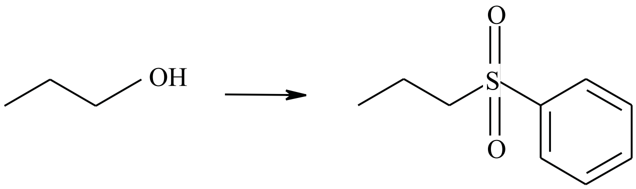
(b)



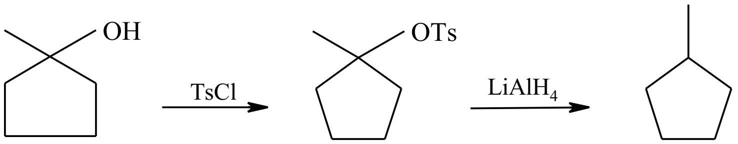
(c)



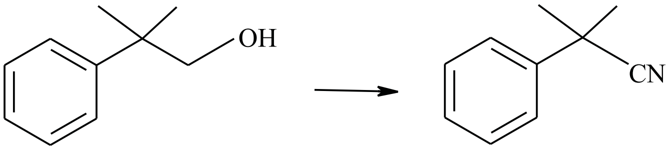
(d)

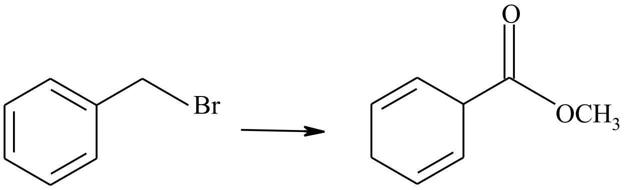


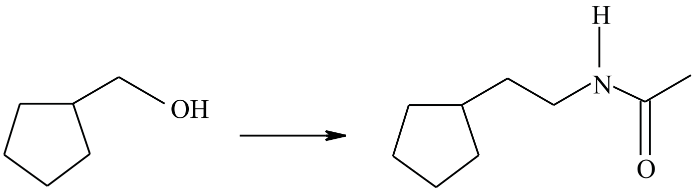
PROBLEM 968 The conversion A into B by the reaction sequence below does not work well. Explain why this is the case and provide a better way of doing this.



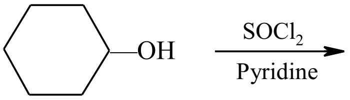
PROBLEM 969 Bring about the following transformations:

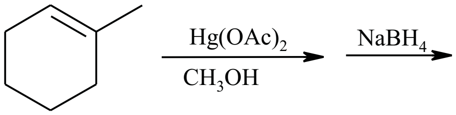
(a)


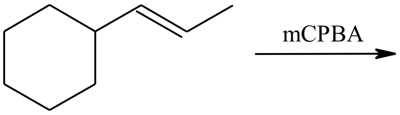
(b)


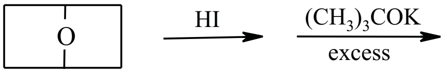
(c)


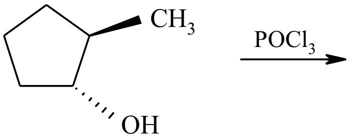
PROBLEM 970 Provide products in the following reactions:

(a)


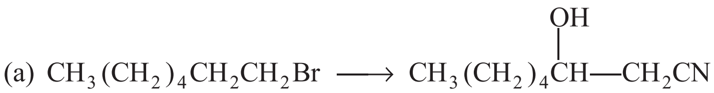
(b)


(c)


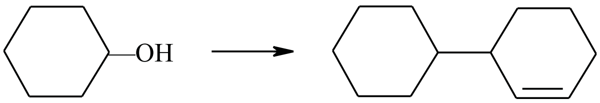
(d)


(e)


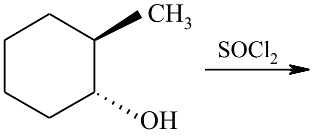
PROBLEM 971 Bring about the following transformations:

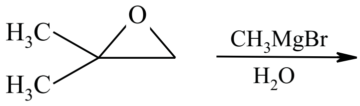


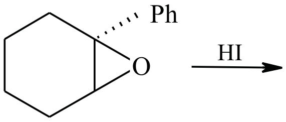
$$\text{(a) } CH_3(CH_2)_4CH_2CH_2Br \longrightarrow CH_3(CH_2)_4\underset{}{\overset{\displaystyle OH \atop |}{C}}H{-}CH_2CN$$

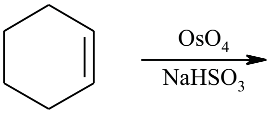
(b) 

Problem 972 Complete the following reactions:

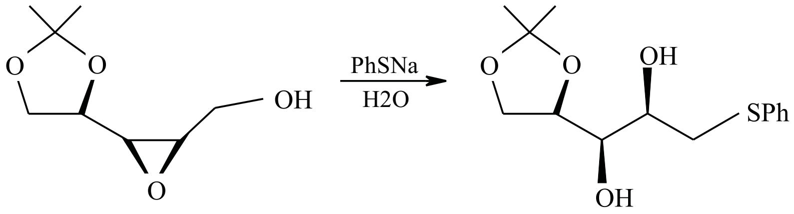
(a) 

(b) 

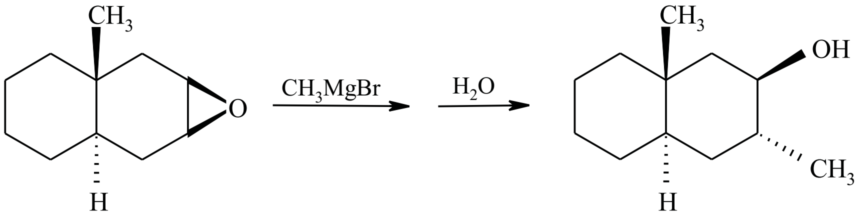
(d) 

(d) 

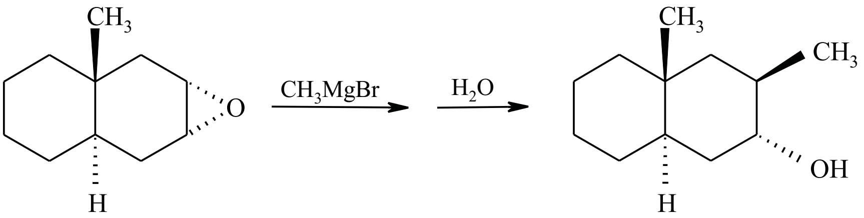
Problem 973 Propose mechanism of the following reaction:



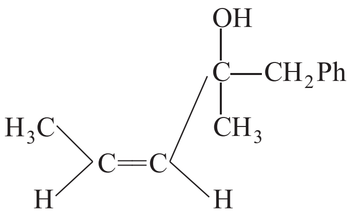
Problem 974 Explain the following observation:

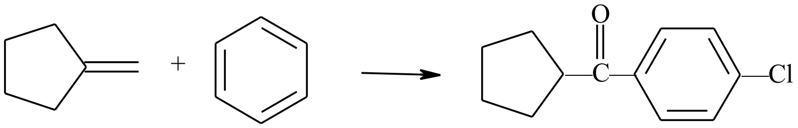


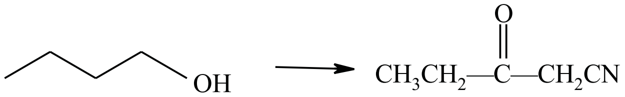
but



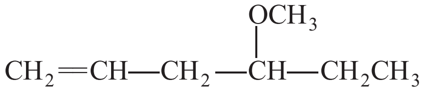
Problem 975 Bring about the following transformations:

(a) $PhCH_2CH_2CH_2Br$ ⟶ 

(b) 

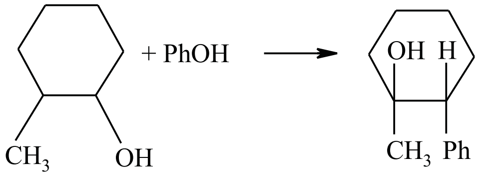
(c) 

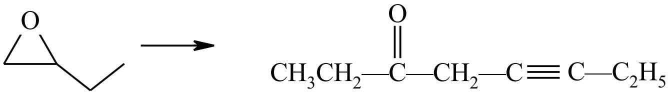
Problem 976 Starting from propene, propanal methylbromide as the only organic reagents, and any other inorganic reagent, synthesize the following compound:



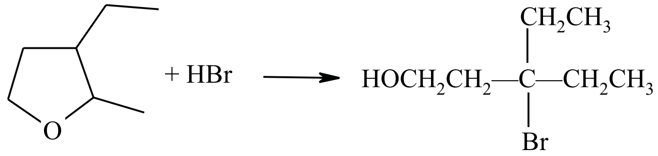
$$CH_2{=}CH{-}CH_2{-}\overset{\displaystyle OCH_3}{\overset{|}{C}H}{-}CH_2CH_3$$

Problem 977 Bring about the following transformations starting from indicated materials:

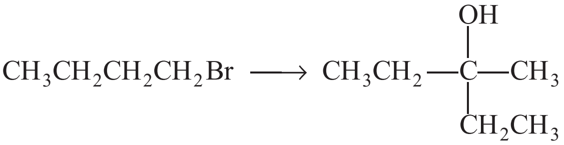
(a) 

(b) 

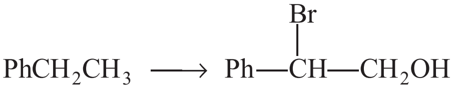
Problem 978 Propose mechanism:



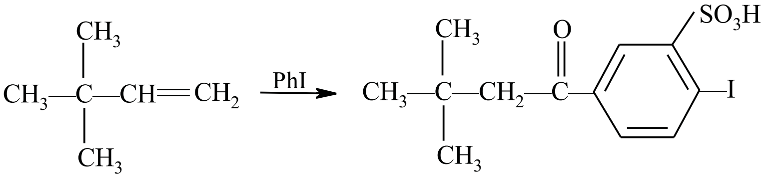
Problem 979 Bring about the following transformations:

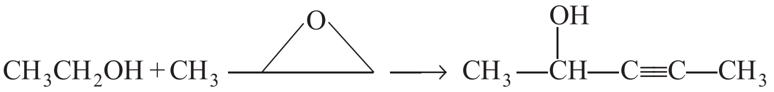
(a) 

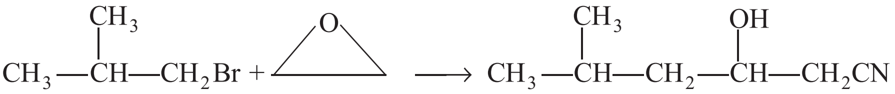
$$CH_3CH_2CH_2CH_2Br \longrightarrow CH_3CH_2{-}\overset{\displaystyle OH}{\underset{\displaystyle CH_2CH_3}{C}}{-}CH_3$$

(b) 

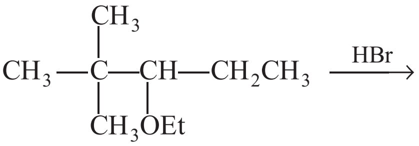
$$PhCH_2CH_3 \longrightarrow Ph{-}\overset{\displaystyle Br}{C}H{-}CH_2OH$$

(c) 

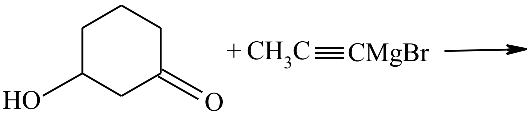
(d) 

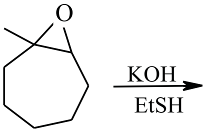
(e) 

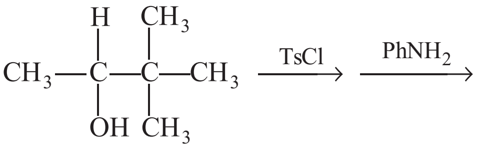
Problem 980 Complete the following reactions and indicate stereochemistry of product where appropriate:

(a) 

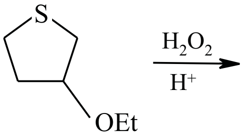
$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-\underset{\displaystyle OEt}{CH}-CH_2CH_3 \xrightarrow{HBr}$$

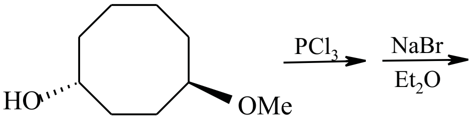
(b) 

(c) 

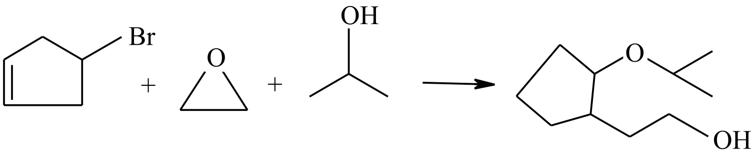
(d) 

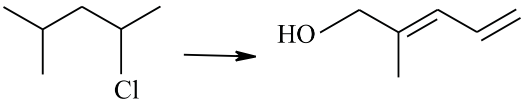
$$CH_3-\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_3 \xrightarrow{TsCl}\xrightarrow{PhNH_2}$$

(e) 

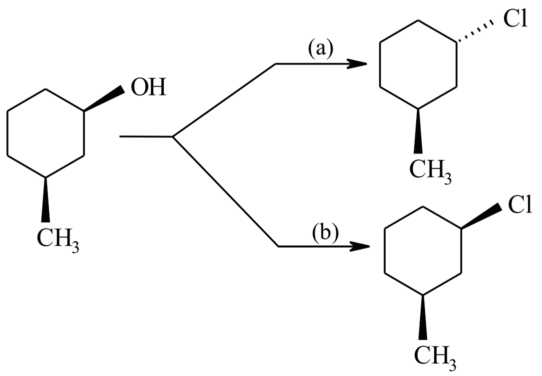
(f) 

Problem 981 Synthesize the products from indicated reagents and other inorganic reagents required.

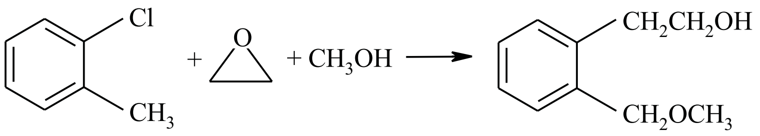
(a) 

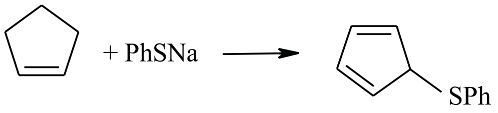
(b) 

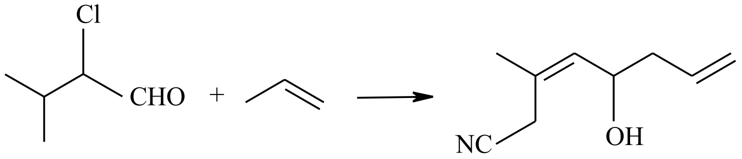
PROBLEM 982 Bring about the following transformations:

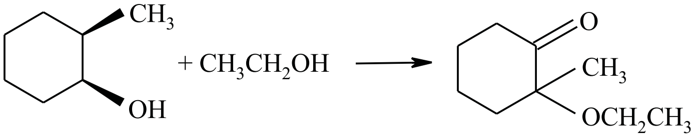


PROBLEM 983 Synthesize the products from indicated starting materials and any other inorganic reagents needed:

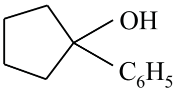
(a)


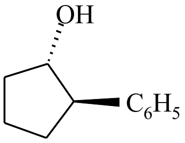
(b)


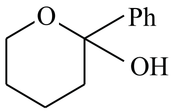
(c)


(d)


PROBLEM 984 Show how the following compounds can be synthesized from cyclopentanol?

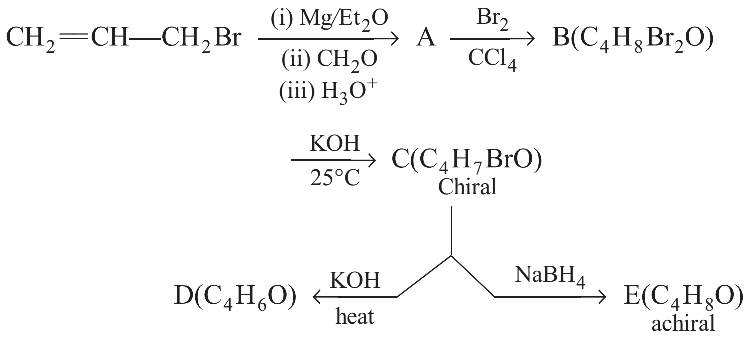
(a)


(b)


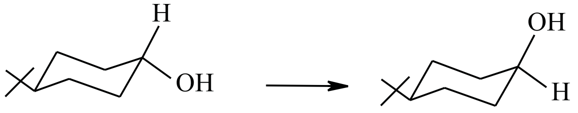
(c)


PROBLEM 985 When enantiomerically pure (+)-2-phenyl-2-butanol is allowed to stand in methanol containing a few drops of H_2SO_4, racemic 2-methoxy-2-phenyl butane is formed. Suggest a plausible mechanism.

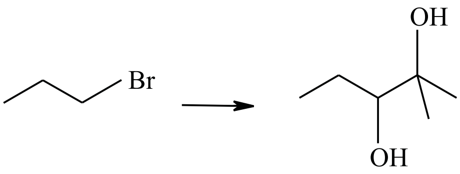
PROBLEM 986 Deduce structures of missing species in the following sequence of reaction:



PROBLEM 987 Bring about the following transformation:

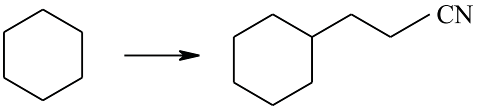


PROBLEM 988 Bring about the folllowing transformations:

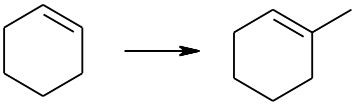


PROBLEM 989 Convert:

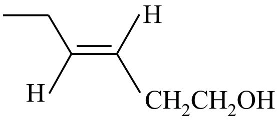
(a)



(b)

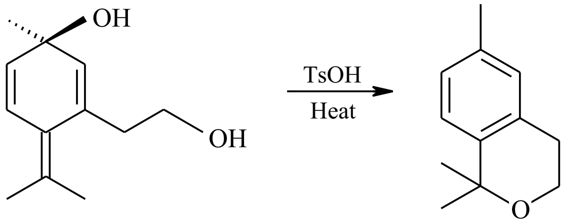


(c) $CH_3CH_2C\equiv CH \longrightarrow$



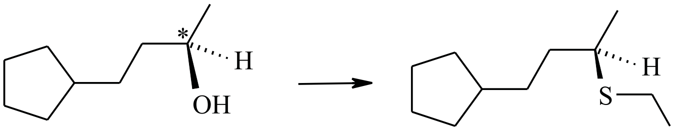
PROBLEM 990 An organic compound *A* has molecular formula $C_8H_{16}O_2$ and it can be resolved into enantiomers. *A* on treatment with acidified dichromate solution yields $B(C_8H_{14}O_4)$ which is achiral. *A* on treatment with PCC/CH_2Cl_2 yields another achiral compound $C(C_8H_{14}O_2)$. *C* on refluxing with dilute Na_2CO_3 solution yields $D(C_8H_{14}O_2)$ which is distereomeric. *D* on heating in presence of H_2SO_4 yields $E(C_8H_{12}O)$ which is still chiral. *E* on heating strongly in stream of H_2/Pt yields 1,3-dimethylcyclohexane. Identify *A* to *E*.

PROBLEM 991 Provide a detailed, step-by-step mechanism for the following:

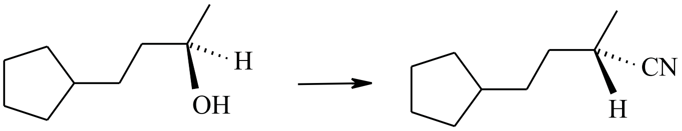


PROBLEM 992 Provide an ordered sequence of reagents that will convert the single enantiomer (indicated by *) of a starting material into the desired single enantiomer of product.

(a)

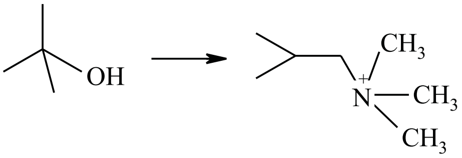


(b)

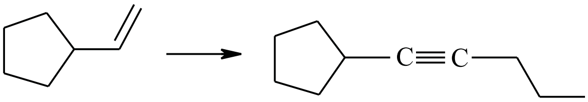


PROBLEM 993 Bring about the following transformations:

(a)

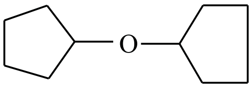


(b)

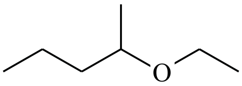


PROBLEM 994 Devise synthesis of the following ethers from an alkyl halide and an alcohols:

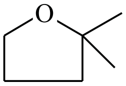
(a)



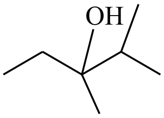
(b)



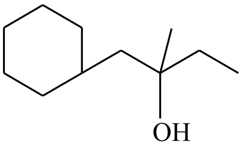
(c)



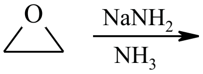
PROBLEM 995 Beginning with alcohols containing not more than three carbons, synthesize:

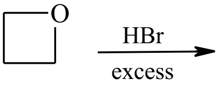


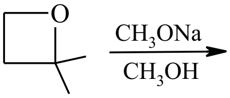
PROBLEM 996 Starting with alcohol containing not more than six carbon synthesize:

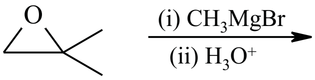


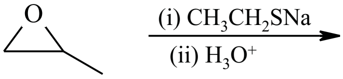
PROBLEM 997 Predict major product in the following reactions:

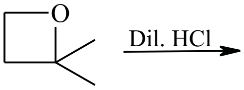
(a)


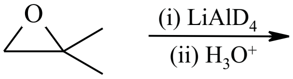
(b)


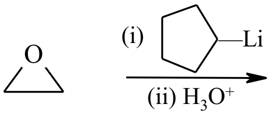
(c)


(d)


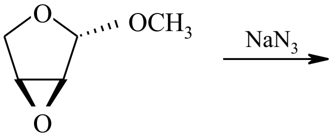
(e)


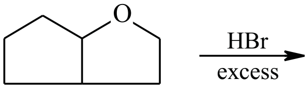
(f)


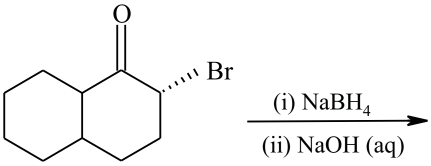
(g)


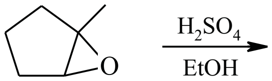
(h)


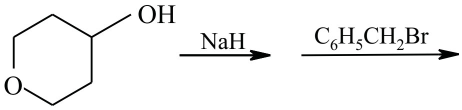
PROBLEM 998 Predict product in the following reactions:

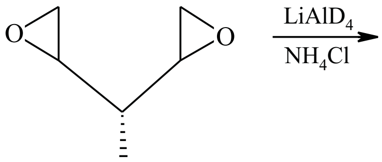
(a)


(b)


(c)


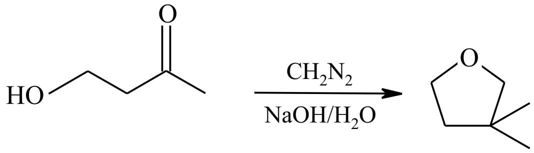
(d)


(e)


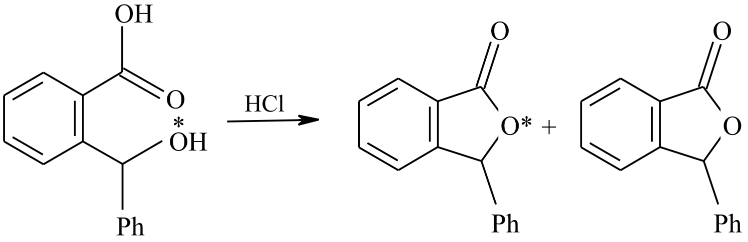
(f)


PROBLEM 999 Accounts for the following observations : 2,2-dimethyl oxirane is hydrolyzed at faster rate than oxirane in acid medium but reverse is true in alkaline medium.

PROBLEM 1000 Propose mechanism:

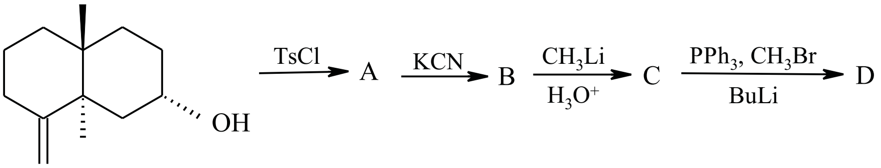


PROBLEM 1001 Propose mechanism:

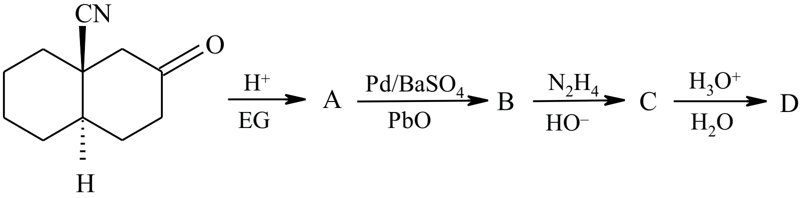


PROBLEM 1002 Identify the missing species:

(a)

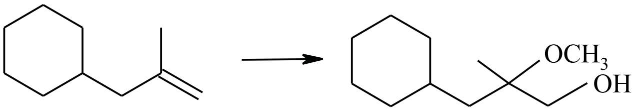


(b)

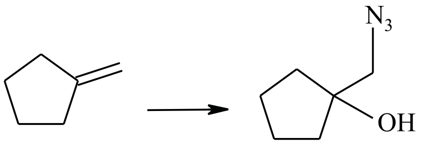


PROBLEM 1003 Provide reagents necessary for the following transformation:

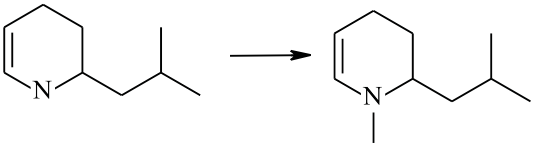
(a)



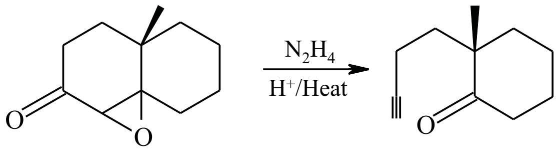
(b)



(c)

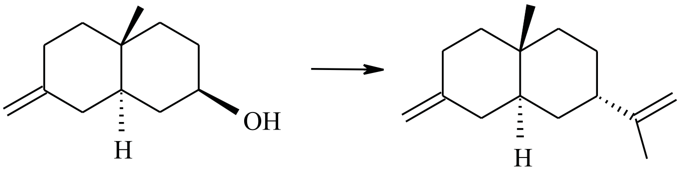


Problem 1004 Propose mechanism:

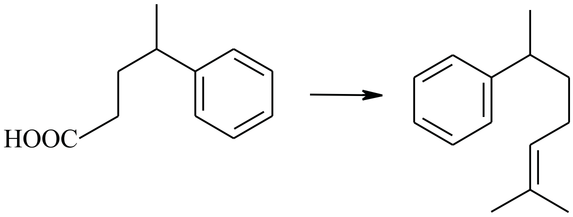


Problem 1005 Synthesize the indicated product from the supplied starting materials:

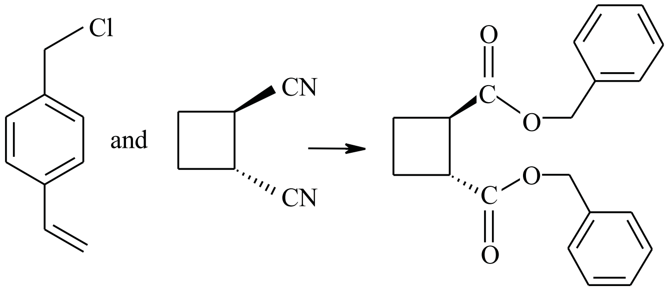
(a)



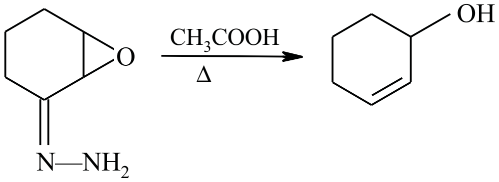
(b)



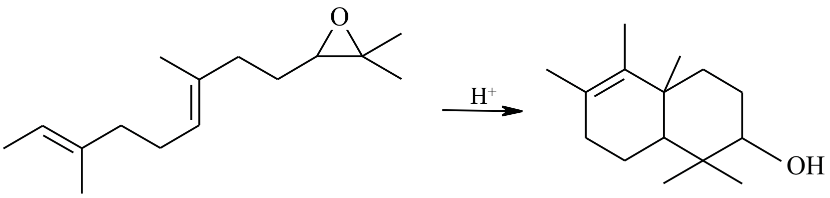
(c)



Problem 1006 Suggest mechanism of the following reaction:

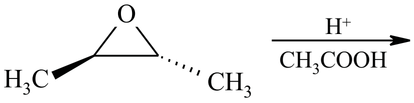


Problem 1007 Propose mechanism of the following reaction:

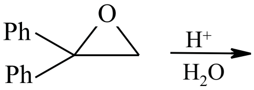


PROBLEM 1008 Write product of the following reactions and indicate stereochemistry product where appropriate:

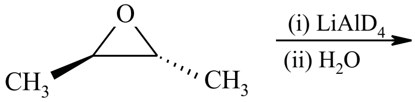
(a)



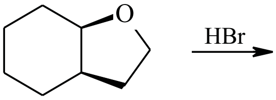
(b)



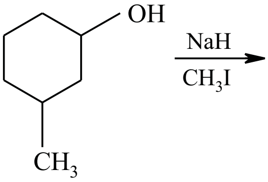
(c)



(d)

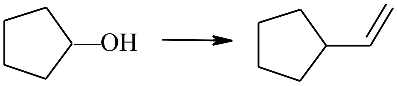


(e)

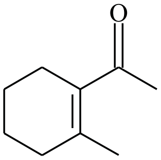


PROBLEM 1009 Bring about the following transformations:

(a)

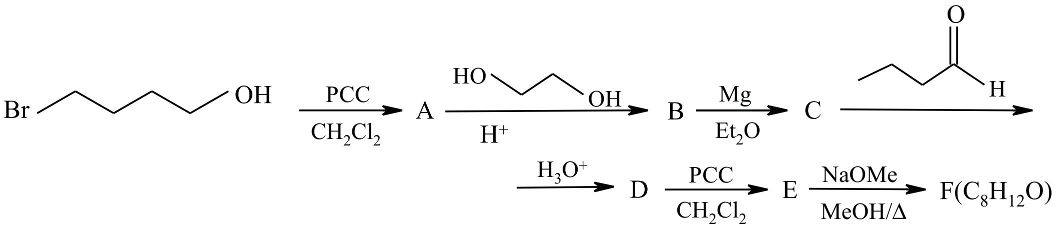


(b)



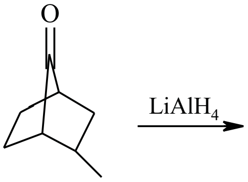
from alcohols containing not more than three carbons.

PROBLEM 1010 The following series of reactions was performed during synthesis of a target molecule. Give structures of each of the indicated compound:

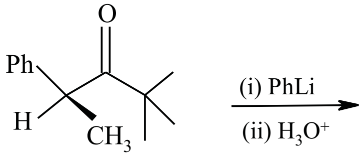


PROBLEM 1011 Predict structures including stereochemistry, of products formed in the following reactions:

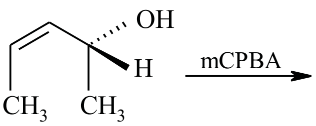
(a)



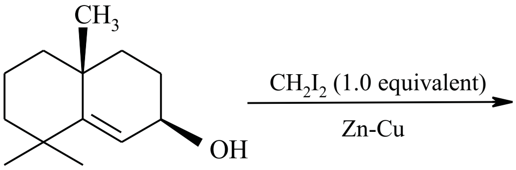
(b)



(c)

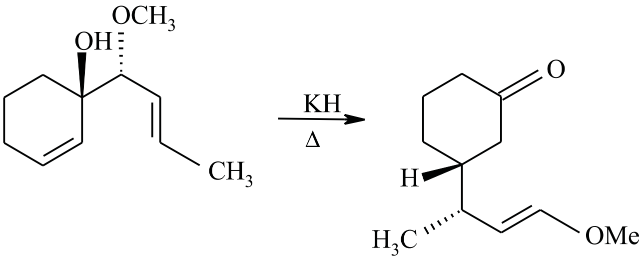


(d)

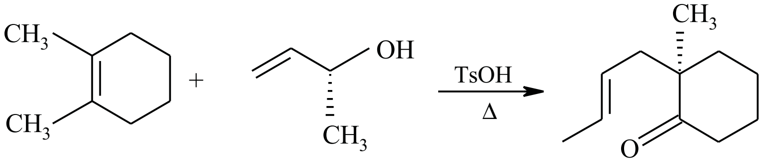


Problem 1012 Propose mechanism of the following reactions:

(a)



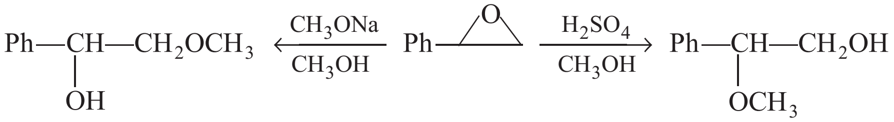
(b)



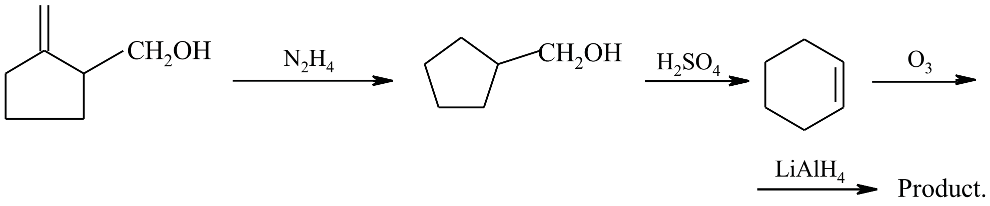
Solutions

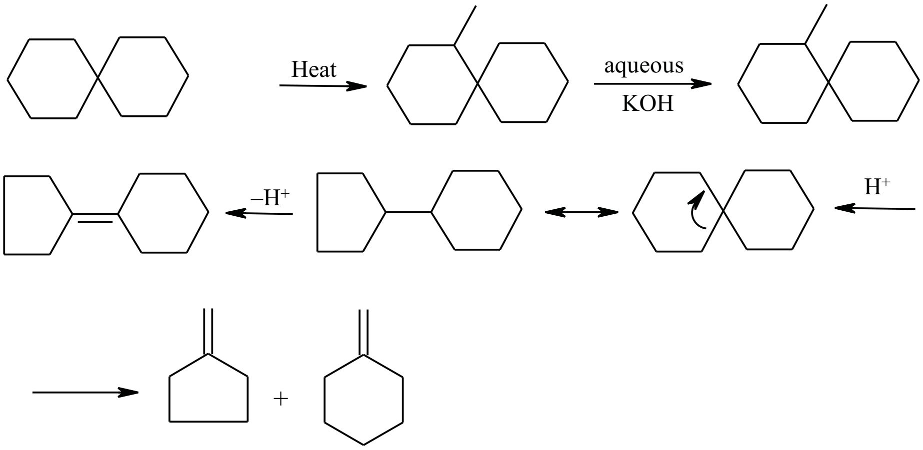
ALCOHOLS AND ETHERS

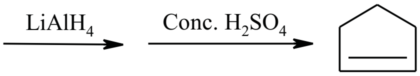
908. Ethylene oxide being a three membered ring, suffers from very large angle strain and therefore highly unstable whereas THF is a five membered ring, it is stable.

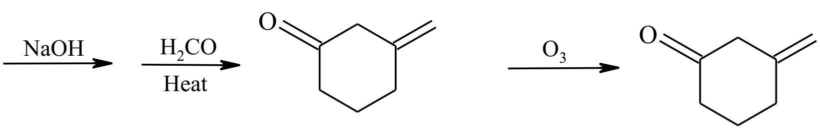
909. 

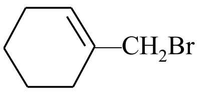
$$\mathrm{Ph{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_2OCH_3} \xleftarrow[\mathrm{CH_3OH}]{\mathrm{CH_3ONa}} \mathrm{Ph{-}epoxide} \xrightarrow[\mathrm{CH_3OH}]{\mathrm{H_2SO_4}} \mathrm{Ph{-}\underset{\displaystyle OCH_3}{\underset{|}{CH}}{-}CH_2OH}$$

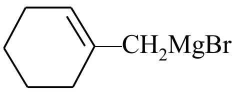


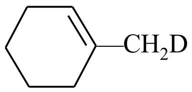


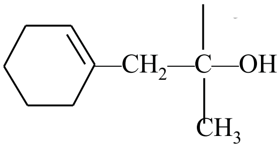


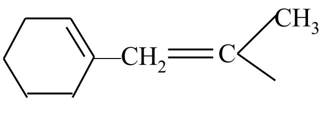






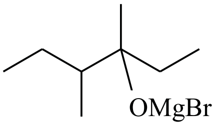






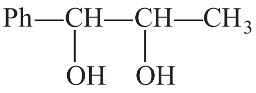
912. At higher temperature, intramolecular dehydration is entropy favoured.

913. 2-butanol *A* 2-butanone *B* 2-bromobutane *C*

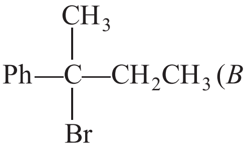


D

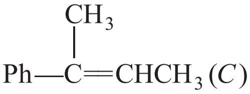
914.



$\mathrm{Ph{-}CH(OH){-}CH(OH){-}CH_3}$ (*A*)



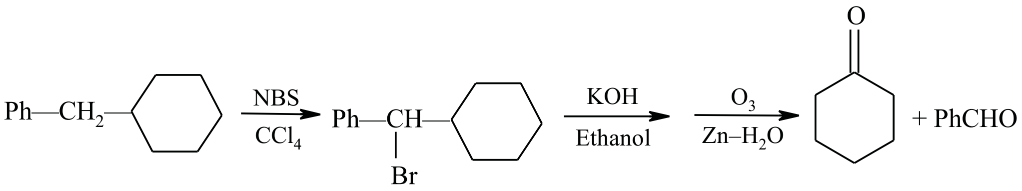
$\mathrm{Ph{-}C(CH_3)(Br){-}CH_2CH_3}$ (*B*)



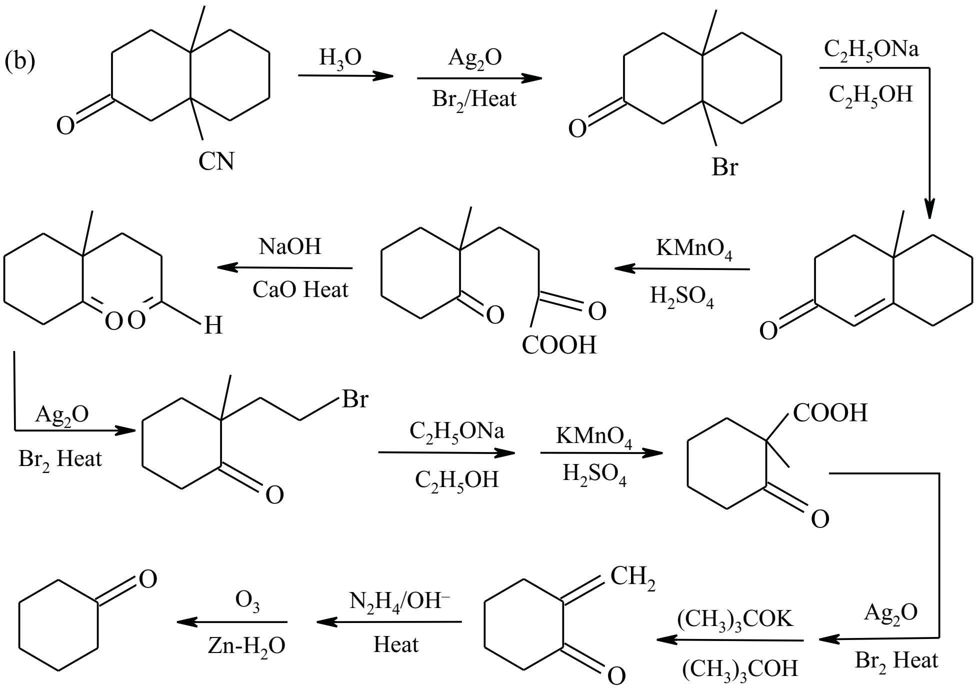
$\mathrm{Ph{-}C(CH_3){=}CHCH_3}$ (*C*)

CH_3COOH(*D*).

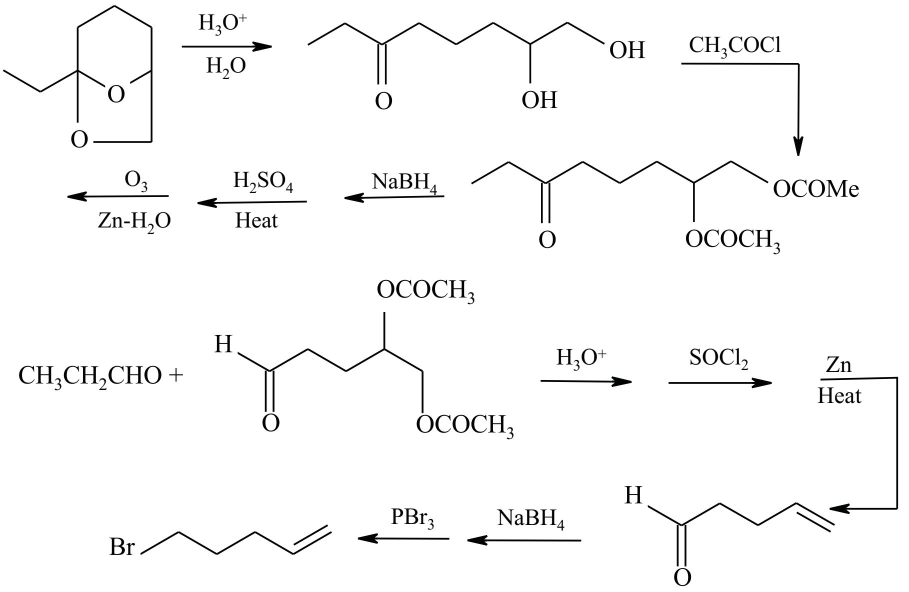
915. (a)



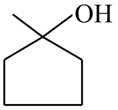
(b)



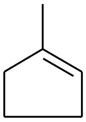
(c)



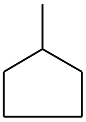
916.



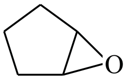
A



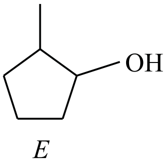
B



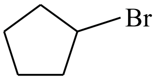
C



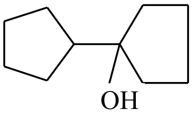
D



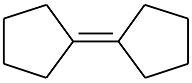
E



F

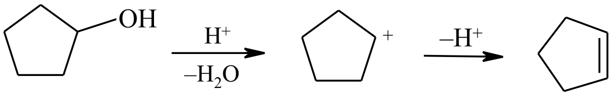


G

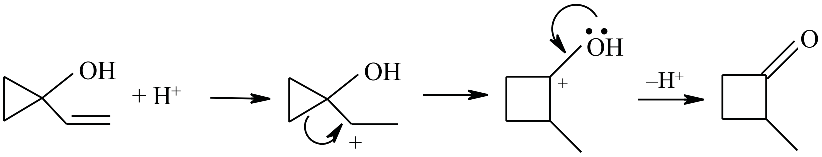


H

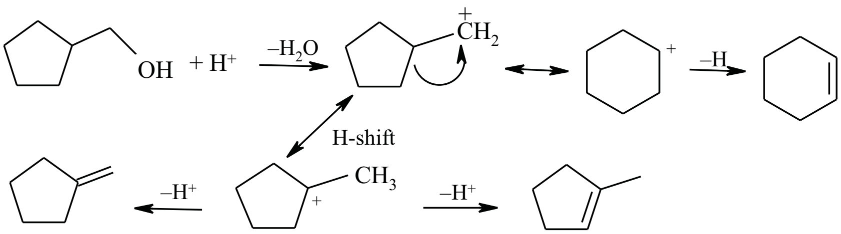
917. (a)



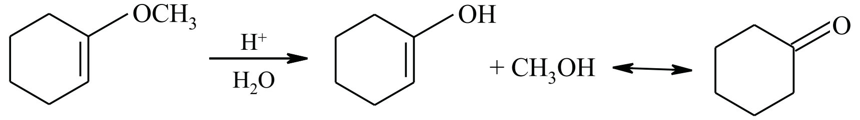
(b)



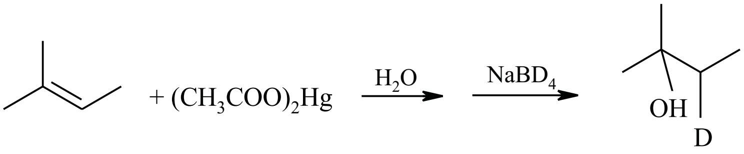
(c)



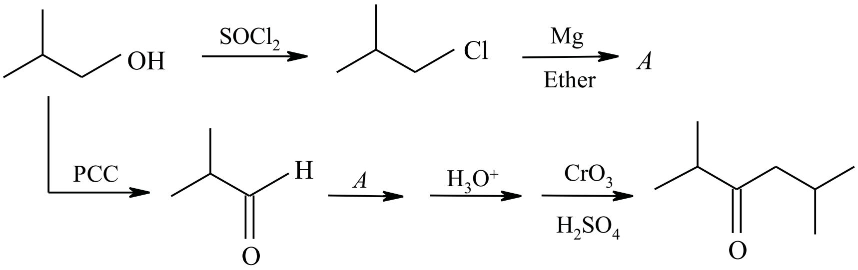
(d)



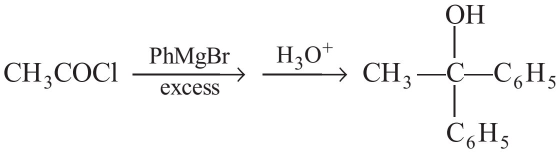
918. (a)



(b)

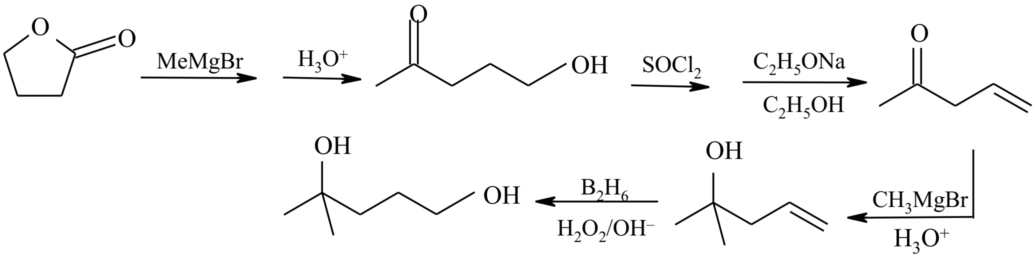


(c)

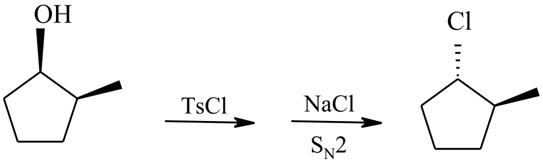


$$CH_3COCl \xrightarrow[\text{excess}]{PhMgBr} \xrightarrow{H_3O^+} CH_3-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle C_6H_5}{|}}{C}}-C_6H_5$$

(d)

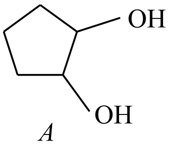


919. (a)

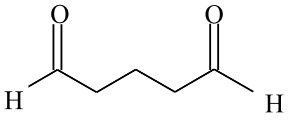


(b) Ethylbromide being a primary halide undergo predominantly S_N2 reaction while cyclohexyl bromide being a secondary halide, undergo E-2 reaction.

920. (a)

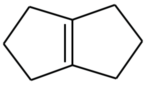


A

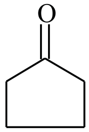


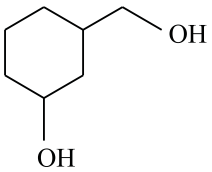
B

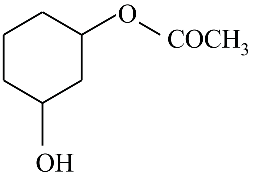
(b)

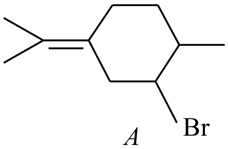


A

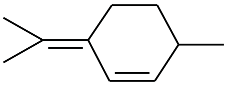
(c) 

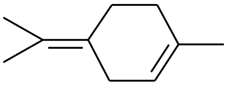
$+ CH_2O$ (d) (i) 

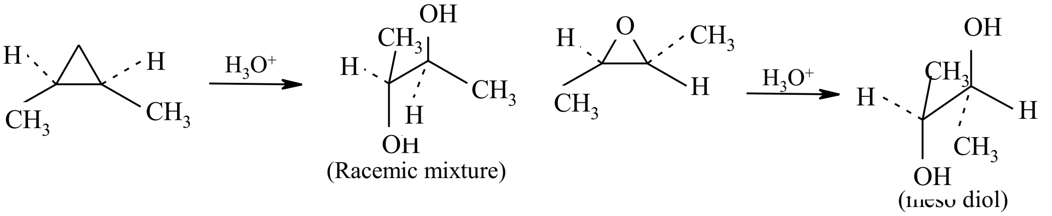
(ii) 

921. 

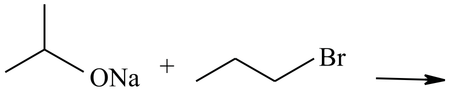
A


B

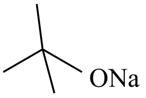

C

922. 

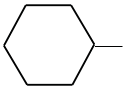
923. Chlorination of alcohols with HCl proceeds by S_N1 mechanism, rearranged products are also obtained. Chlorination of alcohol with $SOCl_2$ proceed by S_N2 mechanism, no rearranged product is obtained.

924. (a) 

Product.

(b) 

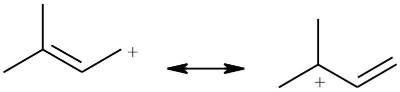
$+ PhCH_2Br \longrightarrow$ Product.

(c) 
$—ONa + CH_3CH_2Br \longrightarrow$ Product.

(d) $CH_3CH_2ONa + CH_2{=}CH—CH_2Br \longrightarrow$ Product.

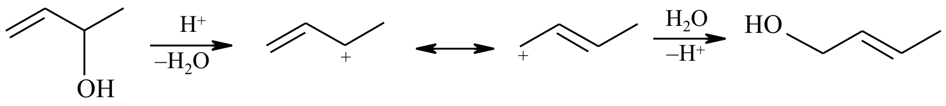
925. The major product is 2-chloro-2-methylbutane.

926. (a) $(CH_3)_2C{=}CHCH_2Cl$ gives a resonance stabilized tertiary carbocation as:

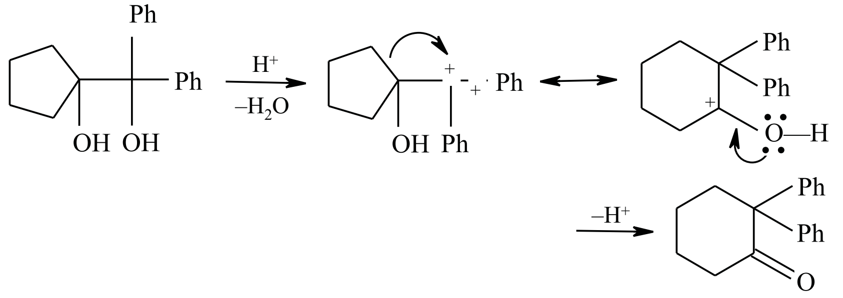


Allyl chloride gives primary carbocation and therefore less stable than the above mentioned carbocation.

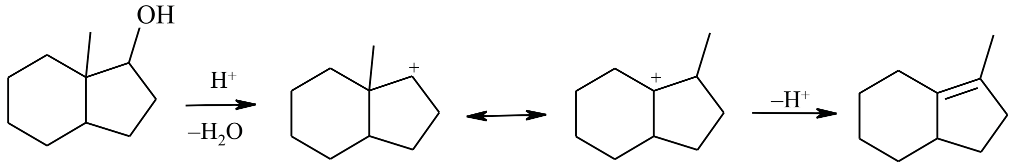
(b) In acidic medium alcohol undergo isomerization via carbocation intermediate as:



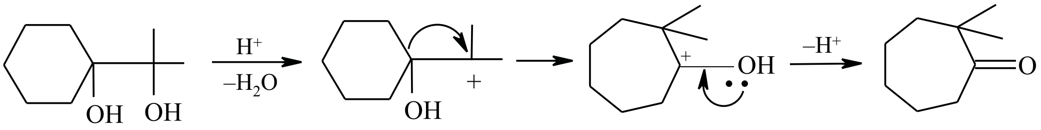
927. (a)



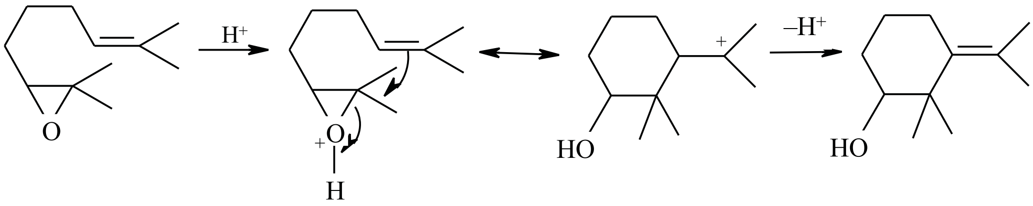
(b)



(c)

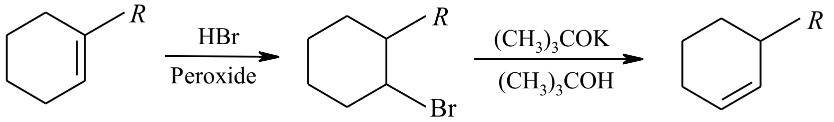


(d)

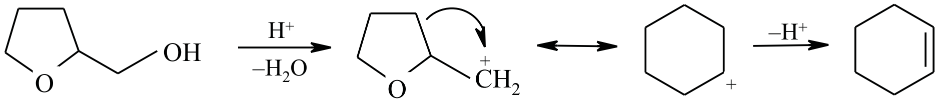


928. $\underset{X}{PhCH(OH)CH_2Ph}$ $\underset{Y}{PhCOCH_2Ph}$

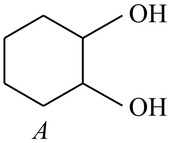
929. (a)



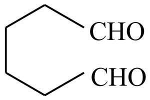
(b)



(c) (i)

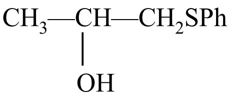


A



B

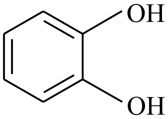
(ii)



$$\underset{\displaystyle OH}{CH_3—\overset{}{C}H—CH_2SPh}$$

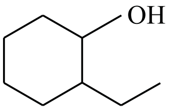
C

(iii)



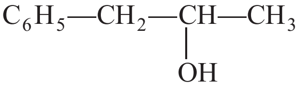
D

(iv)



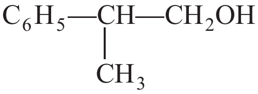
E

930.



$$C_6H_5—CH_2—\underset{\displaystyle OH}{CH}—CH_3$$

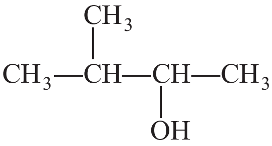
(*A*)



$$C_6H_5—\underset{\displaystyle CH_3}{CH}—CH_2OH$$

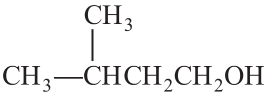
(*B*)

931.



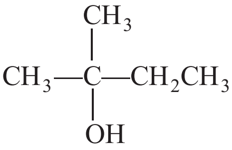
$$CH_3—\overset{\displaystyle CH_3}{CH}—\underset{\displaystyle OH}{CH}—CH_3$$

(*A*)



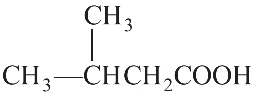
$$CH_3—\overset{\displaystyle CH_3}{CH}CH_2CH_2OH$$

(*B*)



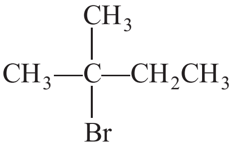
$$CH_3—\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}—CH_2CH_3$$

(*C*)



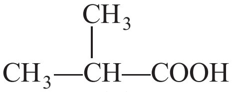
$$CH_3—\overset{\displaystyle CH_3}{CH}CH_2COOH$$

(*D*)



$$CH_3—\overset{\displaystyle CH_3}{\underset{\displaystyle Br}{C}}—CH_2CH_3$$

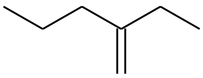
(*E*)



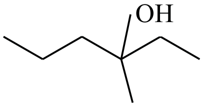
$$CH_3—\overset{\displaystyle CH_3}{CH}—COOH$$

(*F*)

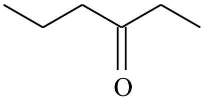
932.



A

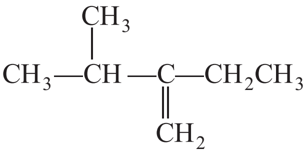


B



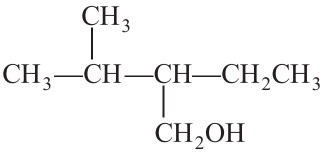
C

933.



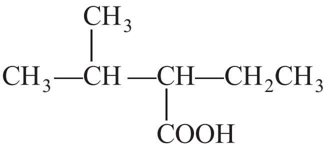
$$CH_3—\overset{\displaystyle CH_3}{CH}—\underset{\displaystyle CH_2}{\overset{\|}{C}}—CH_2CH_3$$

(*A*)



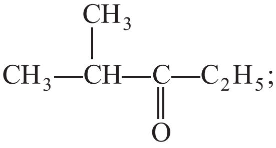
$$CH_3—\overset{\displaystyle CH_3}{CH}—\underset{\displaystyle CH_2OH}{CH}—CH_2CH_3$$

(*B*)



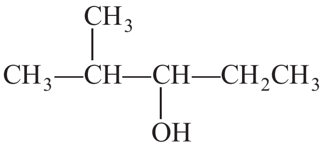
$$CH_3—\overset{\displaystyle CH_3}{CH}—\underset{\displaystyle COOH}{CH}—CH_2CH_3$$

(*C*)



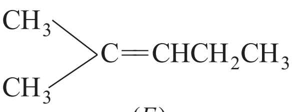
$$CH_3—\overset{\displaystyle CH_3}{CH}—\underset{\displaystyle O}{\overset{\|}{C}}—C_2H_5;$$

(*D*)



$$CH_3—\overset{\displaystyle CH_3}{CH}—\underset{\displaystyle OH}{CH}—CH_2CH_3$$

(*E*)

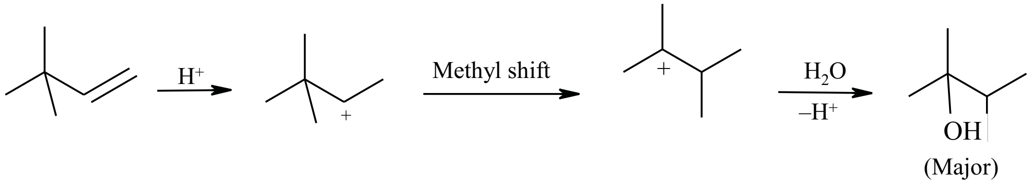


$$(CH_3)_2C{=}CHCH_2CH_3$$

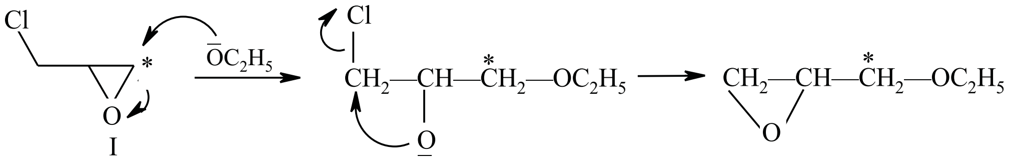
(*F*)

936. 1,3-butandiol (*A*) 3-ketobutanoic acid (*B*).

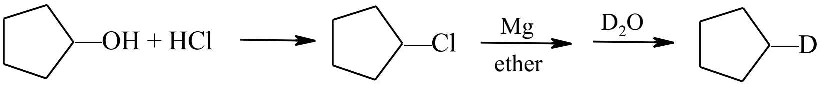
934.



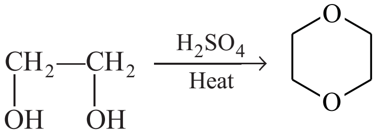
935.



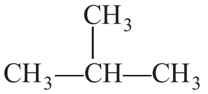
937. (a)



(b) $CH_2{=}CH_2$ + Cold, dilute, alkaline $KMnO_4 \longrightarrow$

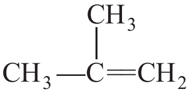


938. (a)



$CH_3{-}\underset{}{\overset{CH_3}{\overset{|}{C}H}}{-}CH_3 + Br_2 \xrightarrow{\text{Heat}} (CH_3)_3CBr$

(b) $(CH_3)_3CBr$ (from a) + $C_2H_5ONa \xrightarrow[\text{E-2}]{C_2H_5OH}$



$CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}CH_2$

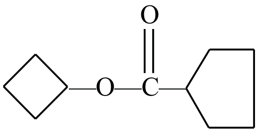
(c) $(CH_3)_2C{=}CH_2 + HBr \xrightarrow{\text{Peroxide}} (CH_3)_2CHCH_2Br$

(d) $(CH_3)_2CHCH_2Br \xrightarrow[S_N2]{CH_3ONa} (CH_3)_2CHCH_2OCH_3$

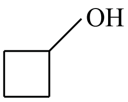
(e) $(CH_3)_2CHCH_2Br + CH_3COONa \longrightarrow (CH_3)_2CHCH_2OCOCH_3$

(f) $(CH_3)_2CHCH_2Br + KCN(aq) \longrightarrow (CH_3)_2CHCH_2CN$

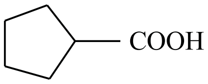
939.



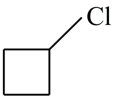
A



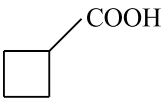
B



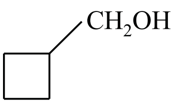
C



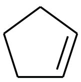
D



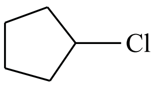
E



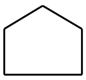
F



G

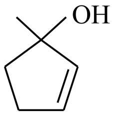


H

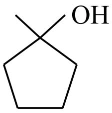


I

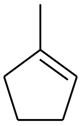
940.



A

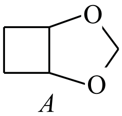


B

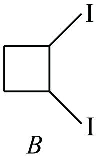


C

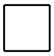
941.



A



B



C

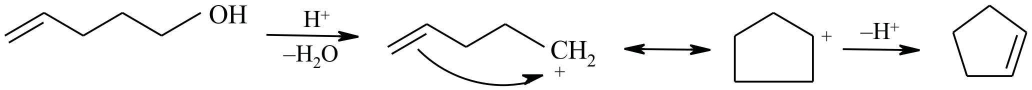
942. (a) 2-methyl propene + $B_2H_6 \xrightarrow[NaOH]{H_2O_2}$ Product

(b) 2-methyl propene + $B_2D_6 \xrightarrow{CH_3COOT}$ Product.

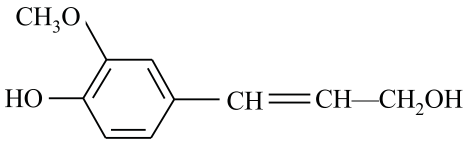
(c) 2-methyl propene + $B_2H_6 \xrightarrow{CH_3COOT}$ Product.

(d) 2-methylpropene + $B_2H_6 + H_2O_2 \xrightarrow{NaOH} (CH_3)_2CHCH_2OH \xrightarrow{NaH} \xrightarrow{C_2H_5Br}$ Product.

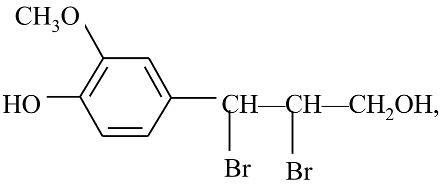
943.



944.



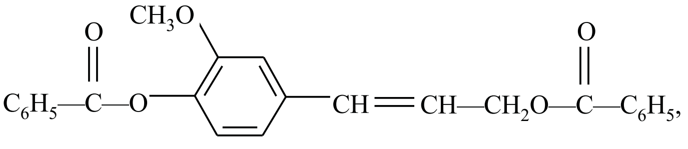
X



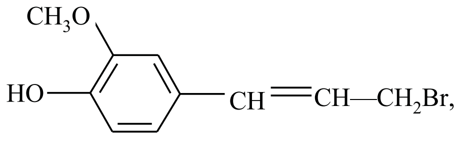
A

HO—CH$_2$—CHO

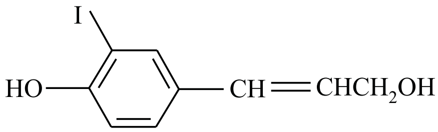
B



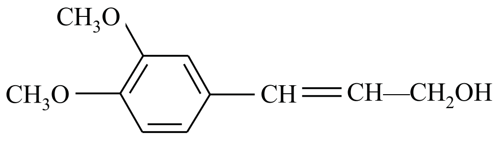
C



D

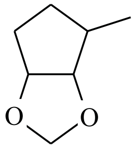


E

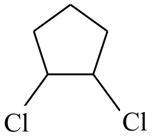


F

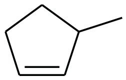
945.



A

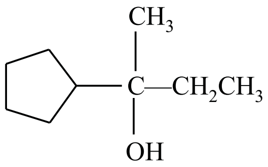


B

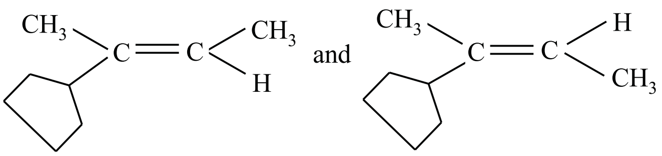


C

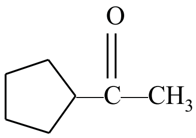
946.



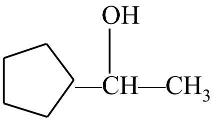
A



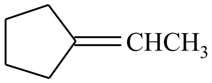
B



C

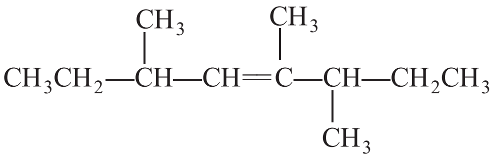


D



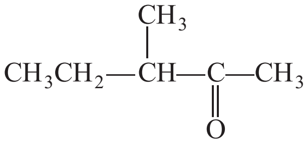
E

947.



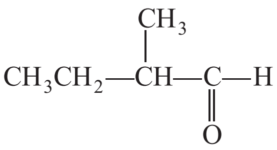
$$\mathrm{CH_3CH_2-\overset{CH_3}{\overset{|}{C}}H-CH=\overset{CH_3}{\overset{|}{C}}-\underset{\underset{CH_3}{|}}{CH}-CH_2CH_3}$$

A



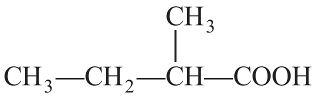
$$\mathrm{CH_3CH_2-\overset{CH_3}{\overset{|}{C}}H-\underset{\underset{O}{\|}}{C}-CH_3}$$

B



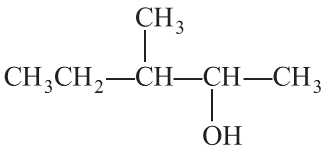
$$\mathrm{CH_3CH_2-\overset{CH_3}{\overset{|}{C}}H-\underset{\underset{O}{\|}}{C}-H}$$

C



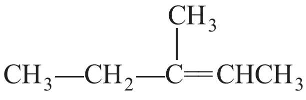
$$\mathrm{CH_3-CH_2-\overset{CH_3}{\overset{|}{C}}H-COOH}$$

D



$$\mathrm{CH_3CH_2-\overset{CH_3}{\overset{|}{C}}H-\underset{\underset{OH}{|}}{CH}-CH_3}$$

E

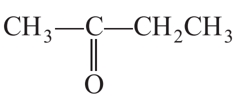


$CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CHCH_3$

F

CH_3CHO

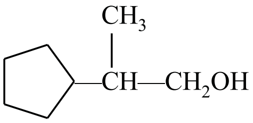
G



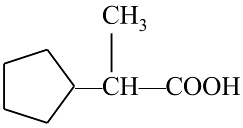
$CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-CH_2CH_3$

H

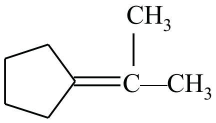
948.



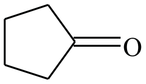
A



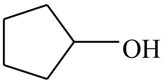
B



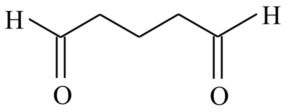
C



D

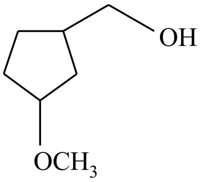


E

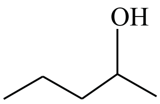


F

949. (a)

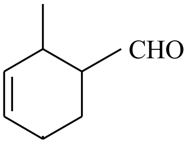


(b)

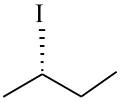


(enantiomers)

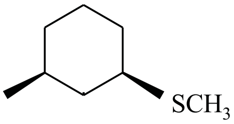
(c)



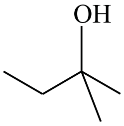
(d)



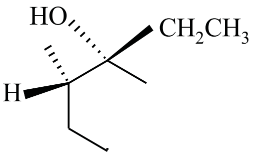
(e)



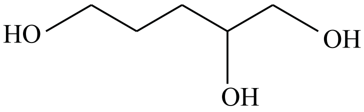
(f)



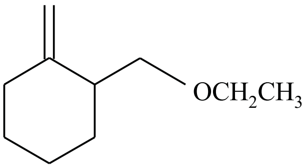
(g)



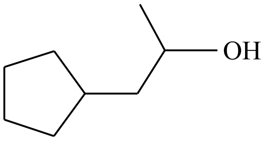
(h)



(i)



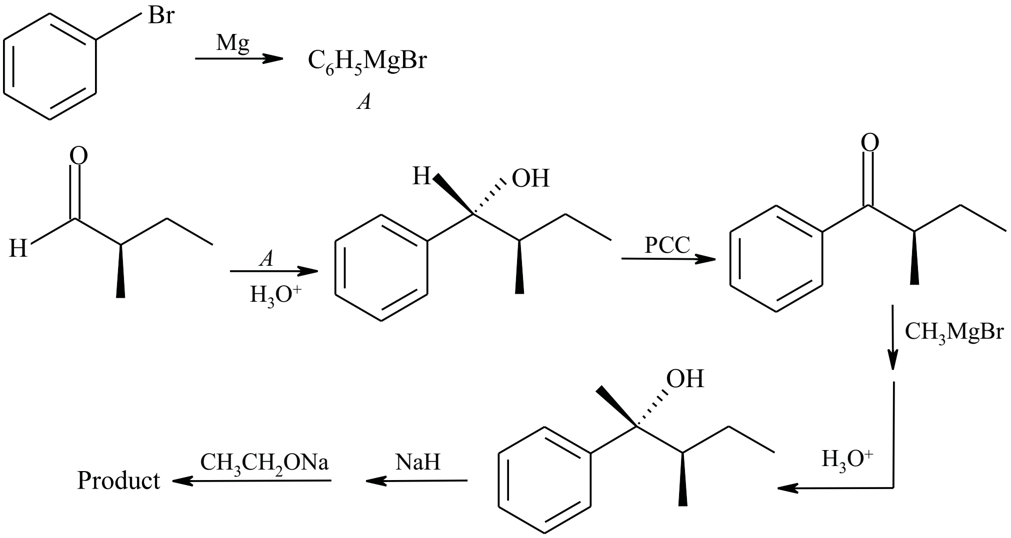
(j)



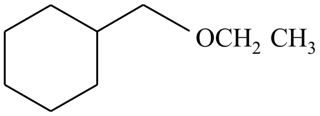
(enantiomers)

950. (a) PCC, (b) $NaBH_4$, H_3O^+, (c) Pd/C, (d) Mg, Ethyleneoxide, H_3O^+, PBr_3,
(e) TsCl, CH_3ONa, (f) $SOCl_2$, Mg/ether, CH_2O, H_3O^+,
(g) Ethylene glycol/ H^+, $LiAlH_4$, H_3O^+, (h) CH_3MgBr, H_3O^+.

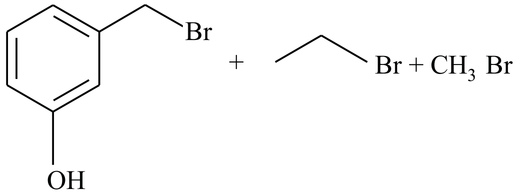
951.



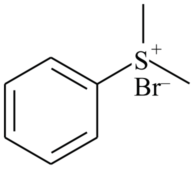
952. (a)



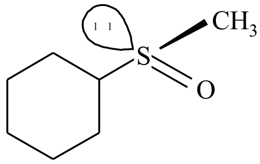
(b)



(c)

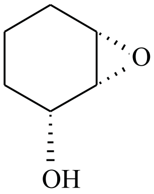


(d)

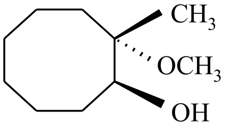


enantiomers

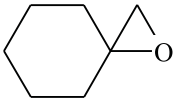
(e)



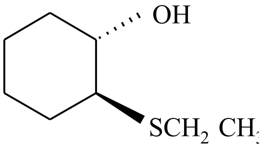
(f)



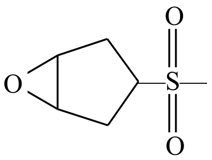
(g)



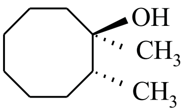
(h)



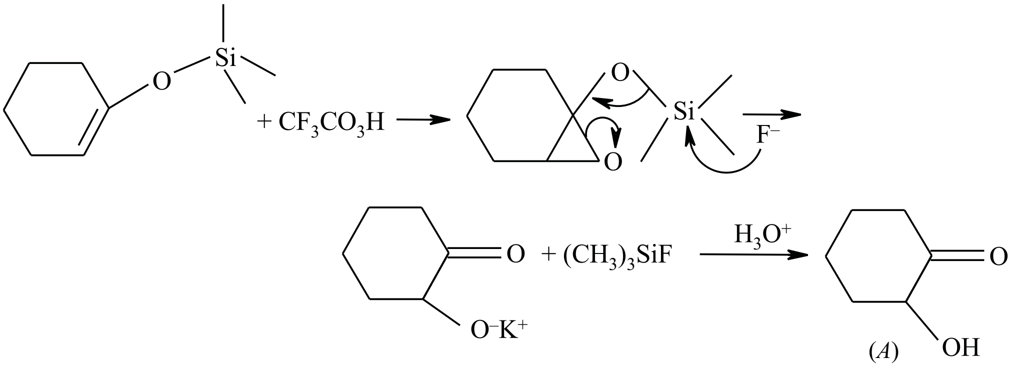
(i)



(j)

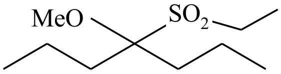


953.

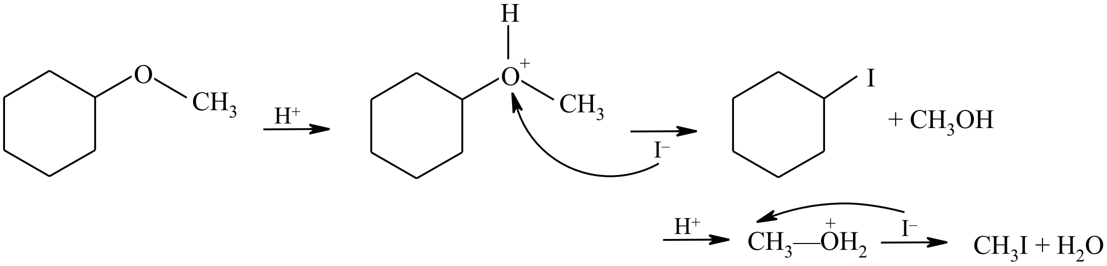


954. *A* : CH_3MgBr/Ether, H_3O^+; *B* : $NaOCH_3$, H_3O^+, NaH/CH_3CH_2Br; *C* : mCPBA;

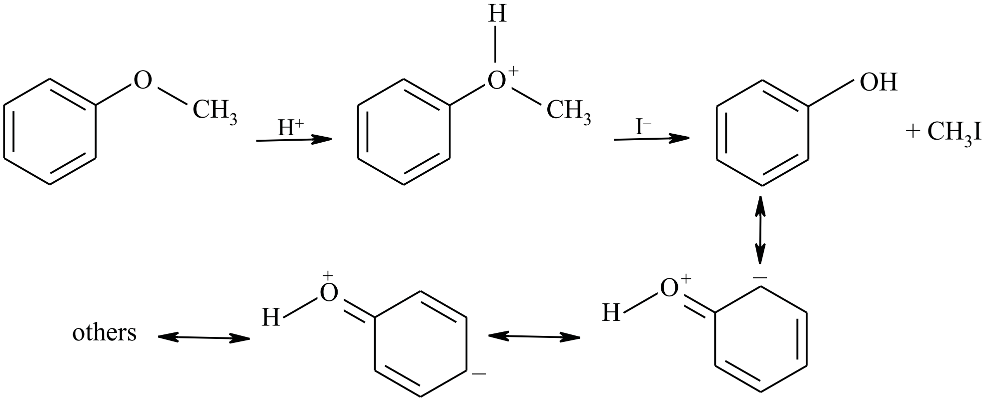
D : $Hg(OAc)_2$, CH_3OH, $NaBH_4$; *E* : CH_3CH_2SNa/H_3O^+ *F* :



955. In case of reaction 1, the mechanism is a series of protonation and S_N2 reactions as:

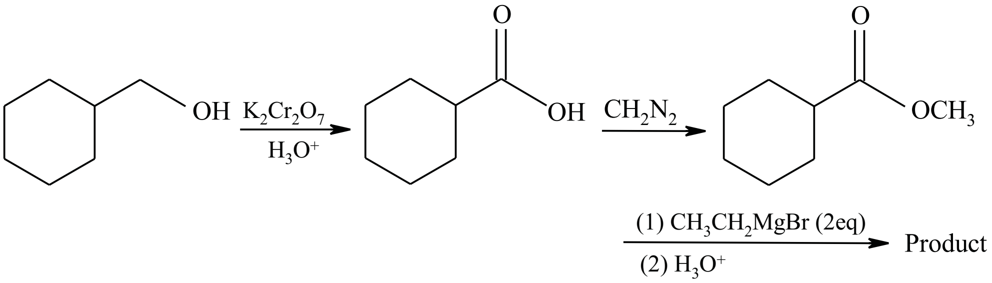


In the case of reaction 2, the mechanism is also a series of protonation and S_N2 reaction. However, phenol is not converted to iodobenzene because of protonated phenol can't be substituted by iodide ion (I^-) due to strong C—O bond in phenol:

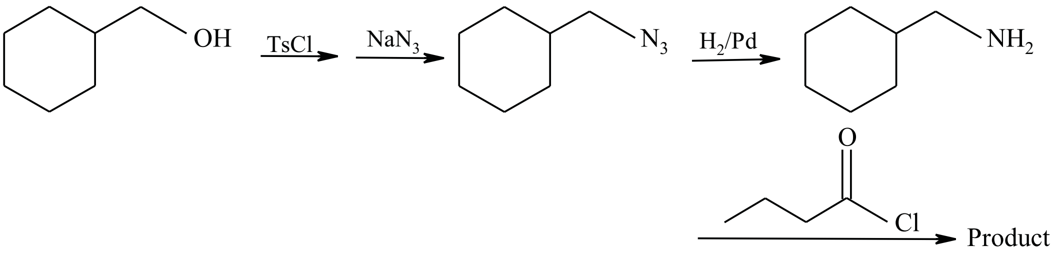


Carbon-oxygen bond acquire partial double bond character, can't be substituted under S_N2 conditions.

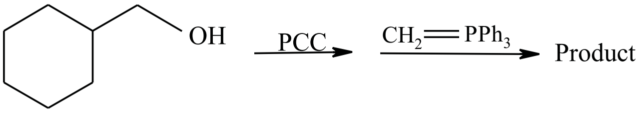
956. (a)



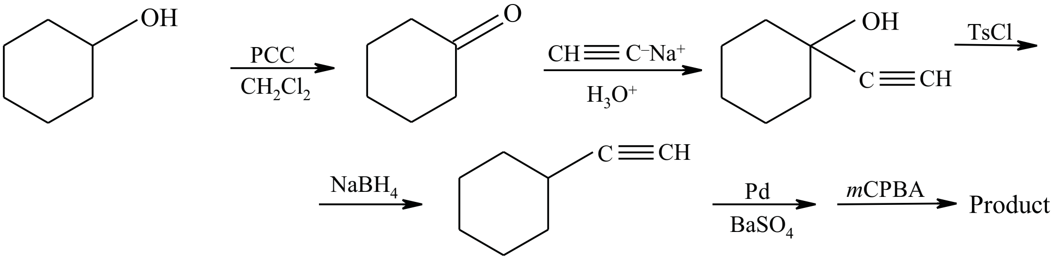
(b)



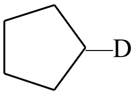
(c)



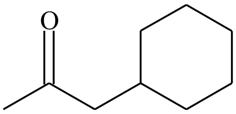
(d)



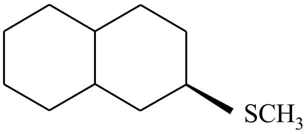
957. (a)



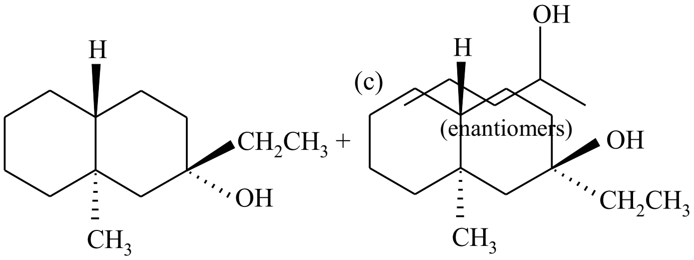
(b)



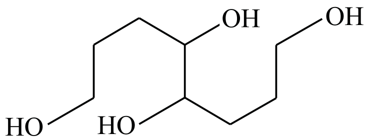
(d)



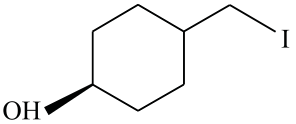
(e)



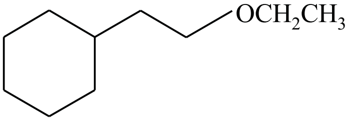
(f)



(g)

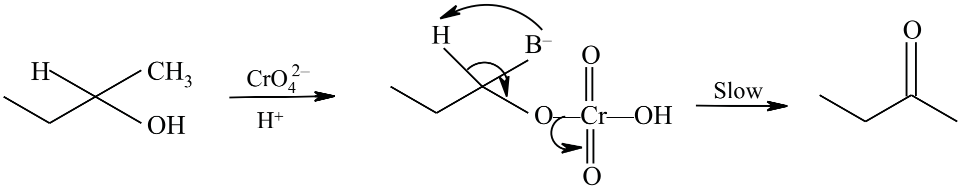


(h)



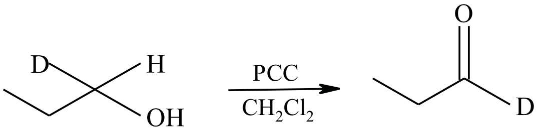
958. (a) (1) PCC, (2) CH_3Li, (3) H_3O^+; (b) HI/Red P; (c) (1) $SOCl_2$, (2) Mg/ether; (3) , (4) H_3O^+; (d) (1) PCC, (2) $NaBH_4$, (3) H_3O^+.

959.



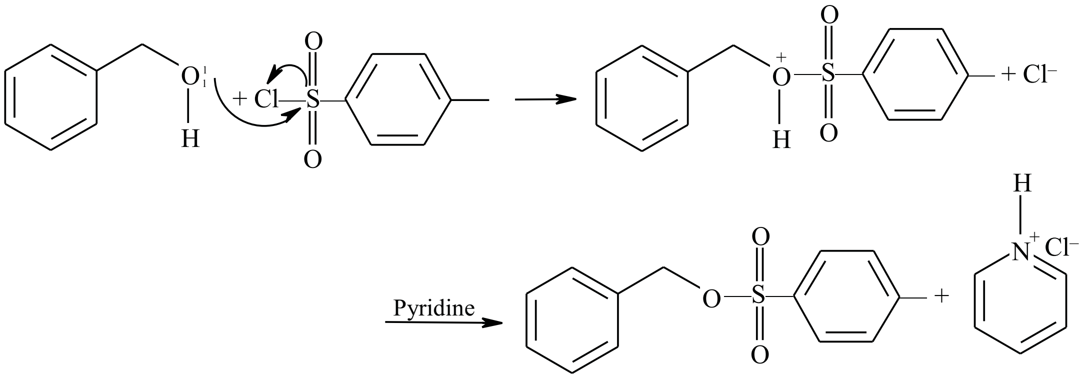
C—H bond cleavage occur in slow rate determing step. Therefore, replacement of H by D will slow down the rate of reaction.

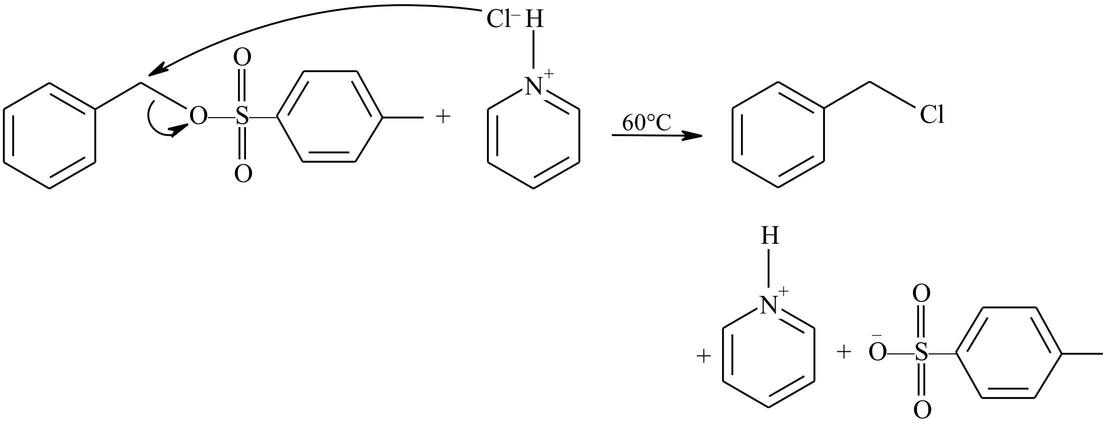
C :



C—H bond will be broken in preference to C—D bond.

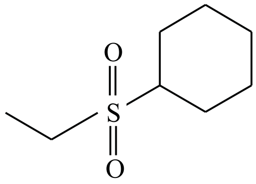
960.



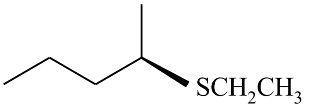


Higher temperature promotes SN–2 reaction of tosylate by chloride ion generated in the first step of reaction.

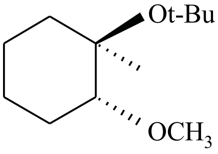
961. (a)



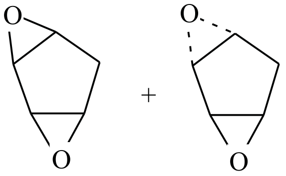
(b)



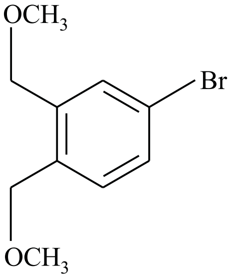
(c)



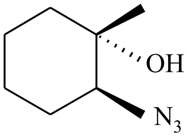
(d)



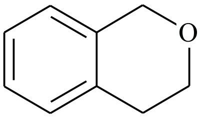
(e)



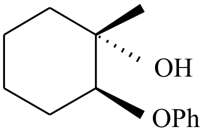
(f)



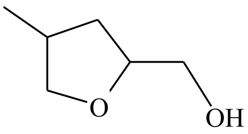
(g)



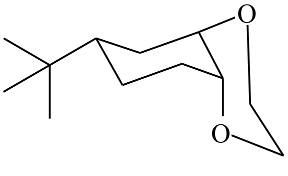
(h)



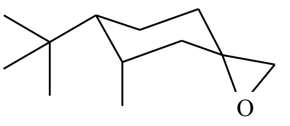
(i)



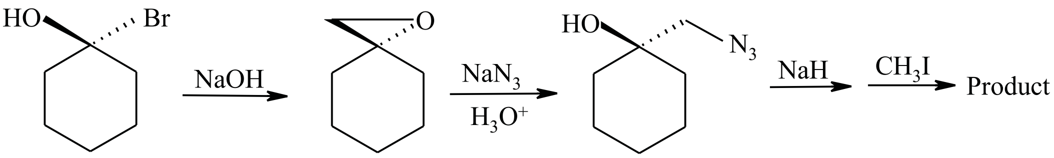
(j)



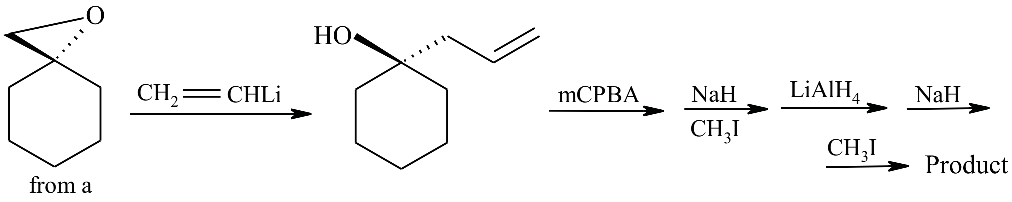
(k)



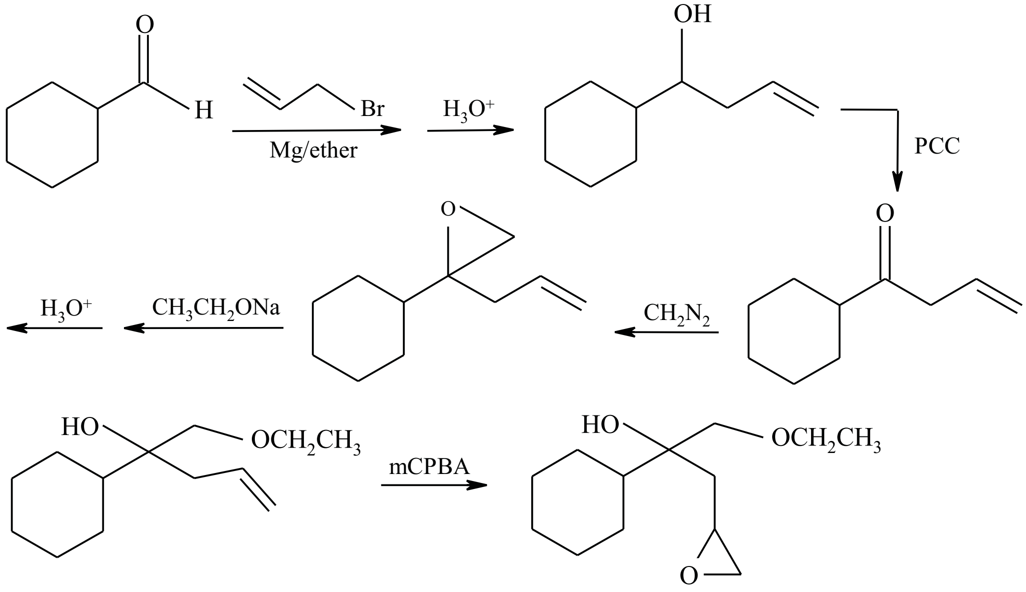
962. (a)



(b)

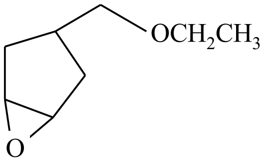


963.

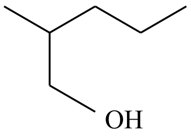


964. I > II > III > IV.

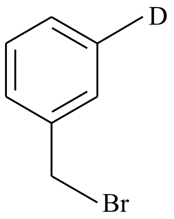
965. (a)



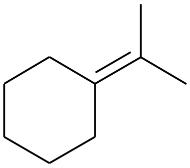
(b)



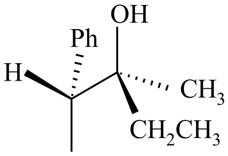
(c)



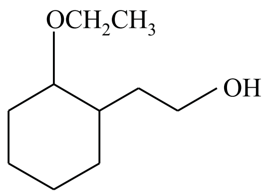
(d)



(e)

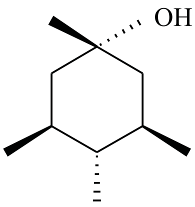


966. (a)



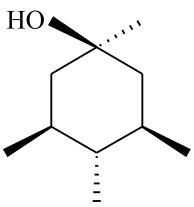
(enantiomers)

(b)



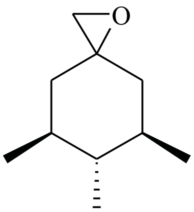
(Major)

(c)

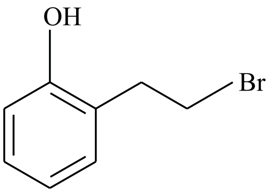


(Major)

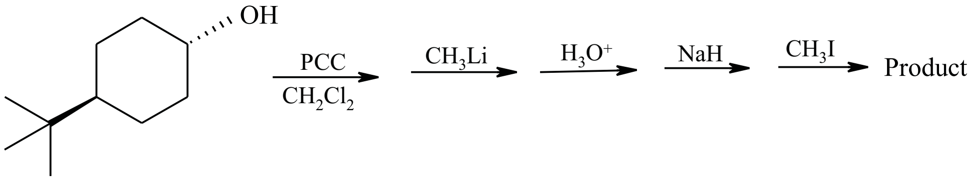
(d)



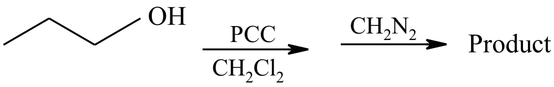
(e)



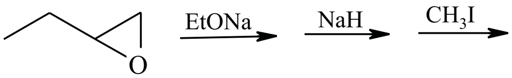
967. (a)



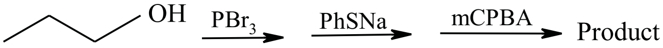
(b)



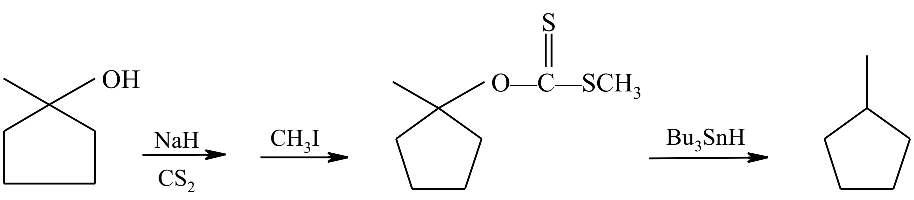
(c)



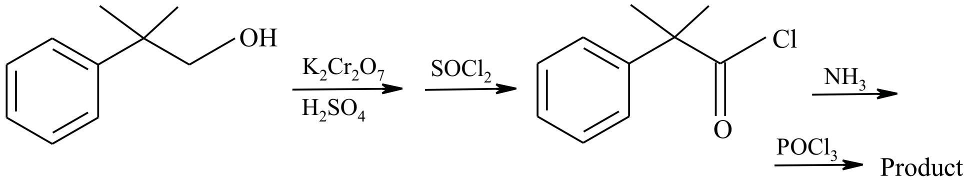
(d)



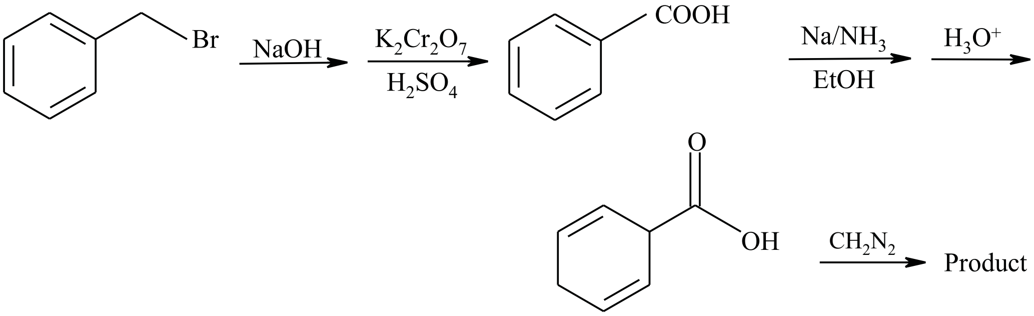
968. There are two problems with the route outlined above. First, because the above alcohol is tertiary, it will be difficult to make the tosylate, which is a large, sterically demanding group. If you can make it, the second step is also difficult as it require SN–2 reaction of a tertiary tosylate by H. This system is very hindered and will not readily undergo susbtitution reaction. Elimination will be a serious competition reaction. A better method would be as follows:



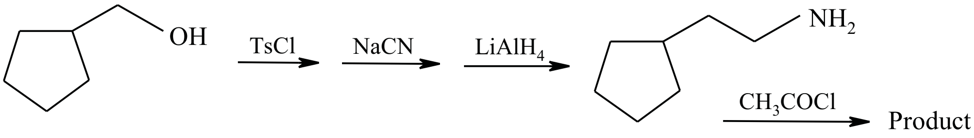
969. (a)



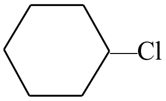
(b)



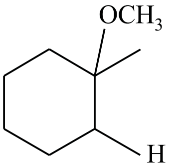
(c)



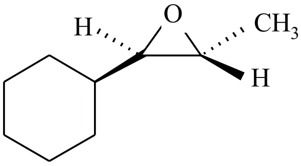
970. (a)



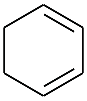
(b)



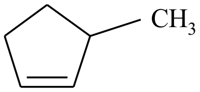
(c)



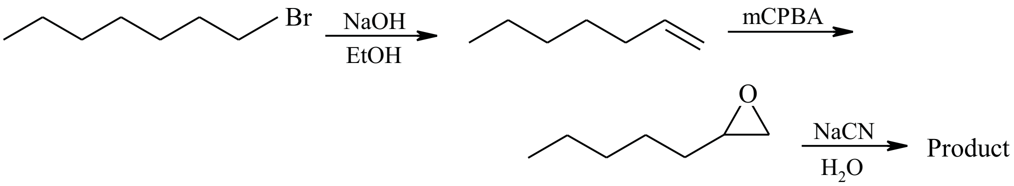
(d)



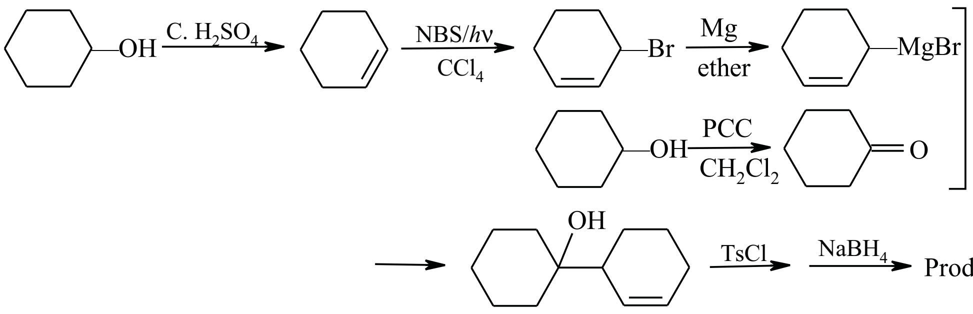
(e)



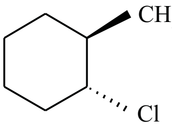
971. (a)



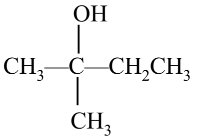
(b)



972. (a)

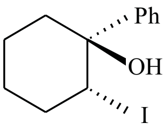


(b)

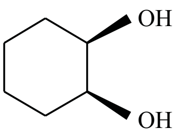


$\mathrm{CH_3{-}\underset{CH_3}{\overset{OH}{C}}{-}CH_2CH_3}$

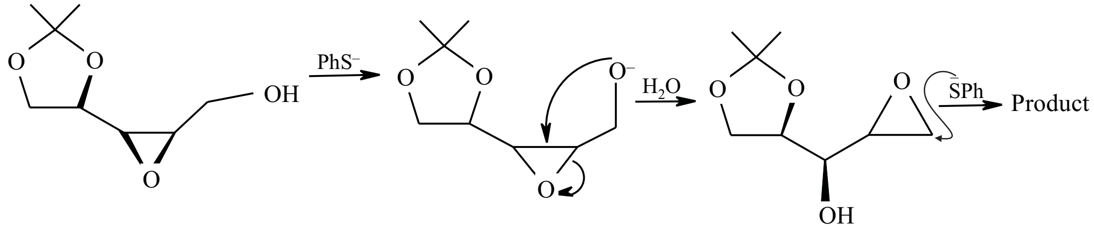
(c)



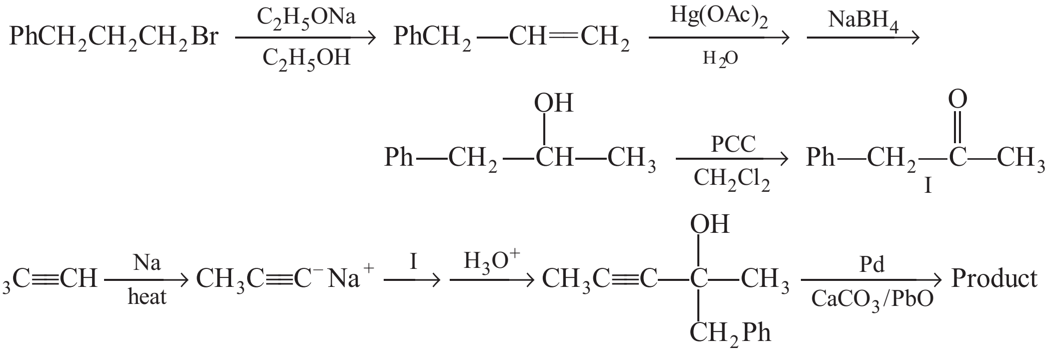
(d)



973.



975. (a)

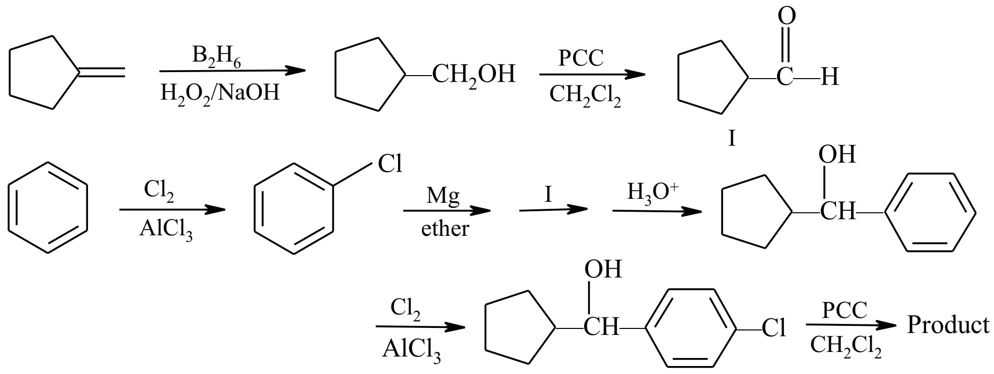


$$\mathrm{PhCH_2CH_2CH_2Br}\xrightarrow[\mathrm{C_2H_5OH}]{\mathrm{C_2H_5ONa}}\mathrm{PhCH_2{-}CH{=}CH_2}\xrightarrow[\mathrm{H_2O}]{\mathrm{Hg(OAc)_2}}\xrightarrow{\mathrm{NaBH_4}}$$

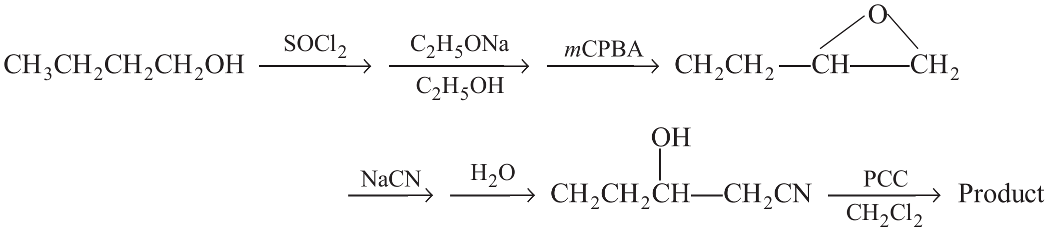
$$\mathrm{Ph{-}CH_2{-}\overset{OH}{CH}{-}CH_3}\xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{PCC}}\mathrm{Ph{-}CH_2{-}\underset{I}{\overset{O}{\overset{\|}{C}}}{-}CH_3}$$

$$\mathrm{CH_3C{\equiv}CH}\xrightarrow[\text{heat}]{\mathrm{Na}}\mathrm{CH_3C{\equiv}C^-Na^+}\xrightarrow{\mathrm{I}}\xrightarrow{\mathrm{H_3O^+}}\mathrm{CH_3C{\equiv}C{-}\underset{CH_2Ph}{\overset{OH}{C}}{-}CH_3}\xrightarrow[\mathrm{CaCO_3/PbO}]{\mathrm{Pd}}\text{Product}$$

(b)



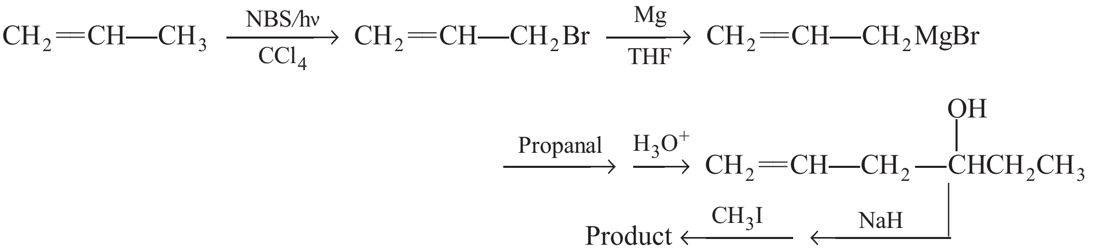
(c)



$$CH_3CH_2CH_2CH_2OH \xrightarrow{SOCl_2} \xrightarrow[C_2H_5OH]{C_2H_5ONa} \xrightarrow{mCPBA} CH_2CH_2-\overset{\;O\;}{CH-CH_2}$$

$$\xrightarrow{NaCN} \xrightarrow{H_2O} CH_2CH_2\overset{OH}{\overset{|}{C}}H-CH_2CN \xrightarrow[CH_2Cl_2]{PCC} \text{Product}$$

976.

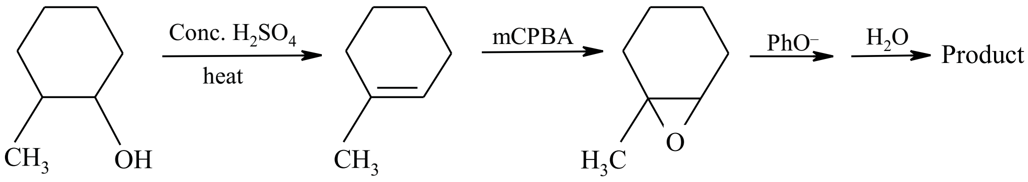


$$CH_2{=}CH-CH_3 \xrightarrow[CCl_4]{NBS/h\nu} CH_2{=}CH-CH_2Br \xrightarrow[THF]{Mg} CH_2{=}CH-CH_2MgBr$$

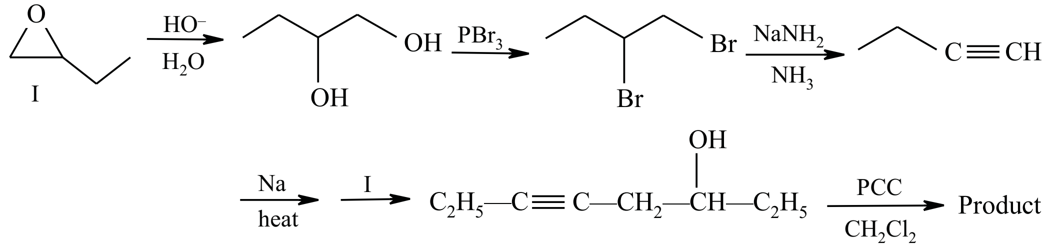
$$\xrightarrow{\text{Propanal}} \xrightarrow{H_3O^+} CH_2{=}CH-CH_2-\overset{OH}{\overset{|}{C}}HCH_2CH_3$$

$$\text{Product} \xleftarrow{CH_3I} \xleftarrow{NaH}$$

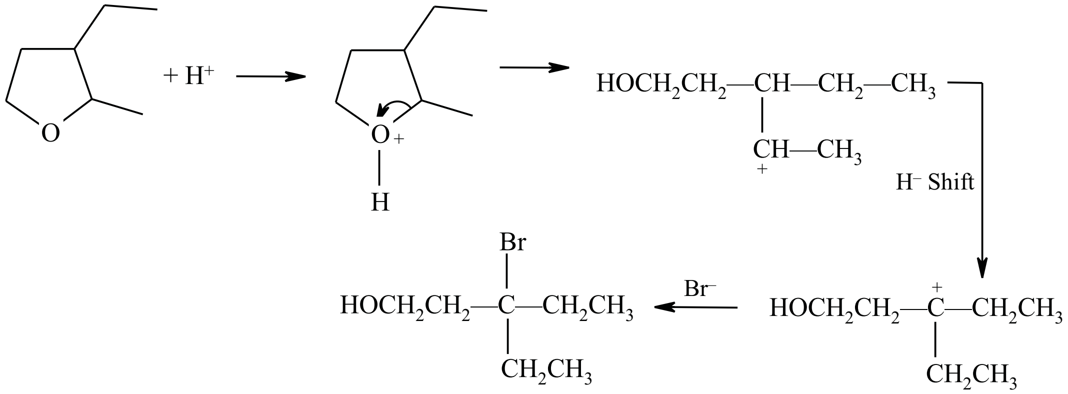
977. (a)



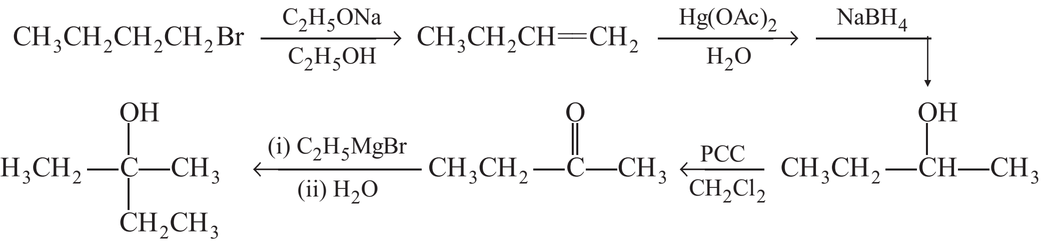
(b)



978.

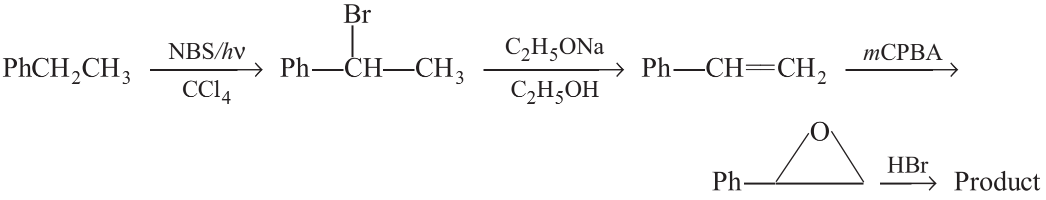


979. (a)

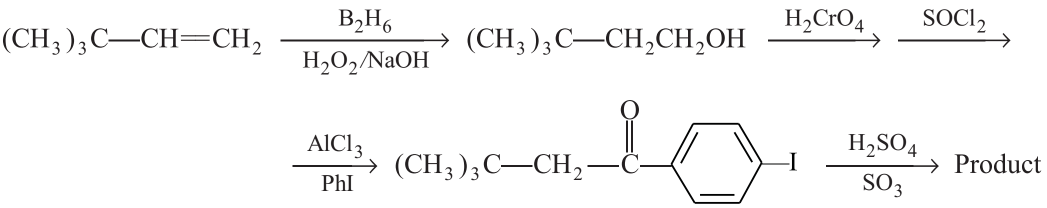


$$CH_3CH_2CH_2CH_2Br \xrightarrow[C_2H_5OH]{C_2H_5ONa} CH_3CH_2CH{=}CH_2 \xrightarrow[H_2O]{Hg(OAc)_2} \xrightarrow{NaBH_4} CH_3CH_2-\overset{OH}{\overset{|}{CH}}-CH_3 \xrightarrow[CH_2Cl_2]{PCC} CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[(ii)\ H_2O]{(i)\ C_2H_5MgBr} CH_3CH_2-\underset{CH_2CH_3}{\overset{OH}{C}}-CH_3$$

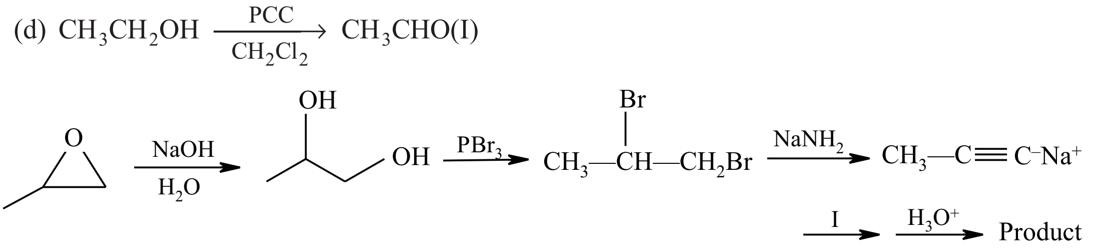
(b)



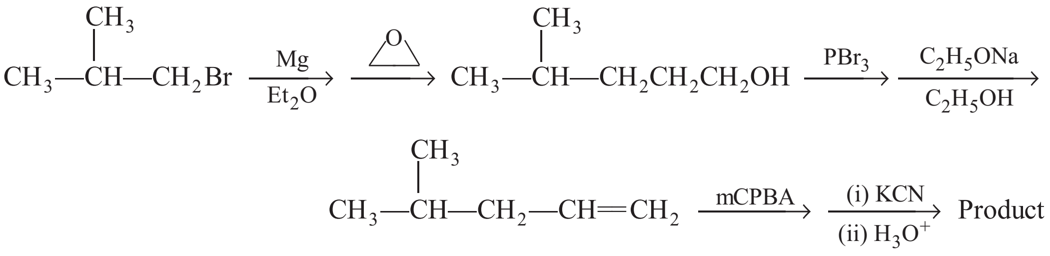
(c)



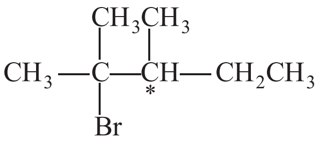
(d)



(e)



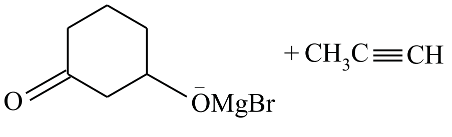
980. (a)



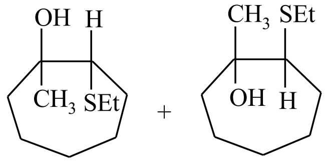
$$CH_3-\underset{Br}{\overset{CH_3}{C}}-\underset{*}{\overset{CH_3}{CH}}-CH_2CH_3$$

(Racemic)

(b)

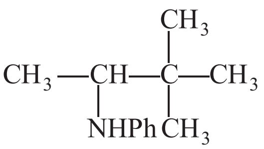


(c)



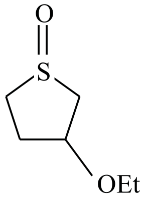
(Racemic)

(d)

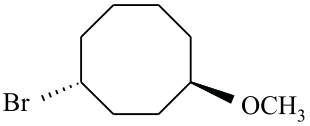


$$CH_3-\underset{NHPh}{CH}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$

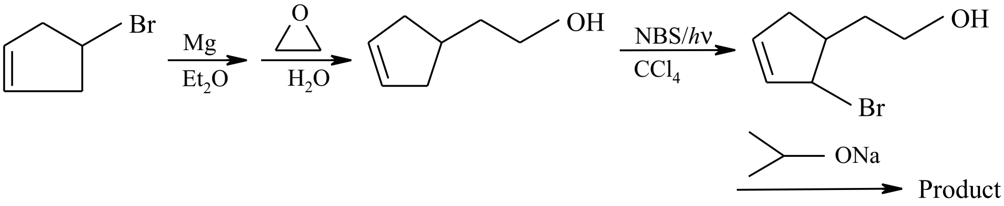
(e)



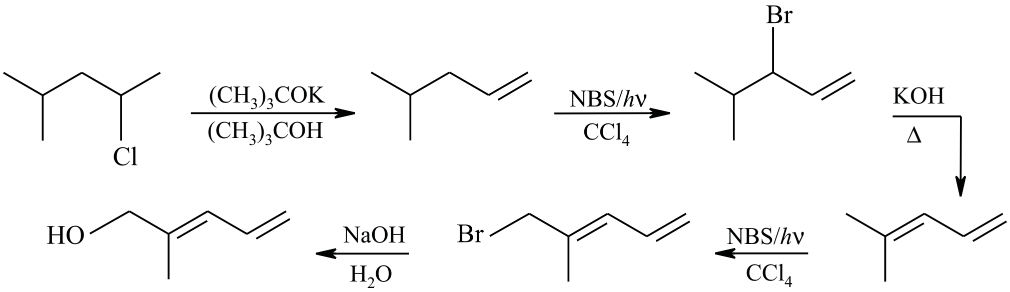
(f)



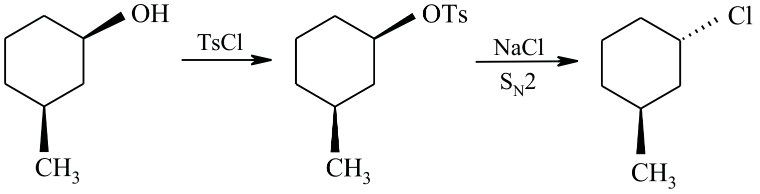
981. (a)



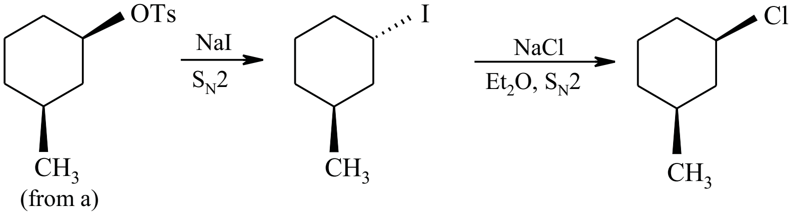
(b)



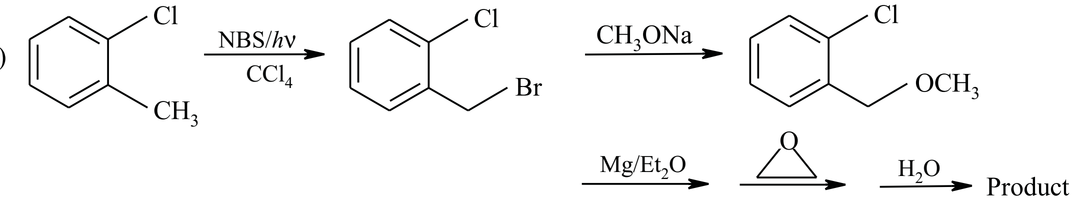
982. (a)



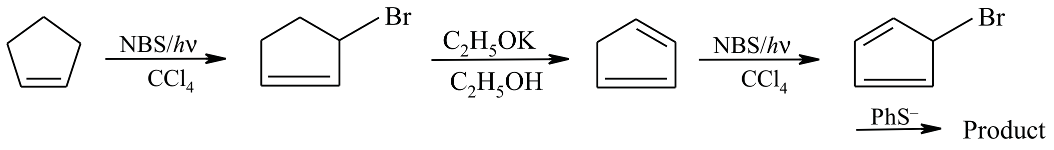
(b)



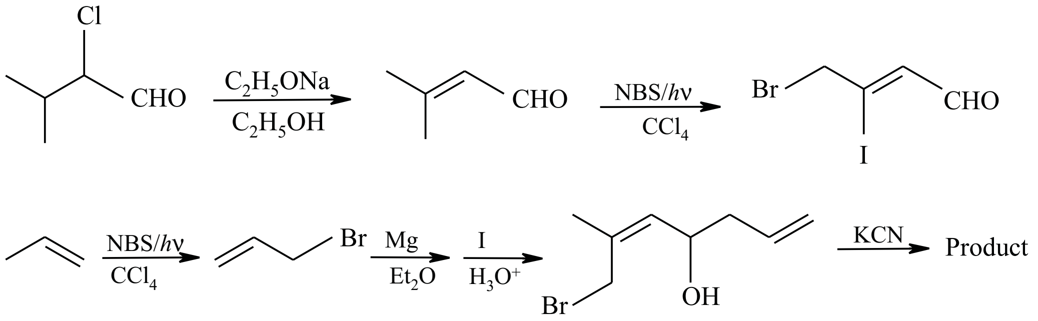
983. (a)



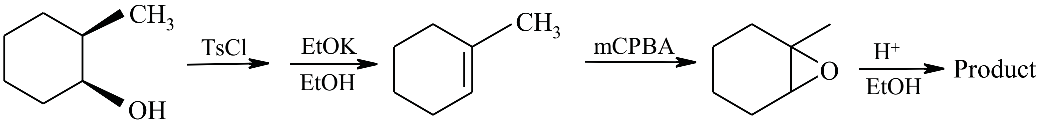
(b)



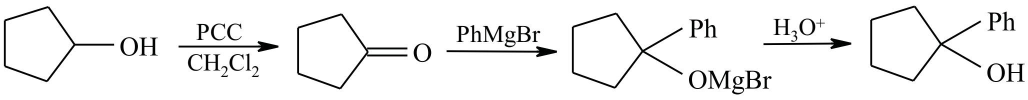
(c)



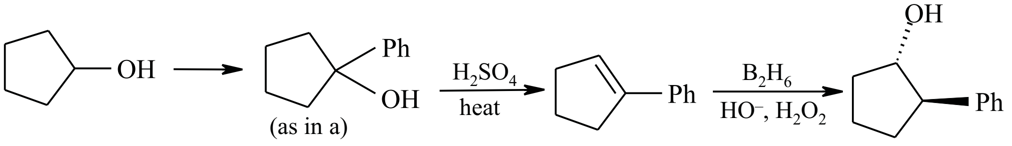
(d)



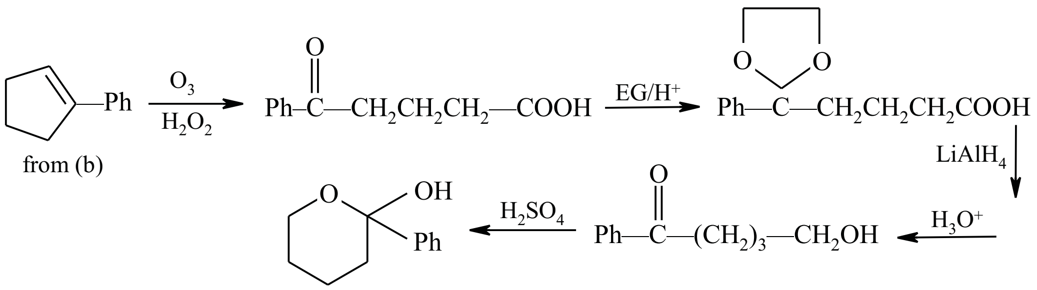
984. (a)



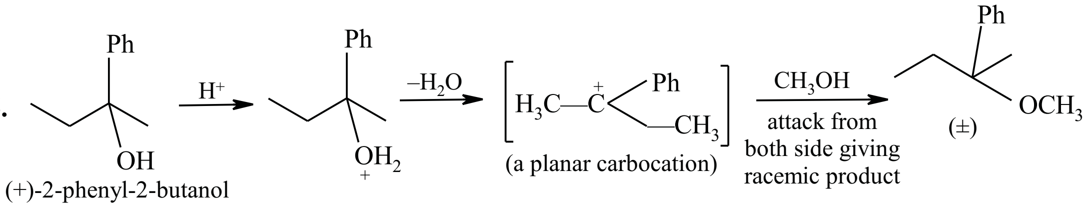
(b)



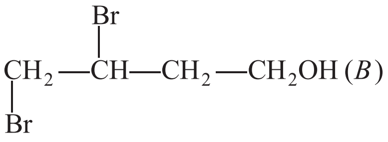
(c)



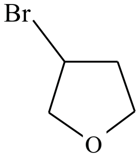
985.



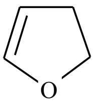
986. $CH_2{=}CH—CH_2CH_2OH$ (*A*)



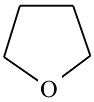
$\underset{\displaystyle Br}{CH_2}—\overset{\displaystyle Br}{CH}—CH_2—CH_2OH$ (*B*)



C

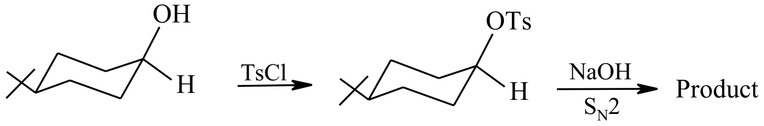


D

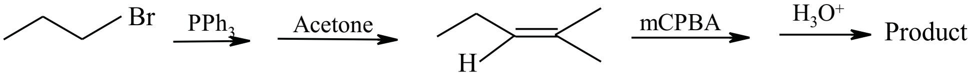


E

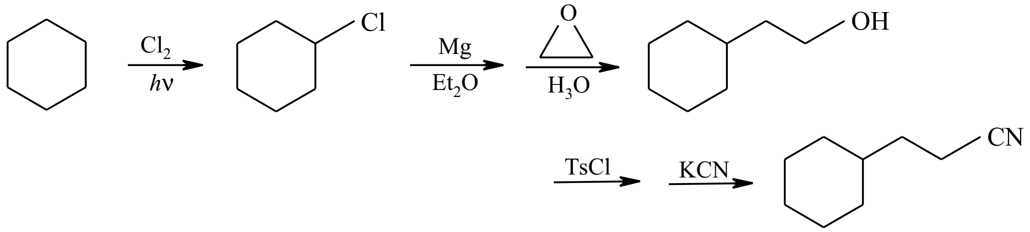
987.



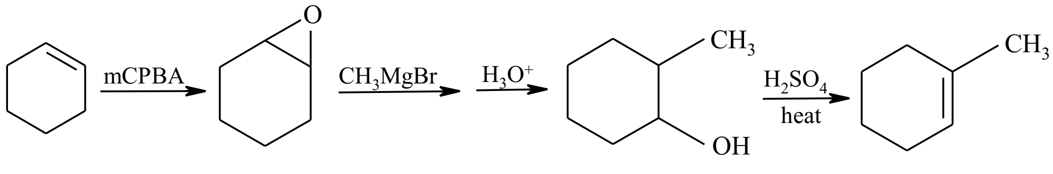
988.



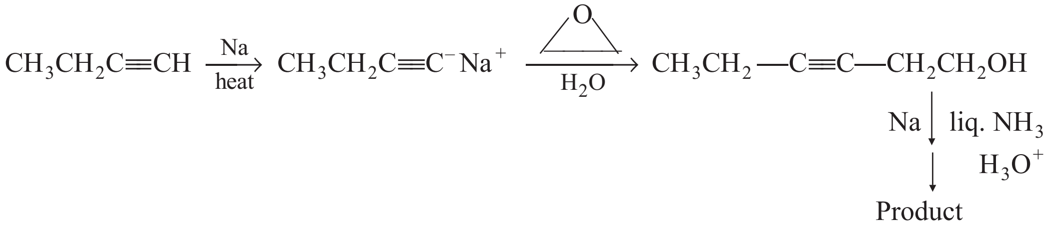
989. (a)



(b)



(c)

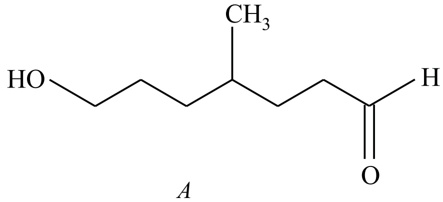


$$CH_3CH_2C{\equiv}CH \xrightarrow[\text{heat}]{\text{Na}} CH_3CH_2C{\equiv}C^-Na^+ \xrightarrow[H_2O]{\text{O}} CH_3CH_2—C{\equiv}C—CH_2CH_2OH$$

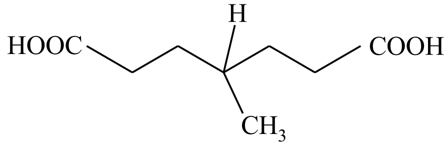
$$\downarrow \text{Na} \mid \text{liq. } NH_3,\ H_3O^+$$

Product

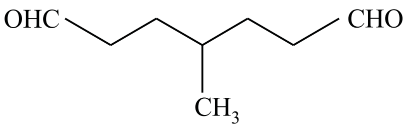
990.



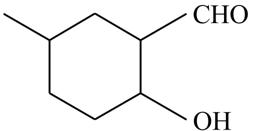
A



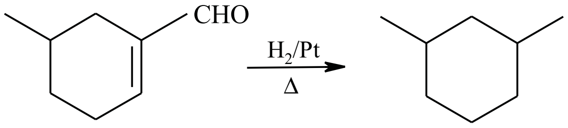
B



C

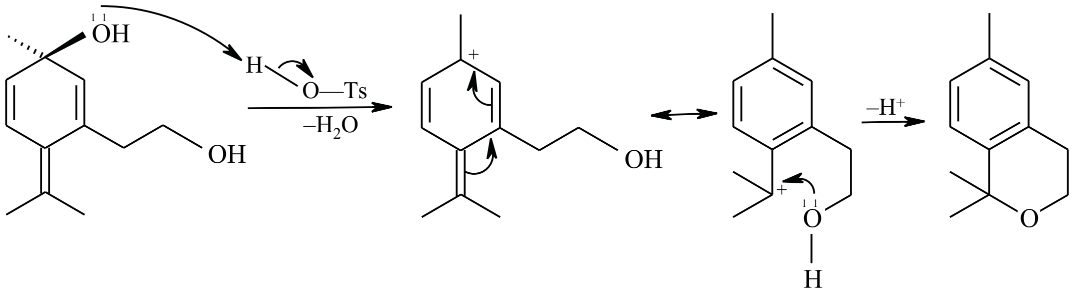


D



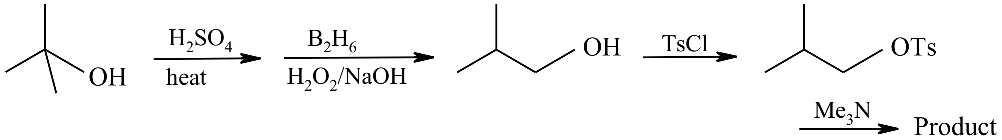
E

991.

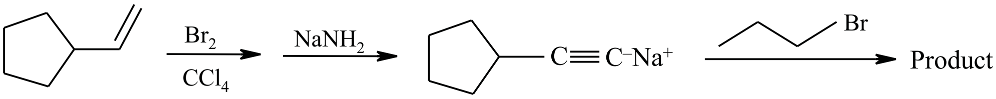


992. (a) PBr_3 (SN – 2) ⟶ C_2H_5SNa(SN–2) : Two inversion will finally lead to retention.
(b) TsCl⟶ NaCN

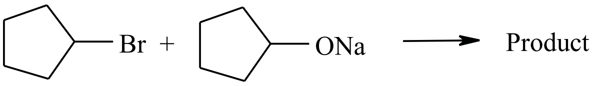
993. (a)



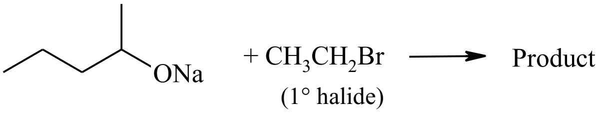
(b)

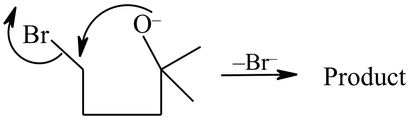


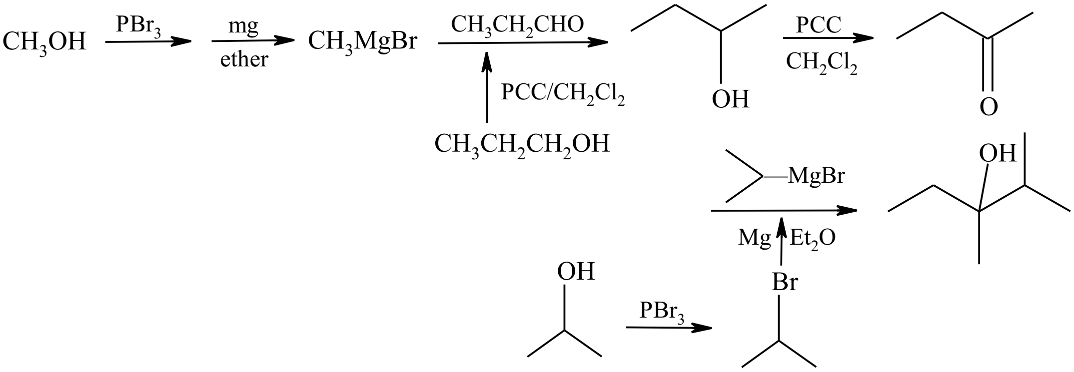
994. (a)

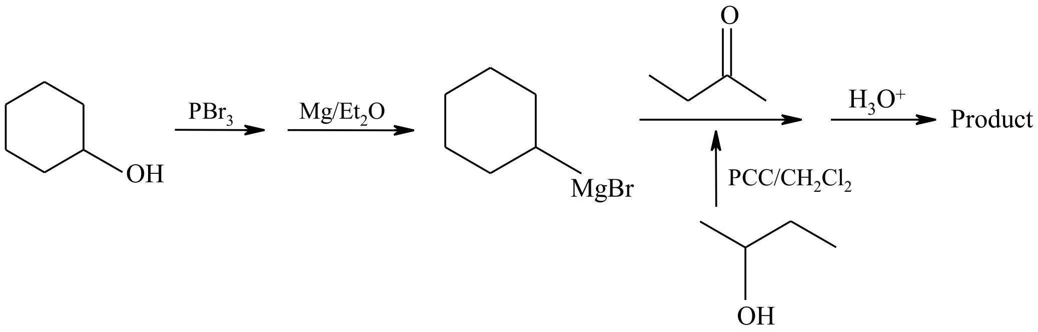


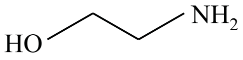
(b)

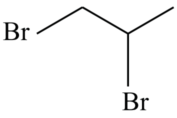


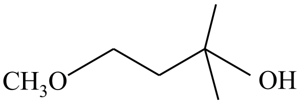
(c) 

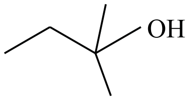
995. 

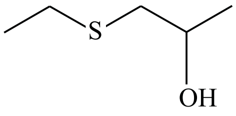
996. 

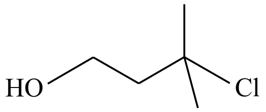
997. (a) 

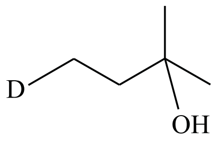
(b) 

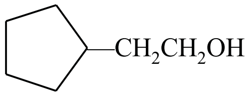
(c) 

(d) 

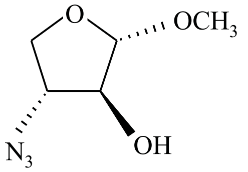
(e) 

(f) 

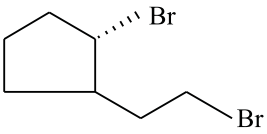
(g) 

(h) 

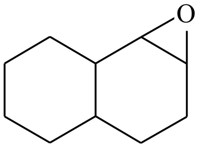
998. (a)



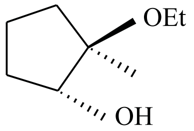
(b)



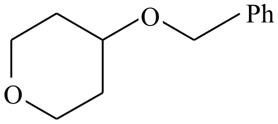
(c)



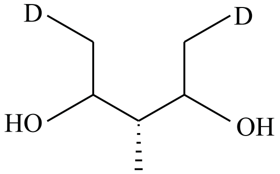
(d)



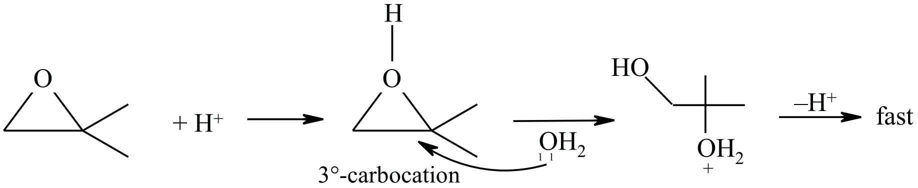
(e)

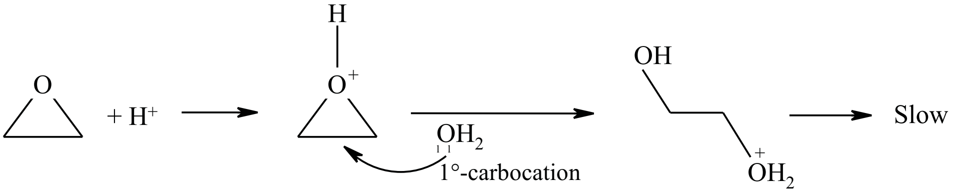


(f)

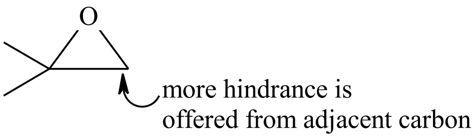


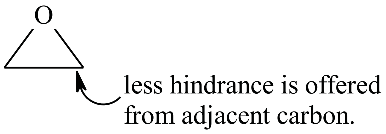
999. In acid catalyzed hydrolysis, protonation activate the reaction and stability of carbocation intermediate decides the reactivity:



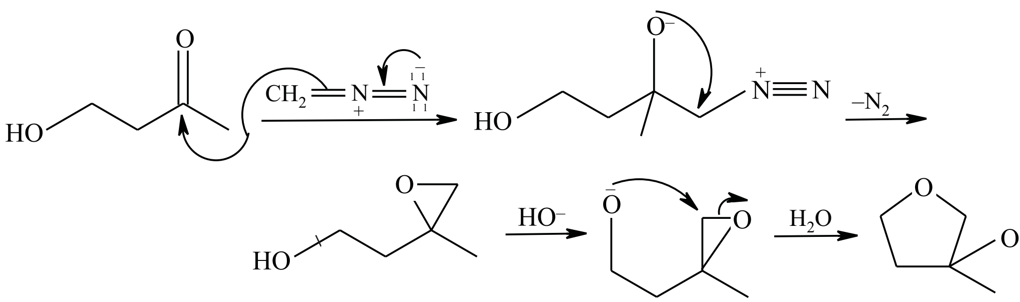


In alkaline medium, the first step is nucleophilic attack of hydroxide ion,which preferably occur at less hindered carbon:

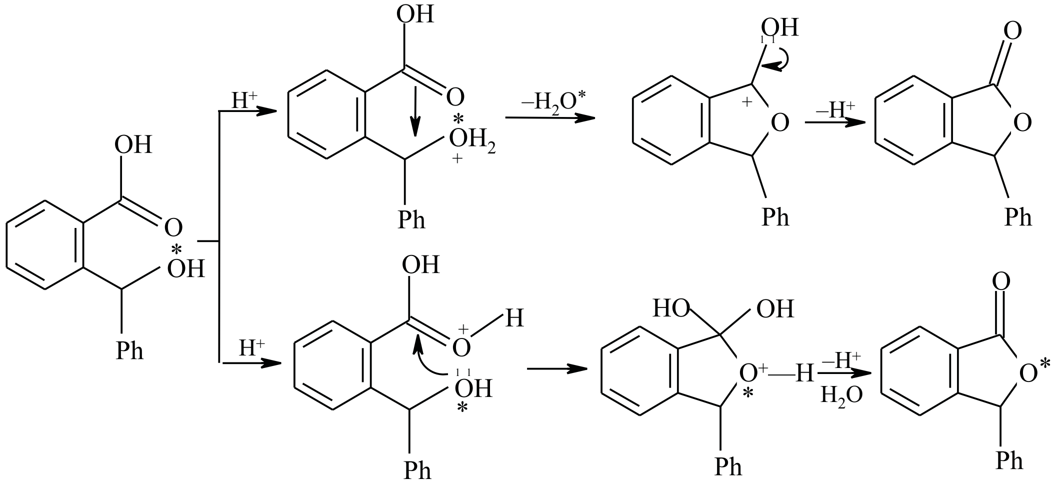




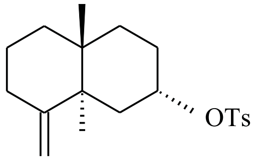
1000.



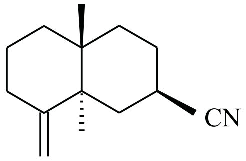
1001.



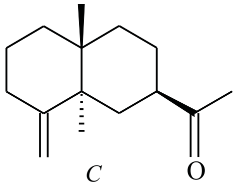
1002. (a)



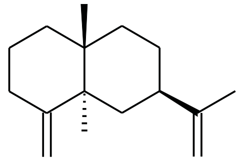
A



B

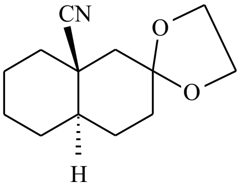


C

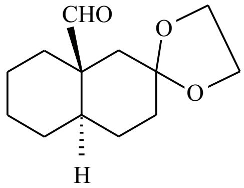


D

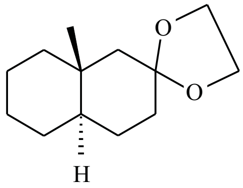
(b)



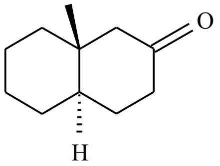
A



B



C



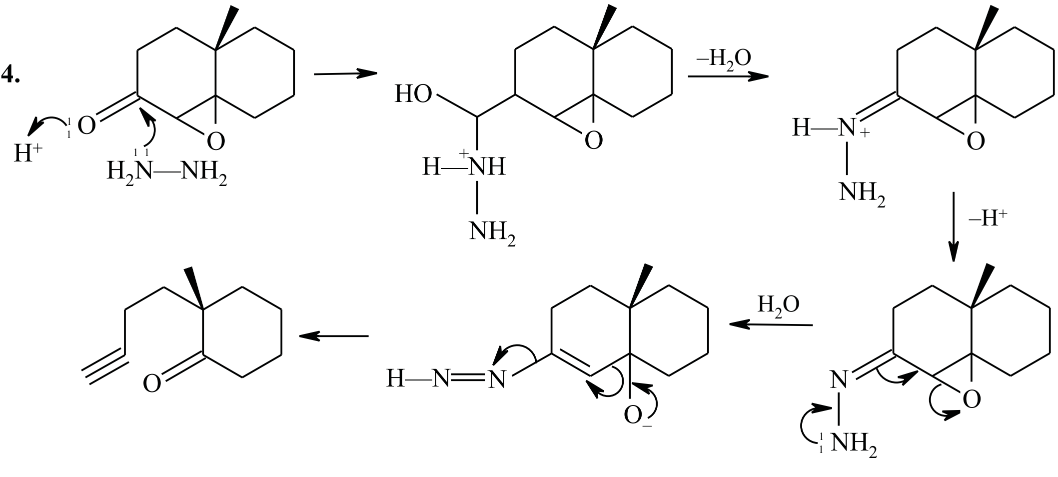
D

1003.(a) mCPBA $\longrightarrow$ H^+/MeOH,

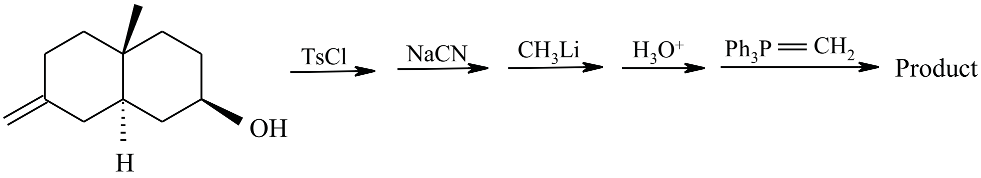
(b) mCPBA $\longrightarrow$ NaN_3/H_2O,

(c) $(CH_3)_3SBr$.

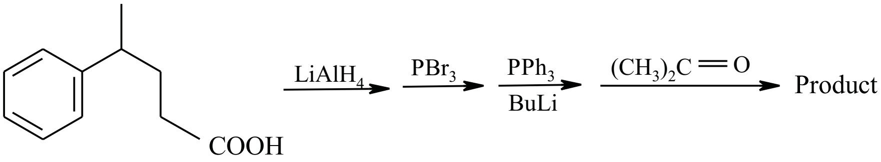
1004.



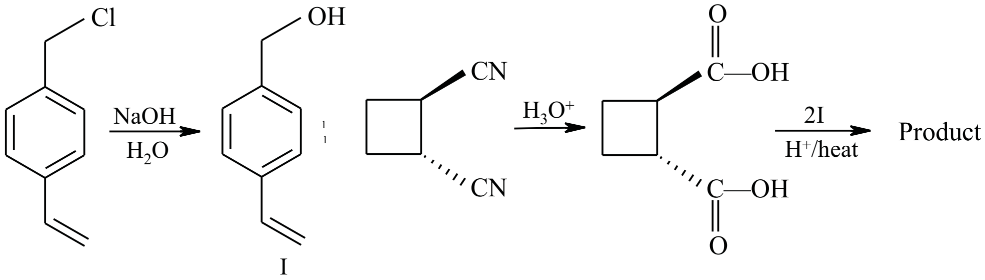
1005. (a)



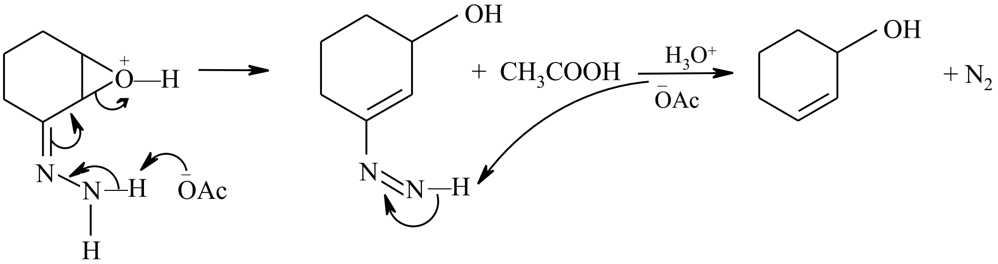
(b)



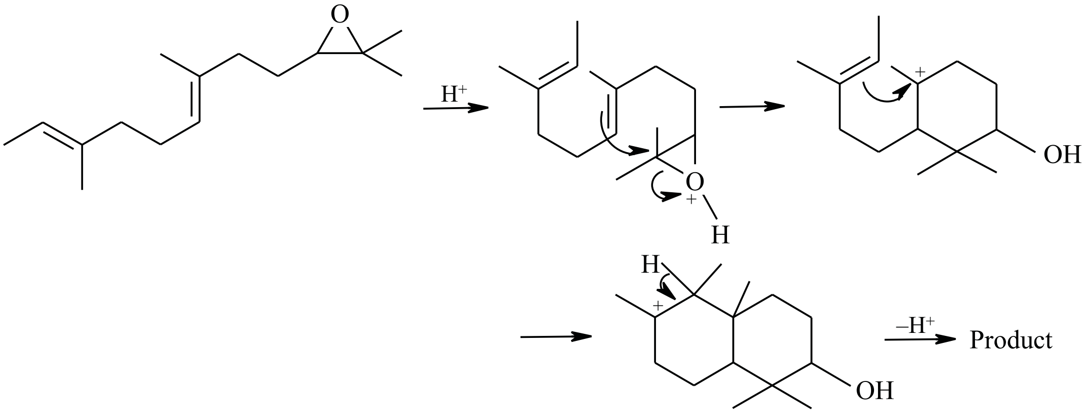
(c)

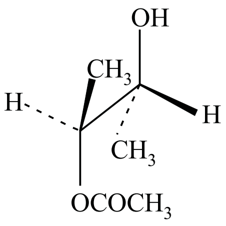


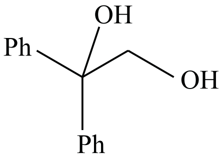
1006.

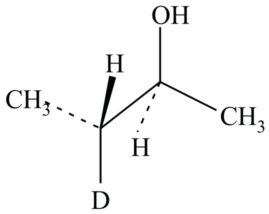


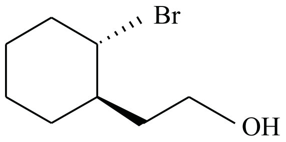
1007.

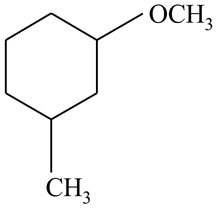


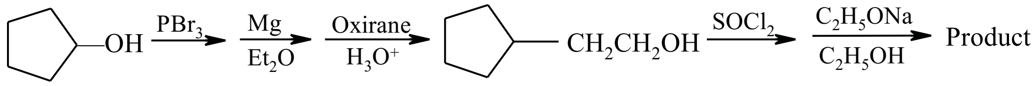
1008. (a) 

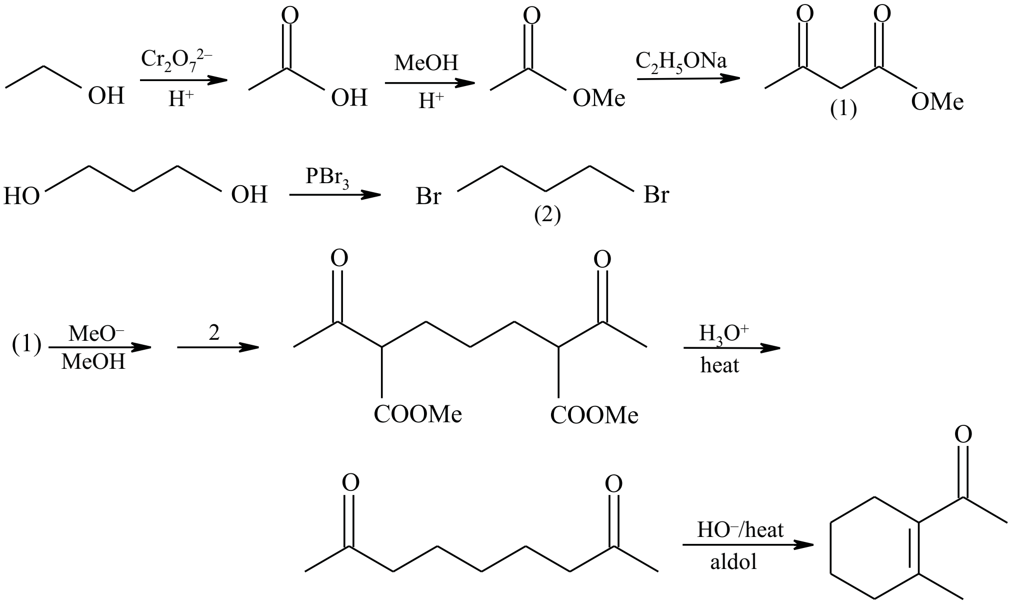
and its enantiomer. (b) 

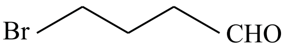
(c) 

(d) 

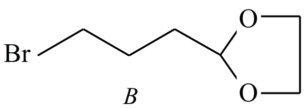
(e) 

1009. (a) 

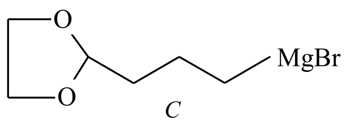
(b) 

1010. 

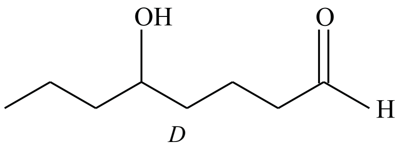
A



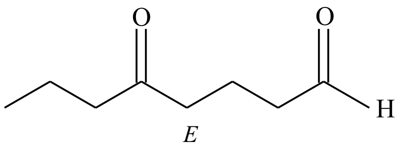
B



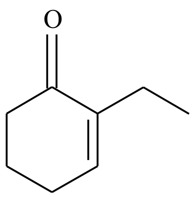
C



D

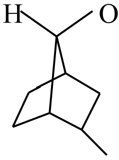


E



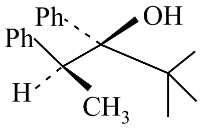
F

1011. (a)



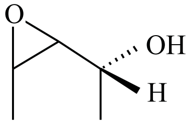
(Racemic)

(b)

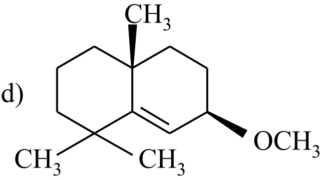


(Phenyl attack from back side, *i.e.*, from H-side to steric reason).

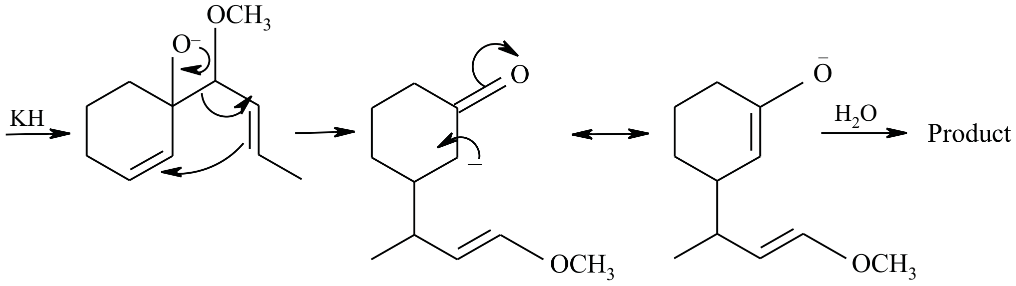
(c)



(d)



1012. (a)



(b)