

HYDROCARBONS

PROBLEM 772 A hydrocarbon *A* has molecular formula $C_{10}H_{10}$ and decolourise brown colour of bromine water. *A* on treatment with $HgSO_4/H_2SO_4$ produces two isomeric compounds *B* and *C*, both having molecular formula $C_{10}H_{12}O$. Compound *B* forms an yellow coloured precipitate on treatment with alkaline solution of I_2 while *C* does not. Also *A* on treatment with O_2 followed by work-up with H_2O_2 yields *D* ($C_8H_8O_2$) as one of the product. Heating *D* with soda lime ($NaOH/CaO$) yields *E* (C_7H_8). *E* on treatment with chlorine in presence of sunlight yields *F* (C_7H_7Cl) as single isomer while *E* on treatment with Cl_2 in dark but in presence of $AlCl_3$ produces two isomeric compounds with their molecular formula C_7H_7Cl . Deduce structures of *A* to *F*.

PROBLEM 773 An organic compound *A* has molecular formula $C_8H_{12}O$ and it evolve a colourless gas on treatment with Na-metal. Also *A* forms a white precipitate with Tollen's reagent. *A* on treatment with $HgSO_4/H_2SO_4$ yields *B* ($C_8H_{14}O_2$) which of reduction with $NaBH_4$ yields a resolvable compound *C* ($C_8H_{16}O_2$). *A* on boiling with aqueous $KMnO_4$ gives *D* ($C_7H_{12}O_3$). *D* can also be obtained by treatment of aqueous KCN with cyclohexanone followed by hydrolysing the product with dilute H_2SO_4 . Deduce structures of *A* to *D*.

PROBLEM 774 A hydrocarbon *A* has molecular formula $C_{10}H_{10}$ and decolourises brown colour of bromine water. *A* on treatment with ozone followed by work-up with dimethyl sulphide $(CH_3)_2S$ yields *B* ($C_{10}H_{10}O_2$). *B* gives positive iodoform test as well as positive Tollen's test. *A* on boiling with acidic $KMnO_4$ yield *C* ($C_8H_6O_4$) as one of the product. *C* on heating with P_2O_5 dehydrate to yield *D* ($C_8H_4O_3$). *C* does not decolourise brown colour of bromine water. Identify *A* to *D*.

PROBLEM 775 A hydrocarbon *A* has molecular formula $C_{11}H_{18}$ and it decolourise bromine water solution. *A* has a chiral centre and structure of four stereo-isomers can be drawn for *A*. *A* on treatment with H_2/Pt yields *B* ($C_{11}H_{22}$) which contain two chiral centre. *A* on treatment with O_3 followed by work-up with $Zn - H_2O$ yields the following compound and ethanol. Deduce structures of *A* and *B* and

draw structures of all stereo-isomers of *A*. $CH_3CH_2-\underset{\substack{| \\ CHO}}{CH}-CH_2-\overset{\overset{O}{||}}{C}-CH_2-\overset{\overset{O}{||}}{C}-CH_3$.

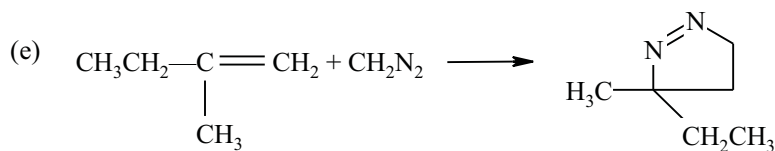
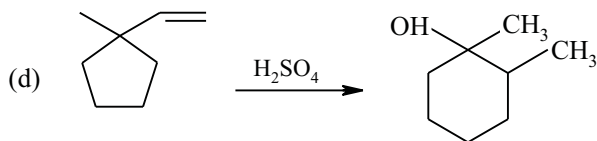
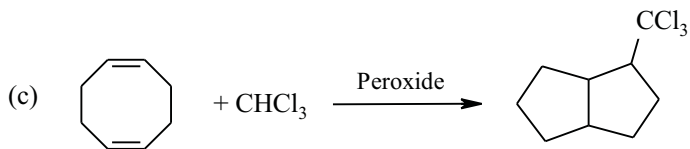
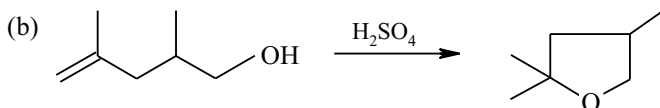
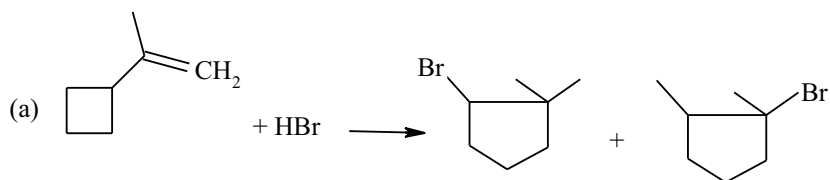
PROBLEM 776 A hydrocarbon *A* has molecular formula $C_{10}H_{18}$ and it decolourise purple colour of cold, dilute and alkaline permanganate solution. *A* on treatment with HBr yields *B* ($C_{10}H_{19}Br$) which can't be resolved into enantiomers while *A* on treating with HBr in presence of a peroxide yields, *C* an isomer of *B*, but *C* can be resolved into enantiomers. Also *A* on treatment with acidic $KMnO_4$ produces *D* ($C_7H_{12}O_2$) as one of the product which on heating with $NaOH/CaO$ yields *E* (C_6H_{12}). *E* on treating with $Cl_2(g)$ in presence of sunlight yields $C_6H_{11}Cl$ as single mono-chloro derivative. Deduce structures of *A* to *E*.

PROBLEM 777 An organic compound *A* has molecular formula $C_{13}H_{10}O$. *A* decolourises Bayer's solution but does not evolve any gas on treatment with Na-metal. *A* on controlled hydrogenation yields *B* ($C_{13}H_{14}O$) which does not decolourise brown colour of bromine water solution. *A* on treatment with O_3 followed by work-up with H_2O_2 yields *C* ($C_8H_8O_2$) and *D* ($C_5H_4O_3$). Heating *C* with $NaOH/CaO$ yields

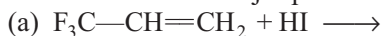
$E(C_7H_8)$ while similar treatment on D yields furan. E on heating with Br_2 yields $F(C_7H_7Br)$ F on treatment with aqueous solution of KCN followed by hydrolysis of product with dilute H_2SO_4 yields C . Deduce structures of A to F .

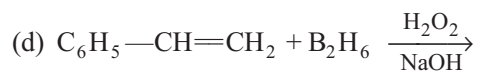
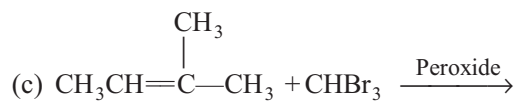
PROBLEM 778 An optical active organic compound A has molecular formula $C_{13}H_{18}O$ and decolourise brown colour of bromine water solution but does not give any gas on heating with sodium metal. A on hydroboration-oxidation yields $B(C_{13}H_{20}O_2)$ which is still resolvable. B on refluxing with dilute solution of H_2SO_4 yields $C(C_7H_8O)$ and $D(C_6H_{14}O_2)$ neither of them can be resolved into enantiomers. C on treating with chromic acid solution gives benzoic acid while D on heating with concentrated solution of H_2SO_4 yields $E(C_6H_{12}O)$. E does not evolve any gas on heating with sodium metal. Deduce structures of A to E .

PROBLEM 779 Propose mechanism of the following reactions :

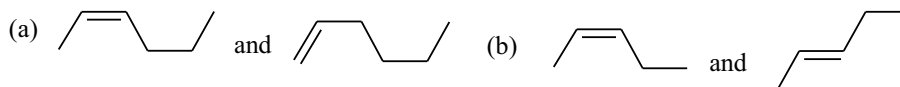


PROBLEM 780 Write major product in the following reactions :

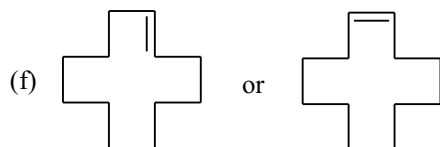
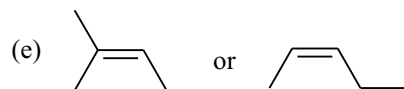
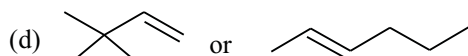
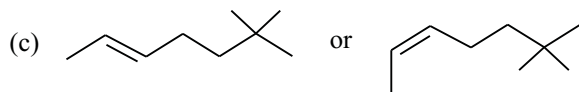
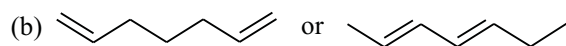
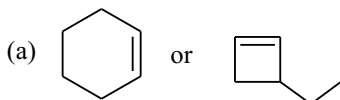




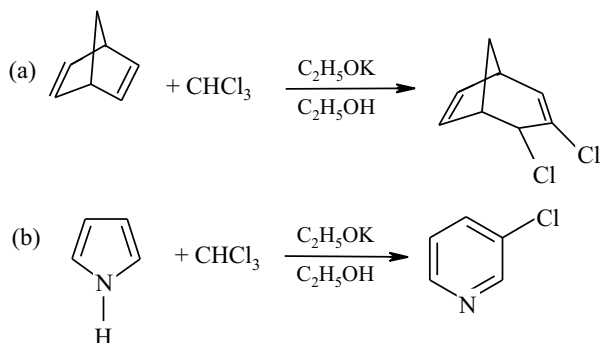
PROBLEM 781 Select one from the following pair of isomer that has higher heat of combustion, justifying your choice :



PROBLEM 782 Select one from the following pair of isomers, that has higher heat of hydrogenation, justifying your choice.



PROBLEM 783 Propose mechanism of the following reactions :



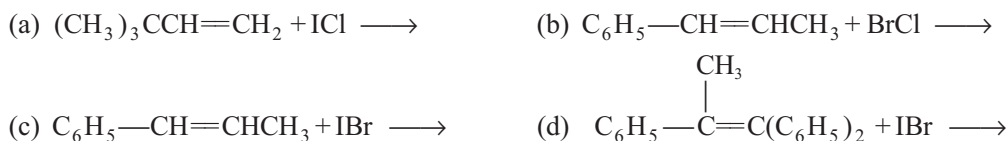
PROBLEM 784 Write mechanism of chlorination of an alkane using sulphuryl chloride (SO_2Cl_2) and a free radical initiator (R_2O_2).

PROBLEM 785 An organic compound *A* has molecular formula C_8H_{18} which on monobromination produced three isomeric products *B*, *C* and *D*. *B* and *C* are enantiomeric whereas *D* is achiral. Treatment of either *C* or *D* with alcoholic KOH solution produced the same product *E* while *B* on similar treatment produced *F* (C_8H_{16}), an isomer of *E* as major product. Establish structures of *A* to *F*.

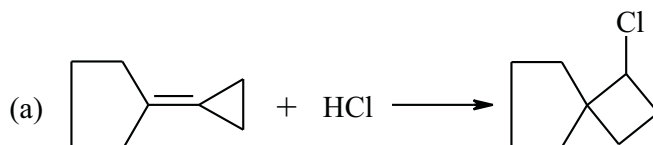
PROBLEM 786 A hydrocarbon *A* (C_8H_{16}) does not decolourise Br_2 -water. *A* on monochlorination produced four isomeric products *B*, *C*, *D* and *E*, among which only *C* and *D* are enantiomeric. Compound *B* is resistant to dehydrohalogenation reaction. Treatment of *C* with alcoholic solution of KOH produced *F* (C_8H_{14}) as only product while similar treatment on *E* produced *G*, an isomer of *F*. *D* on treatment with alcoholic solution of KOH produces both *F* and *G* in comparable amount. Deduce structures of *A* to *G*.

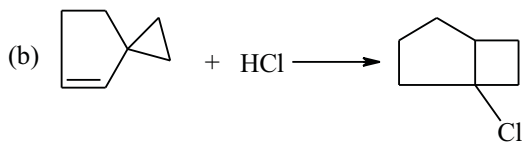
PROBLEM 787 A hydrocarbon *A* (C_8H_{16}) does not decolourise Br_2 water. *A* on monochlorination produced four isomeric products *B*, *C*, *D* and *E* among which only *D* is enantiomeric. Compound *B* is resistant to dehydrohalogenation reaction. Treatment of either *C* or *D* with alcoholic solution of KOH produced the same alkene *F* (C_8H_{14}) as major product which does not rotate the plane polarized light while similar treatment on *E* produced *G*, an isomer of *F* which is enantiomeric. Deduce structures of *A* to *G*.

PROBLEM 788 Predict major addition products in the following reactions:



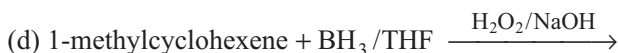
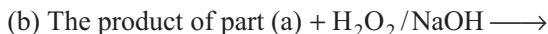
PROBLEM 789 Propose mechanism of formation of the indicated products in the following reactions:



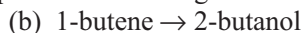
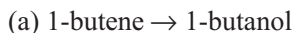


PROBLEM 790 Show how would you convert 1-methylcyclopentanol to 2-methylpentanol.

PROBLEM 791 Predict major products of the following reactions:



PROBLEM 792 Show how would you accomplish the following conversion:

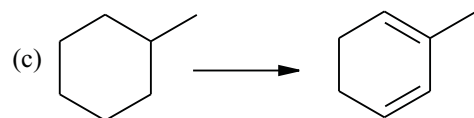
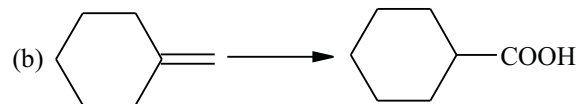
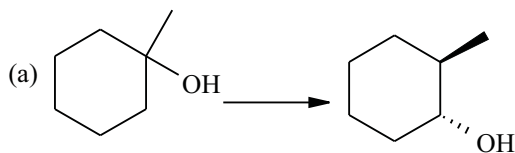


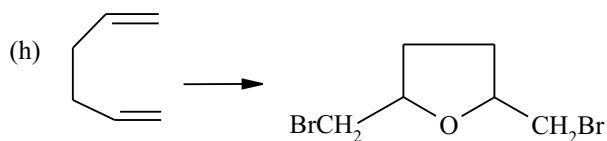
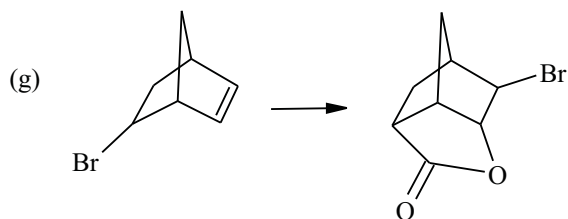
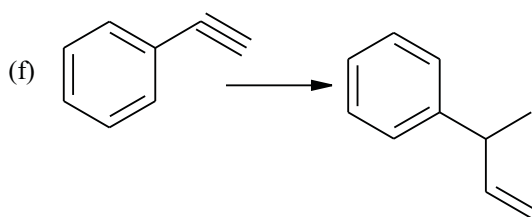
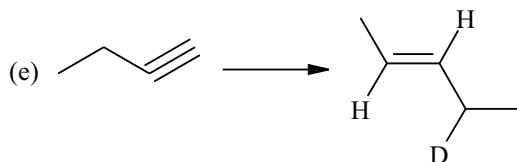
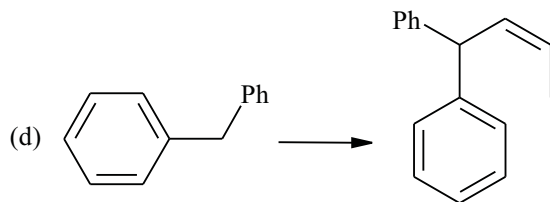
PROBLEM 793 A hydrocarbon $A(\text{C}_6\text{H}_{10})$ on reduction first gives $B(\text{C}_6\text{H}_{12})$ and finally $C(\text{C}_6\text{H}_{14})$. A on ozonolysis followed by work-up with $\text{Zn-H}_2\text{O}$ gives two molecules of aldehydes $\text{C}_2\text{H}_4\text{O}(D)$ and one molecule of aldehyde $E(\text{C}_2\text{H}_2\text{O})$. Oxidation of B with acidified KMnO_4 gives an acid $F(\text{C}_4\text{H}_8\text{O}_2)$. Determine structures of A to F with proper reasoning.

PROBLEM 794 A hydrocarbon exist in two stereomeric forms (A) and (B) with their molecular formula C_8H_{16} . A on treatment with cold, dilute and alkaline solution of KMnO_4 produces $\text{C}_8\text{H}_{18}\text{O}_2(C)$ which is a meso form. B , on the other hand, on similar treatment produces racemic mixture which is isomeric to C . Either A or B on treatment with O_3 followed by work with H_2O_2 produces $D(\text{C}_4\text{H}_8\text{O})$ as the only product. Identify A to D .

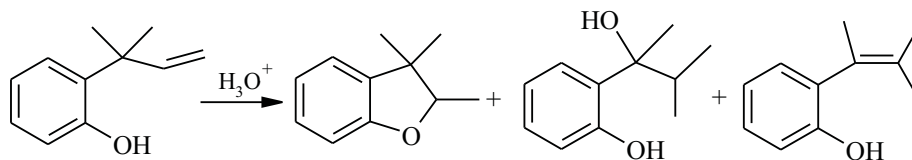
PROBLEM 795 An organic compound $A(\text{C}_{13}\text{H}_{23}\text{Cl})$ exist as diastereomers and decolourise bromine water. A on treatment with ethanolic solution of KOH produces isomeric B and C with their molecular formula $\text{C}_{13}\text{H}_{22}$. Treatment of either B or C with Rany Nickel produces 4-isopropyl-1-tertiarybutyl cyclohexane. A on oxidative ozonolysis gives acetone as one product. Identify A , B and C considering C to be enantiomeric.

PROBLEM 796 Bring about the following conversions:

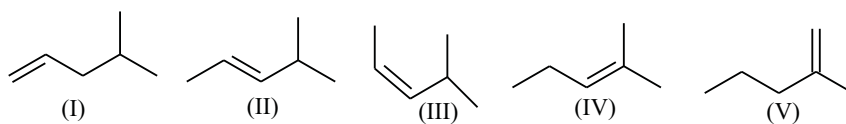




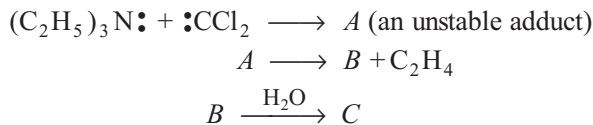
PROBLEM 797 (a) Propose mechanism of formation of products in the following reaction:



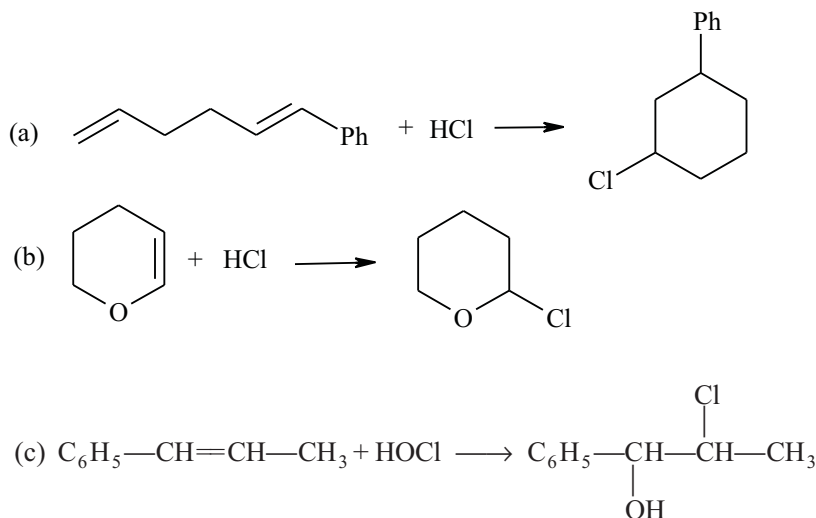
(b) Arrange the following alkenes in increasing order of their heat of hydrogenation explaining reason for your choice:



PROBLEM 798 Draw the structures of compounds *A* to *C*:



PROBLEM 799 Predict mechanism of formation of products in the following reactions:



PROBLEM 800 An optically active hydrocarbon *A* has molecular formula C_8H_{18} . *A* on monochlorination gives five alkyl halide *B* to *F* with their molecular formula $\text{C}_8\text{H}_{17}\text{Cl}$. *B* does not undergo dehydrohalogenation on treatment with alcoholic solution of KOH. Treatment of either *C* or *D* with alcoholic KOH yields same alkene *G* (C_8H_{16}) which on ozonolysis followed by work-up with Zn-dimethyl sulphide gives an optically inactive compound $\text{C}_6\text{H}_{12}\text{O}$ and ethanal. Also *C* is enantiomeric whereas *D* is diastereomeric. *E* on dehydrohalogenation yields an alkene, which on reductive ozonolysis yields *H* ($\text{C}_7\text{H}_{14}\text{O}$) which is optically inactive. *H* on treatment with LiAlH_4 yields *I* ($\text{C}_7\text{H}_{16}\text{O}$) which can be resolved into enantiomers. *F* on dehydrohalogenation yields an alkene (C_8H_{16}) which on reductive ozonolysis yields *J* ($\text{C}_7\text{H}_{14}\text{O}$) which is optically active and have same configuration as that of *A*. Identify *A* to *J* explaining the reactions involved.

PROBLEM 801 A hydrocarbon (*A*) contains five carbon atoms, reacts with cold, dilute and alkaline solution of KMnO_4 to form *B* (resolvable). *B* on oxidation with hot concentrated KMnO_4 solution forms two compounds (*C*) and a neutral (*D*). *C* has molecular formula $\text{C}_2\text{H}_4\text{O}_2$ and turns blue litmus paper red. Compound *D* neither reacts with Fehling solution nor with Tollen's reagent and its formula is $\text{C}_3\text{H}_6\text{O}$. *A* on treatment with Cl_2 in CCl_4 yields another compound *E* ($\text{C}_5\text{H}_{10}\text{Cl}_2$). *E* on treatment with alcoholic solution of KOH yields a stable compound *F* (C_5H_8). Identify *A* to *F*.

PROBLEM 802 An organic compound $A(C_8H_{14})$ on treatment with H_2/Pt gives C_8H_{18} . Ozonolysis of A followed by work-up with Zn-dimethyl sulphide yields three products B , C and D . B reduces Tollen's reagent and gives a yellow precipitate on treatment with $NaOH/I_2$. C doesn't reduce Tollen's reagent but gives yellow precipitate with $NaOH/I_2$. D has molecular formula $C_2H_2O_2$ and on treatment with concentrated solution of $NaOH$ followed by acidification of product yields $E(C_2H_4O_3)$. Deduce structures of A to E .

PROBLEM 803 An organic compound (A) has molecular formula C_5H_{10} , and decolourise bromine-water solution. When A is treated with cold concentrated solution of sulphuric acid followed by refluxing of product, $B(C_5H_{12}O)$ was formed. B turns the orange colour of chromic acid solution to blue-green, converting itself into $C(C_5H_{10}O)$. B and C both react with alkaline solution of iodine producing yellow precipitate and salt of isobutyric acid. Identify A to C .

PROBLEM 804 A hydrocarbon $A(C_8H_{12})$ is optically active and on treatment with H_2/Pt gives (C_8H_{18}) which does not rotate plane polarized light. A does not give any precipitate on treatment with ammoniacal silver nitrate solution. A on treatment with $Pd/BaSO_4$ gives $C(C_8H_{14})$ which is also optically inactive but A on treatment with $Na/liq\ NH_3$ gives D , an isomer of C , which is able to show enantiomerism. Also A on treatment with ozone followed by hydrolysis gives $C_4H_6O_3(E)$ which is optically active. Identify A to E representing their stereochemical structure.

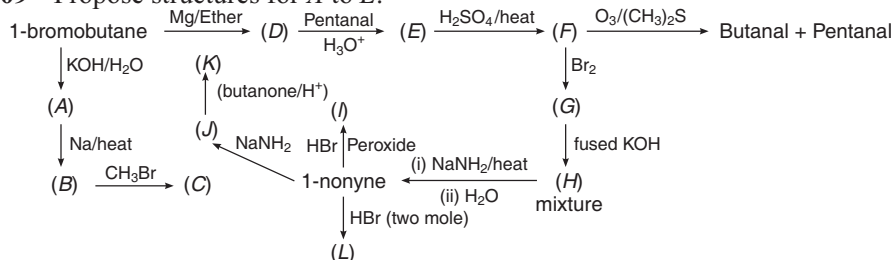
PROBLEM 805 A hydrocarbon A has molecular formula $C_{10}H_{18}$. A on treatment with H_2/Pt gives $B(C_{10}H_{22})$. B on monochlorination gives two isomers C and D with molecular formula $C_{10}H_{21}Cl$. Out of C and D , only C can undergo dehydrohalogenation with alcoholic solution of KOH as well as only C can be resolved into enantiomers. A on addition of one equivalent of Cl_2 in CCl_4 gives a stereomer $E(C_{10}H_{18}Cl_2)$. E on treatment with Bayer's reagent yields a racemic mixture of molecular formula $(C_{10}H_{20}Cl_2O_2)$. Also A on partial hydrogenation with $Pd/BaSO_4/quinone$ gives $F(C_{10}H_{20})$ which on treatment with Bayer's reagent gives a meso compound $G(C_{10}H_{22}O_2)$. Deduce the structures of A to G .

PROBLEM 806 A hydrocarbon $A(C_{10}H_{12})$ has no chiral carbon. A gives a white precipitate with ammoniacal solution of silver nitrate. A on treatment with H_2/Pt gives $B(C_{10}H_{20})$. A on ozonolysis gives $C(C_8H_{12}O_4)$ as one product which on heating with soda lime gives $D(C_6H_{12})$. D on monochlorination with $Cl_2/h\nu$ gives $C_6H_{11}Cl$ as sole isomer. Identify A to D .

PROBLEM 807 An organic compound $A(C_8H_6)$ gives brick red precipitate with ammoniacal solution of Cu_2Cl_2 . A on treatment with acidic solution of $HgSO_4$ yields $B(C_8H_8O)$. B gives positive iodoform test. B can also be prepared by the reaction of benzene with acetic anhydride in presence of $AlCl_3$. Identify A and B .

PROBLEM 808 Potassium hydroxide is mixed with 2,3-dibromohexane, the mixture is sealed in a fusion tube and heated to $200^\circ C$ for one hour. The product mixture (A) is mixed with $Cu(I)$ -ammonia complex and a precipitate forms. The precipitate (B) and liquid phase (C) are separated. The precipitate is acidified and the product (D) is distilled at $71^\circ C$. Product D is treated with $NaNH_2$, followed by acetone and then with dilute acid to give alcohol (F). The liquid phase (C) is distilled and the product alkyne is treated with $NaNH_2$ at $150^\circ C$ for 1.0 hour and product mixture is distilled to give a pure alkyne (E) of boiling point $71^\circ C$. Identify A to F .

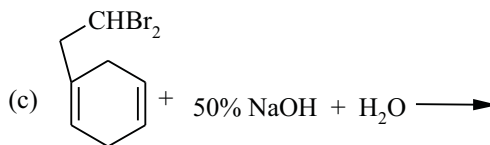
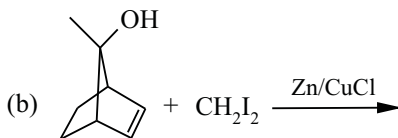
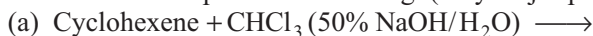
PROBLEM 809 Propose structures for *A* to *L*:



PROBLEM 810 An optically active compound *A* has molecular formula $\text{C}_7\text{H}_{11}\text{Br}$. *A* reacts with HBr , in absence of peroxide to yield isomeric products, *B* and *C* with molecular formula $\text{C}_7\text{H}_{12}\text{Br}_2$. Compound *B* is optically active; *C* is not. Treating *A* with one mole of potassium-*t*-butoxide yields *D* (C_7H_{10}). Subjecting one mole of *D* to ozonolysis followed by treatment with Zn and water yield two moles of formaldehyde and one mole of 1,3-cyclopentandione. *A* on addition of HBr in presence of H_2O_2 produces another isomer of *B* which is *E*, and shows diastereomerism. Deduce structure of *A* to *E*.

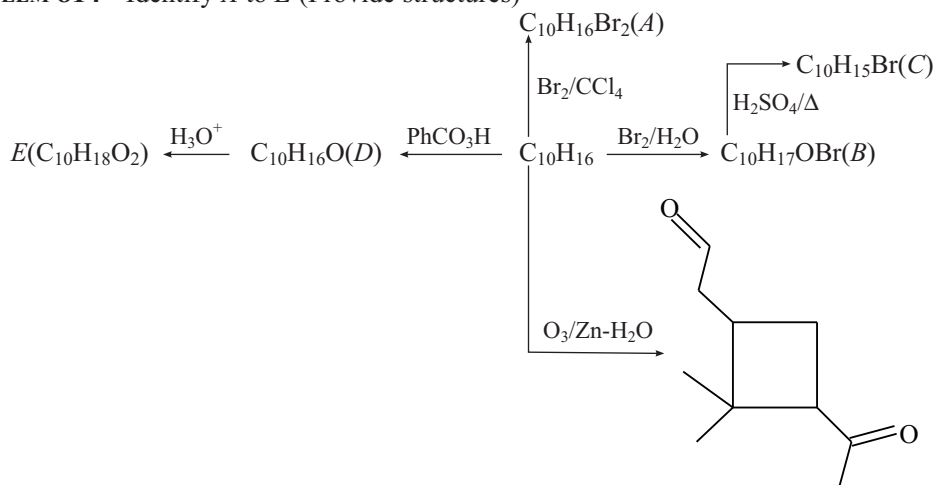
PROBLEM 811 An alkane (*A*) with formula C_6H_{14} reacts with Cl_2 to yield three compounds with formula $\text{C}_6\text{H}_{13}\text{Cl}$, *B*, *C* and *D* of these only *C* and *D* undergo dehydrohalogenation with $\text{C}_2\text{H}_5\text{ONa}/\text{EtOH}$ to produce alkene (*E*). Also *C* can be resolved into enantiomers but *D* is non-resolvable. *E* on addition of HCl produces '*B*' which on treatment with Zn -acetic acid produces *A*. Deduce structure of *A* to *E*.

PROBLEM 812 Complete the following: (only major product)

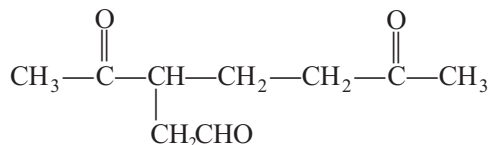


PROBLEM 813 An organic compound *A* has molecular formula $\text{C}_{10}\text{H}_{16}$ and is known not to contain any triple bond. On catalytic hydrogenation of *A*, a new compound *B* ($\text{C}_{10}\text{H}_{22}$) is formed. Ozonolysis of *A* followed by treatment with zinc- H_2O yields two mole of CH_2O , one mole of acetone and a third compound *C* ($\text{C}_5\text{H}_6\text{O}_3$). Deduce the structure of *A*, *B* and *C* considering *C* being optically active.

PROBLEM 814 Identify *A* to *E* (Provide structures)



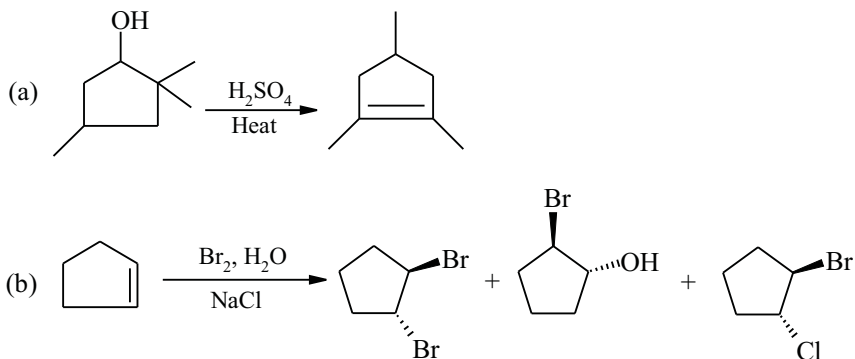
PROBLEM 815 An organic compound *A* ($C_{10}H_{16}$) on catalytic hydrogenation produces 1-isopropyl-4-methylcyclohexane. Ozonolysis of *A* followed by work-up with dimethylsulphide produces formaldehyde and



Deduce structure of *A*.

PROBLEM 816 Three isomeric hydrocarbons *A*, *B* and *C* have molecular formula C_6H_{10} . All three compounds readily decolourise bromine in CCl_4 , compound *A* gives precipitate with $AgNO_3/NH_3$ solution but compound *B* and *C* do not. Compound *A* and *B* both yield hexane when treated with excess of H_2/Pt . Under these conditions, *C* absorbs only one molar equivalent of H_2 and give product with formula C_6H_{12} . When *A* is oxidised with hot basic $KMnO_4$ and resulting solution is acidified, the only organic product that can be isolated is $CH_3(CH_2)_3COOH$. Similar oxidation of *B* gives only CH_3CH_2COOH and similar treatment of *C* gives only $HO_2C(CH_2)_4COOH$. Identify *A*, *B* and *C*.

PROBLEM 817 Propose mechanism:

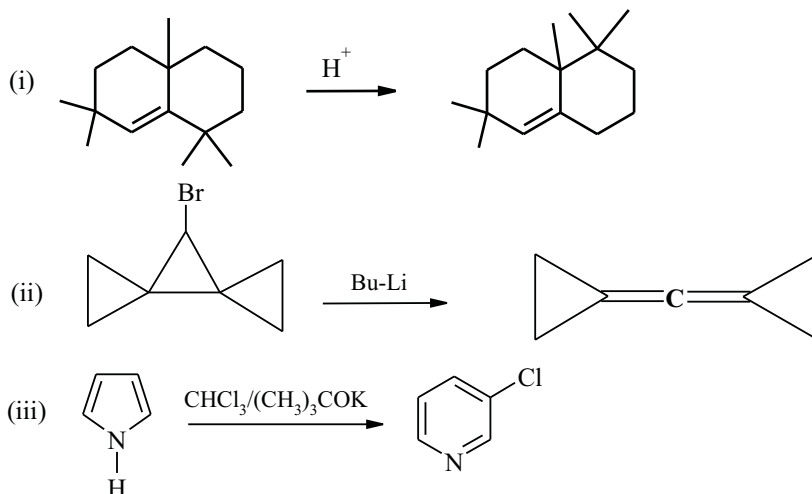


PROBLEM 818 An organic compound *A* has molecular formula C_9H_{14} and on treatment with H_2/Pt gives C_9H_{20} . *A* exist in four stereomeric forms. *A* on treatment with O_3 followed by work-up with $Zn-H_2O$ produced CO_2 , *B* ($C_4H_6O_3$) and *C* (C_4H_8O). *B* rotates plane-polarized light but *C* doesn't. *C* changes the colour of acidic dichromate solution converting itself into an another optically inactive compound *D* ($C_4H_8O_2$). *D* on treatment with $I_2/Red-P$ produced an optically inactive compound *E* ($C_4H_7O_2I$) as the only isomer. Deduce structures of *A* to *E* and draw the structures of all four stereomers of *A*.

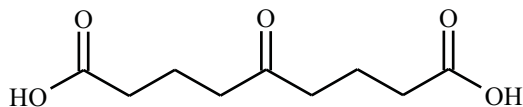
PROBLEM 819 An optically active compound *A* has molecular formula C_9H_{10} . *A* does not decolourise aqueous solution of Br_2 . *A* on treatment with NBS produced another optically active compound *B* (C_9H_9Br). *B* on hydrolyzing in aqueous KOH solution gave *C* ($C_9H_{10}O$) which doesn't change the colour of acidic dichromate solution. *B* on treatment with C_2H_5ONa/C_2H_5OH produced *D* (C_9H_8) which is optically inactive. *D* on oxidative cleavage produced *E* ($C_9H_8O_3$) which is optically inactive. *E* on heating with soda lime gave C_8H_8O , which can also be obtained by Friedel Craft's acylation. Deduce the structures of *A* to *E* describing the reactions involved in each step.

PROBLEM 820 (a) Reagent (two possible isomers) + $KMnO_4/H^+ \longrightarrow$ 3,4-diketo hexandioic acid. Provide structures of the reagent which will lead to the above product.

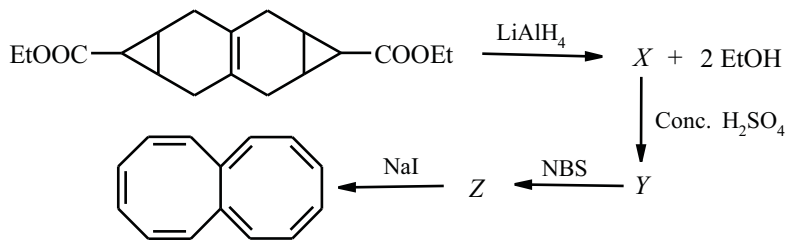
(b) Propose mechanism:



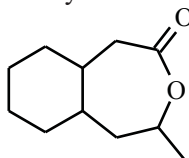
PROBLEM 821 (a) An organic compound $A(C_{12}H_{20})$ on catalytic hydrogenation yields $B(C_{12}H_{24})$. A on ozonolysis followed by work-up with H_2O_2 yields acetone and the following compound. Deduce the structures of A and B .



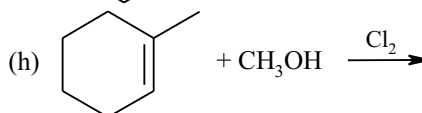
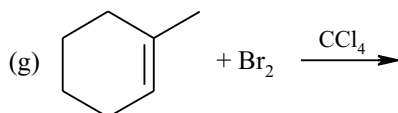
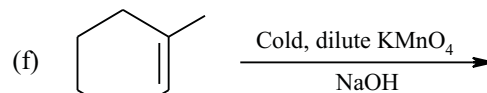
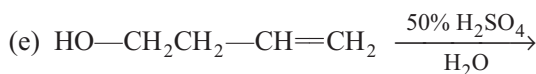
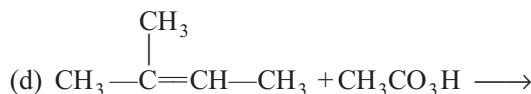
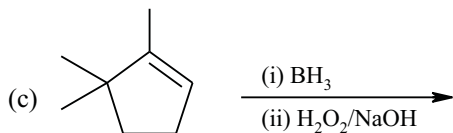
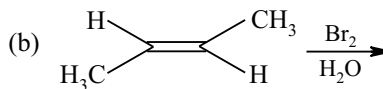
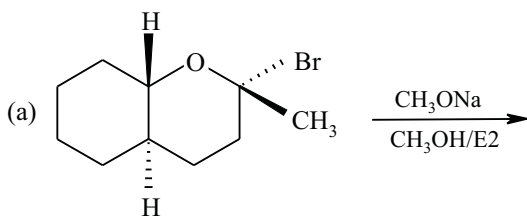
(b) Predict product in the following sequence of reaction:



PROBLEM 822 An organic compound $A(C_{13}H_{21}Br)$ is optically active and decolourise Bayer's reagent. A on treatment with $EtONa/EtOH$ yields two and only two isomers B and C both having molecular formula $C_{13}H_{20}$ with B as major product. Catalytic hydrogenation of either B or C gave the same product $C_{13}H_{24}$ which is optically active. B is stereomeric whereas C is non-stereomeric. C on oxidative cleavage with acidic $KMnO_4$ produced $D(C_{12}H_{18}O_5)$ as one product which on simple heating gave $E(C_{11}H_{18}O_3)$. E gives yellow precipitate with $NaOH/I_2$. E on treatment with $NaBH_4$ gives $F(C_{11}H_{20}O_3)$, an optically active compound. F on heating with catalytic amount of H^+ gave the following compound:

Deduce structure of A to F .

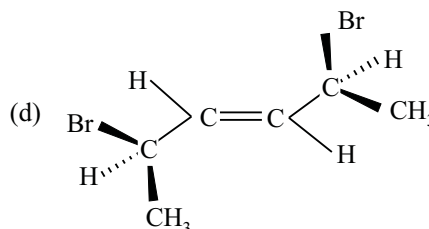
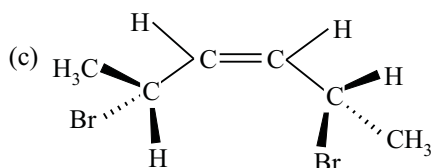
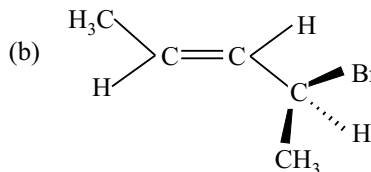
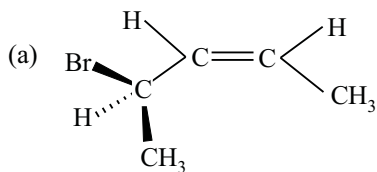
PROBLEM 823 Write structures of single major product of each of the following reactions. If two or more major products are formed, write structures of both. Show stereochemistry of products where appropriate.



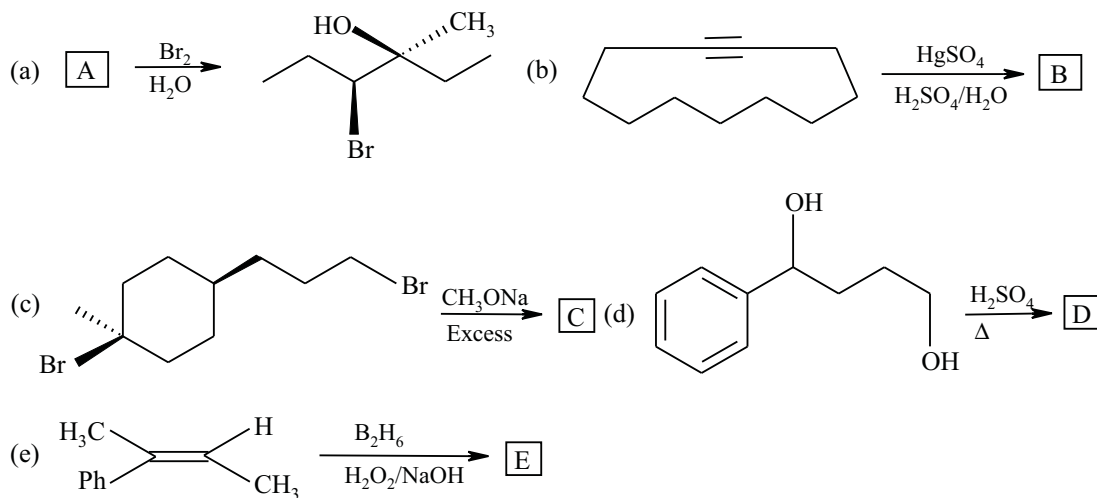
PROBLEM 824 Hydroboration oxidation of *trans*-2-(*p*-anisyl)-2-butene yielded an alcohol *A* whose melting point is 60°C while similar treatment on *cis* isomer yielded an isomeric alcohol which is a liquid at room temperature. Suggest reasonable structures for *A* and *B*.

PROBLEM 825 An optically active alkyne *A* contain 89.25% C and 10.48% H. After hydrogenation with H_2/Pt , it is converted into 1-methyl-4-propyl cyclohexane. *A* gives no gas with CH_3MgBr . Treatment of *A* with acidified KMnO_4 solution yields *B* which gives positive iodoform test and a salt *C*. Acidification of salt *C* yields an optically active compound *D*. Identify *A* to *D*.

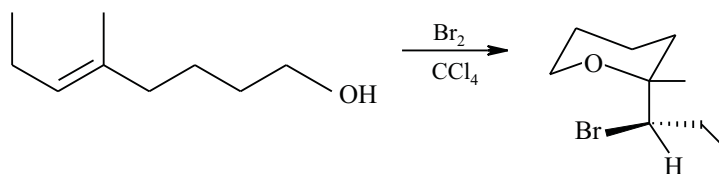
PROBLEM 826 Discuss the stereochemistry of addition of Br_2 to the following alkenes:



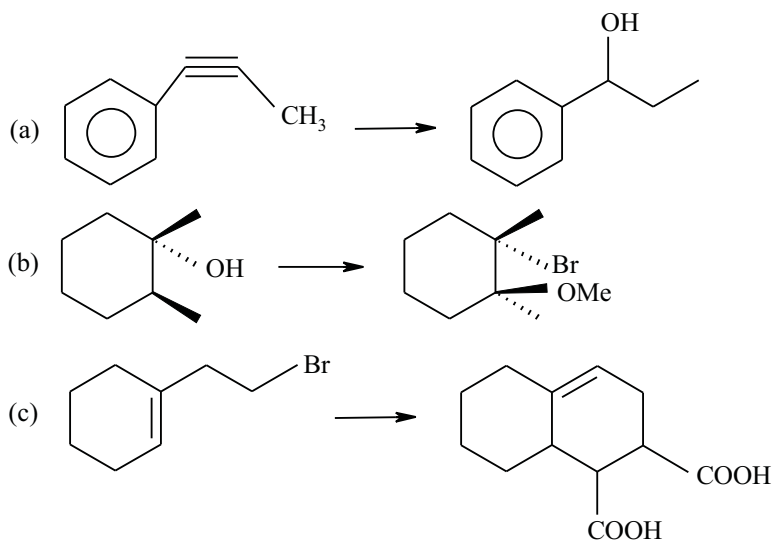
PROBLEM 827 Provide the structures of missing components:



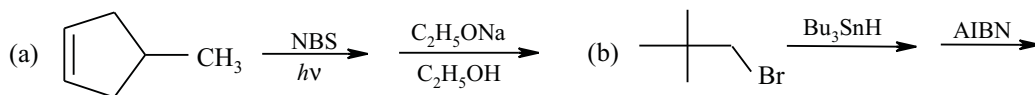
PROBLEM 828 Propose mechanism of the following reaction:



PROBLEM 829 Bring about the following transformations:

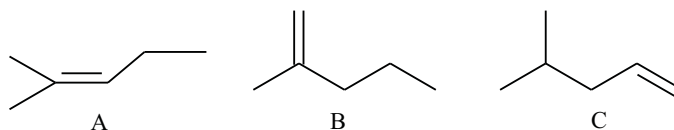


PROBLEM 830 Complete the following reactions:

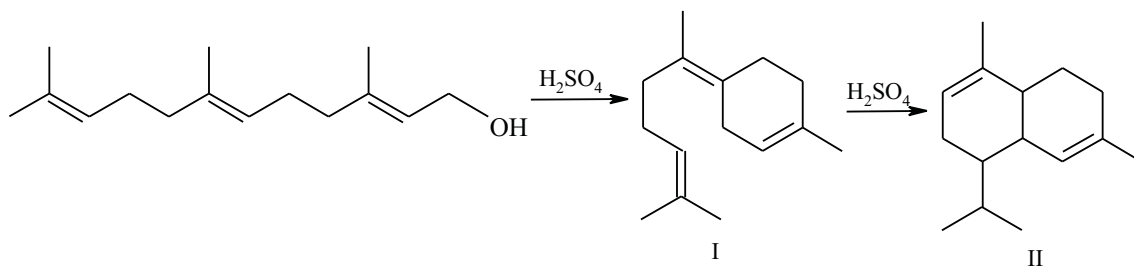


[AIBN : Azobis isobutyronitrile]

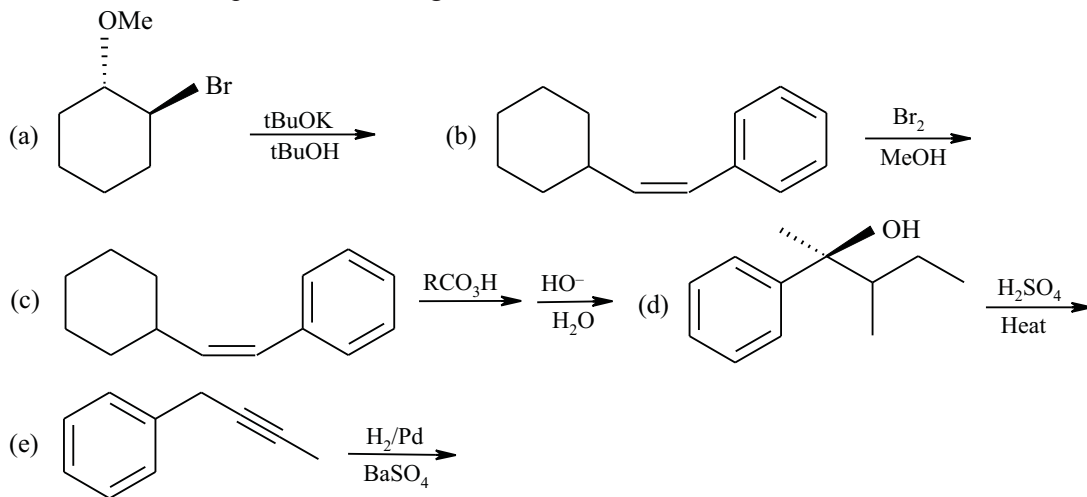
PROBLEM 831 Discuss the relative heat of hydrogenation of following alkenes:



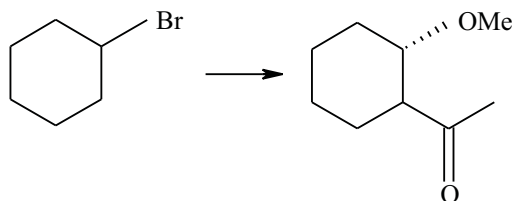
PROBLEM 832 Propose mechanism of the following acid catalyzed reaction:



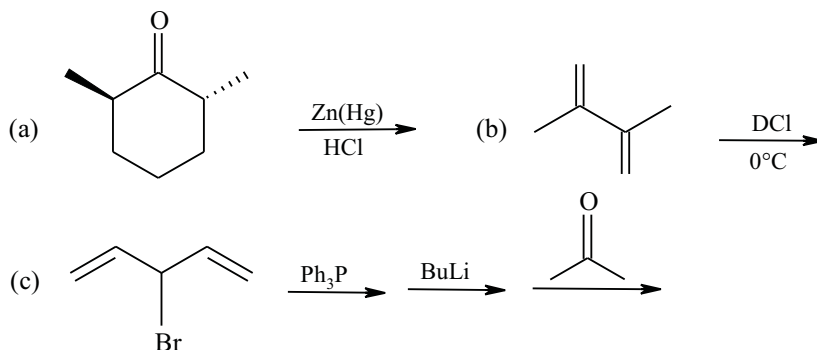
PROBLEM 833 Complete the following reactions:



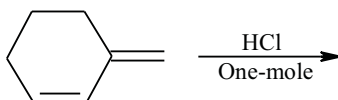
PROBLEM 834 Convert:



PROBLEM 835 Provide structural formula for the major product in the following reactions:



PROBLEM 836 The reaction of the diene shown below with dry HCl can lead to four products. Provide structural formula of all the products.

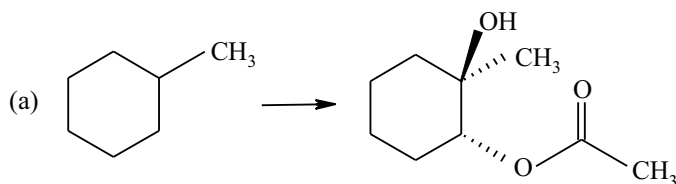


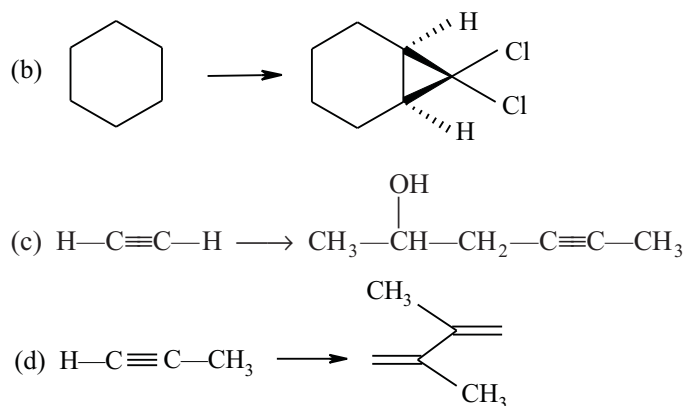
PROBLEM 837 A hydrocarbon *A* has molecular formula “C₁₄H₂₂” and it can be resolved into enantiomers. *A* on hydrogenation with H₂/Pt yields *B* (C₁₄H₃₀) which can't be resolved into enantiomers. Also *A* on partial hydrogenation with H₂ in presence of Pd/BaSO₄/PbO yields *C* (C₁₄H₂₆) which is still resolvable and decolourise brown colour of bromine water solution. *A* on treatment with alkaline permanganate solution yielded *D* (C₉H₁₈O₂), oxalic acid and propanoic acid. *D* can also be resolved into enantiomers. Another organic compound *E* (C₈H₁₆O) forms yellow precipitate on treatment with alkaline iodine solution. *E* on treatment with NaBH₄ yielded a resolvable organic product *F* (C₈H₁₈O). *F* on treatment with *p*-toluenesulphonyl chloride followed by workup with aqueous NaCN yielded *G* (C₉H₁₇N). Hydrolysing *G* with dilute sulphuric acid produced *D*. Identify *A* to *G*.

PROBLEM 838 An organic compound *A* has molecular formula C₁₂H₂₂ and can't be resolved into enantiomers. *A* on ozonolysis followed by work-up with Zn/H₂O yields *B* (C₁₂H₂₂O₂). *B* neither reduces Tollen's reagent nor produced any yellow precipitate with alkaline iodine solution. *B* on exhaustive oxidation with hot, concentrated, acidic permanganate solution produced *C* (C₆H₁₀O₄) as one of the product. *C* on heating with sodalime yielded isobutane. Identify *A*, *B* and *C*.

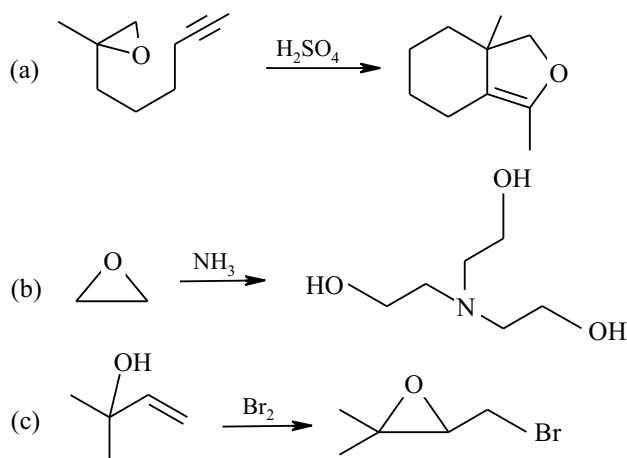
PROBLEM 839 An organic compound C₅H₆O₂ exist in three isomeric forms *A*, *B* and *C* of which only *B* can be resolved into enantiomers. All three evolves a gas on heating with sodium metal but only *A* and *B* evolves gas with NaHCO₃. Also *B* and *C* formed white precipitate with ammonical silver nitrate while *A* didnot. *A* on heating with soda-lime yielded *D* (C₄H₆) which did not yield any precipitate with ammonical silver nitrate. Hydrolysing *C* with aqueous alkali followed by heating with sodalime produced C₃H₄. Identify *A* to *D*.

PROBLEM 840 Propose synthetic routes to accomplish the indicated transformations:

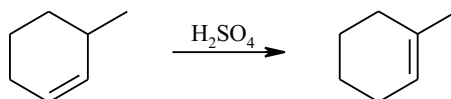




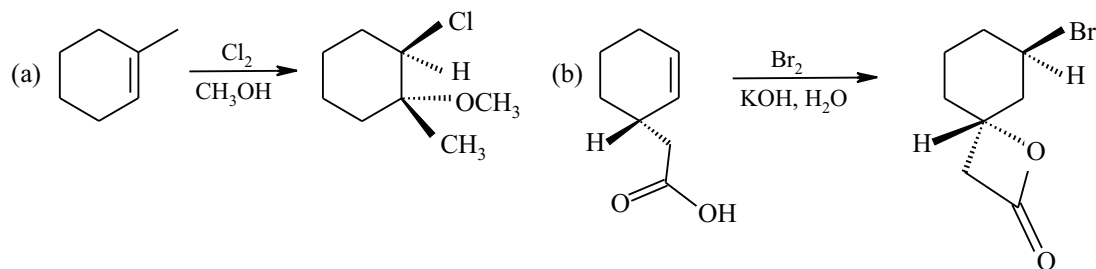
PROBLEM 841 Propose mechanism to account for the following transformations:

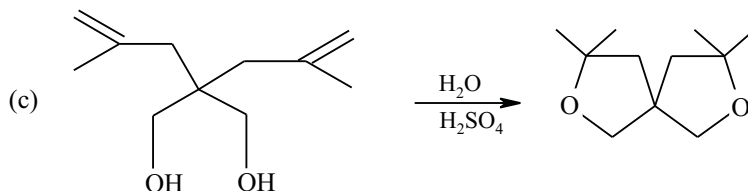


PROBLEM 842 Propose mechanism:



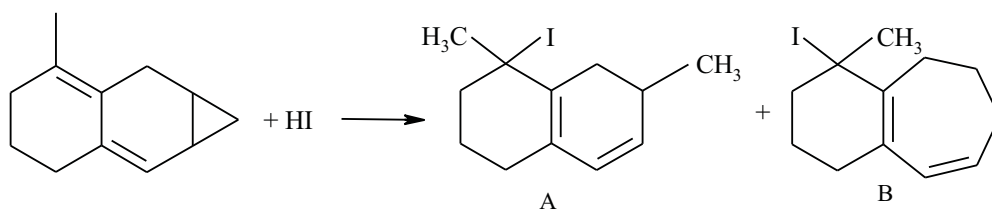
PROBLEM 843 Propose mechanism of the following reactions:



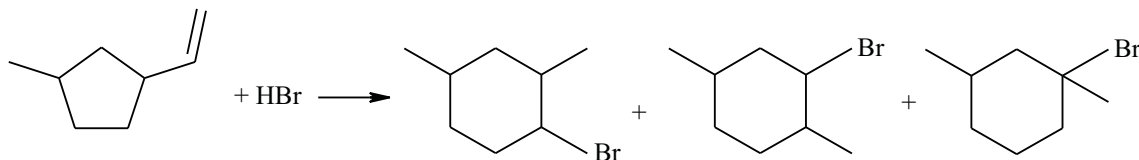


PROBLEM 844 An organic compound *A* has molecular formula $\text{C}_{10}\text{H}_{12}\text{O}$. *A* forms salt with aqueous NaOH but does not exhibit stereo-isomerism. *A* on treatment with HBr yields *B* ($\text{C}_{10}\text{H}_{13}\text{OBr}$) which can be resolved into enantiomers. On the otherhand, if *A* is treated with HBr in presence of a peroxide, it gives *C*, an isomer of *B* but *C* can't be resolved into enantiomer. *C* on treating with potassium tertiary butoxide in tertiary butanol yields *D*, an isomer of *A*, which is still non-resolvable. *D* on hydration in presence of alkaline H_2O_2 catalyzed by B_2H_6 yields *E* ($\text{C}_{10}\text{H}_{14}\text{O}_2$) which can be resolved into enantiomers. Refluxing *E* with dilute sulphuric acid yields *F* ($\text{C}_{10}\text{H}_{12}\text{O}$) which does not forms any salt with aqueous NaOH. Also, *A* on boiling with alkaline solution of potassium permanganate yields 2-hydroxybenzoic acid. Identify *A* to *F*.

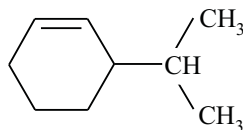
PROBLEM 845 Propose mechanism of the following reactions:



PROBLEM 846 Propose mechanism:

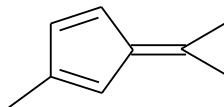


PROBLEM 847 The hydrocarbon shown below is optically active and can be resolved into enantiomers. A pure enantiomer of this compound on refluxing with conc. H_2SO_4 for sometime isomerizes into an optically inactive isomer. Explain the observations with the help of mechanism.



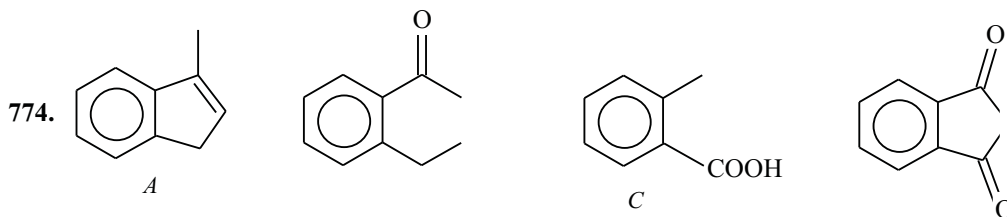
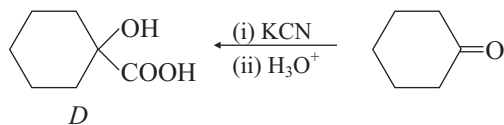
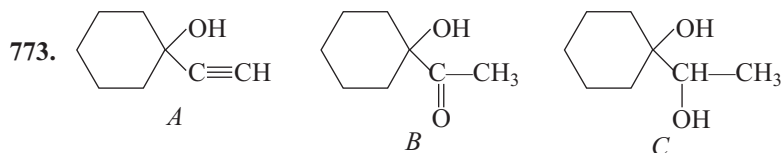
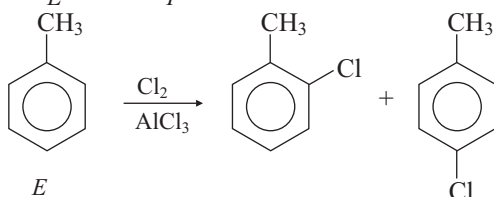
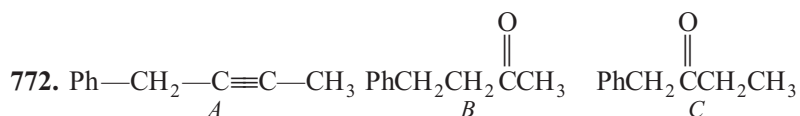
PROBLEM 848 A hydrocarbon *A* has molecular formula C_7H_{12} . *A* on treatment with B_2H_6 followed by work-up with $\text{H}_2\text{O}_2/\text{NaOH}$ produced *B* ($\text{C}_7\text{H}_{14}\text{O}$) as the only product. Reacting *B* with torylchloride followed by workup with KOH yielded *C*, an isomer of *A*, in addition to other olefinic products. Ozonolysis of *C* followed by work-up with $\text{Zn}-\text{CH}_3\text{COOH}$ produced 2-methyl hexan-1,6-diol. Identify *A* to *C*.

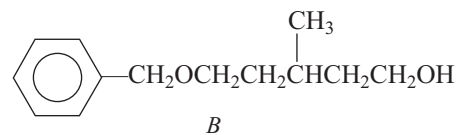
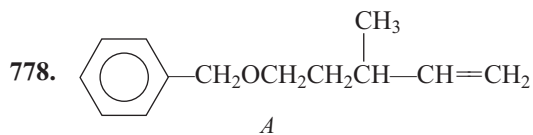
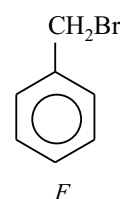
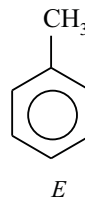
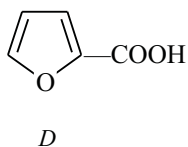
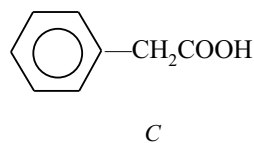
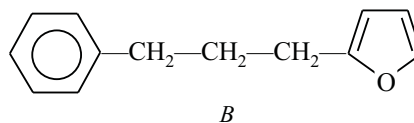
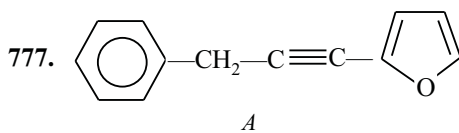
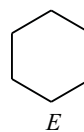
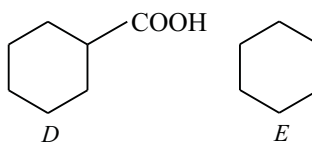
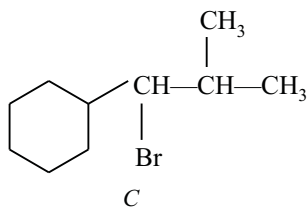
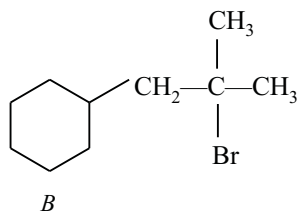
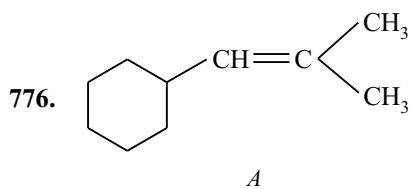
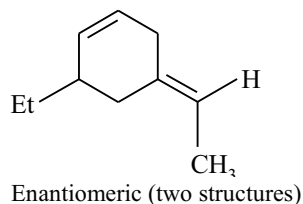
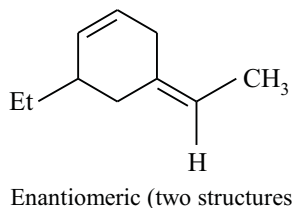
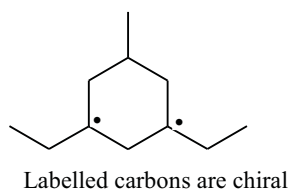
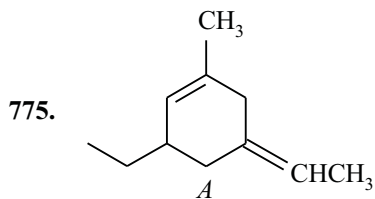
PROBLEM 849 Suggest the most likely site of protonation explaining reason:

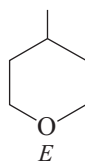
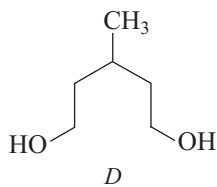
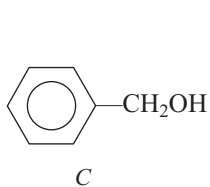


Solutions

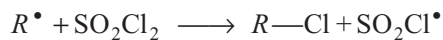
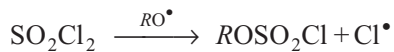
HYDROCARBONS



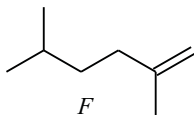
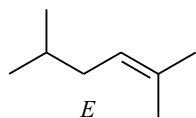
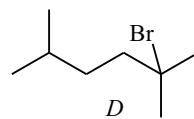
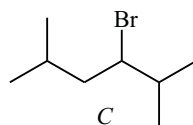
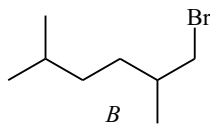
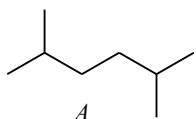




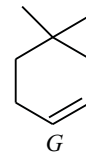
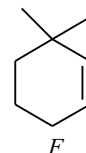
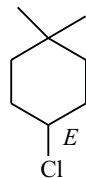
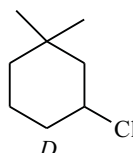
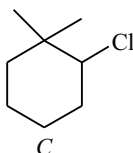
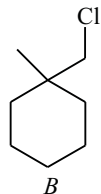
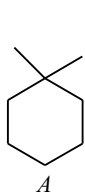
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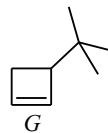
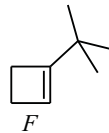
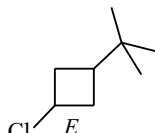
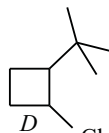
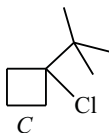
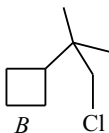
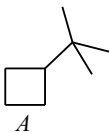
785.



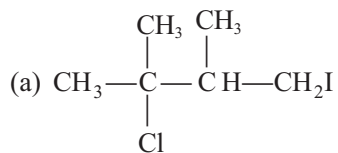
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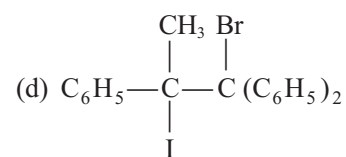
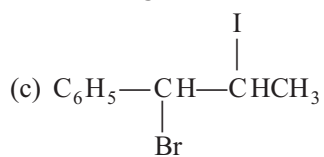
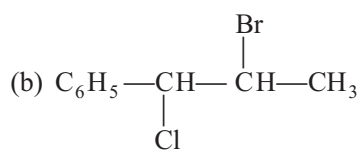
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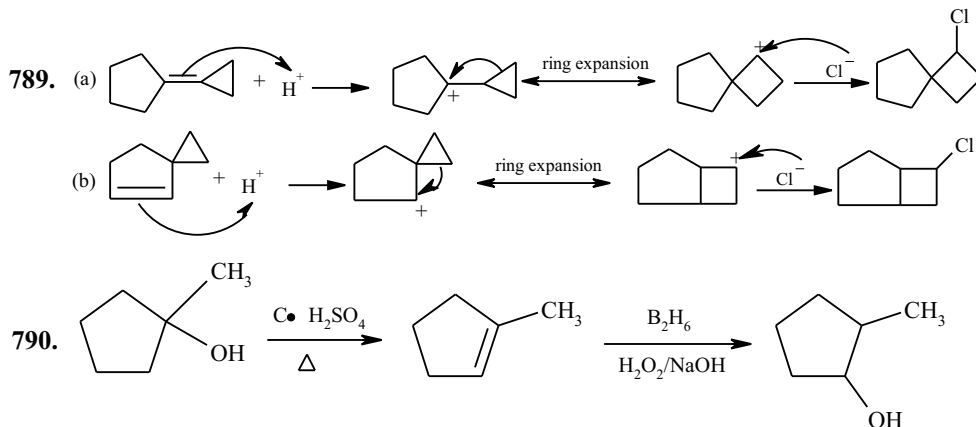


788. (a)

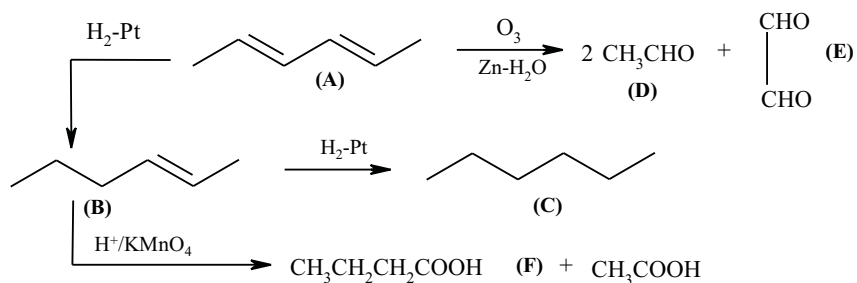


(b)





791. (a) $(\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{B}$ (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
 (c) 2-methyl-3-pentanol (d) 2-methylcyclohexanol.
 792. (a) 1-butene + $\text{BH}_3/\text{H}_2\text{O}_2/\text{NaOH} \longrightarrow$ 1-butanol
 (b) 1-butene + *dil.* $\text{H}_2\text{SO}_4/\text{heat} \longrightarrow$ 2-butanol
 (c) 2-bromo-2,4-dimethylpentane + alcoholic KOH $\longrightarrow$ 2,4-dimethyl-2-pentene
 2,4-dimethyl-2-pentene + $\text{BH}_3/\text{H}_2\text{O}_2/\text{NaOH} \longrightarrow$ product.



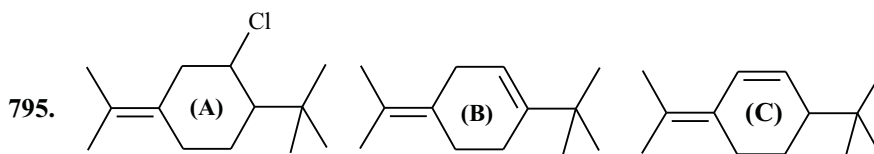
793. Ozonolysis products shows that *A* is a symmetrical diene:

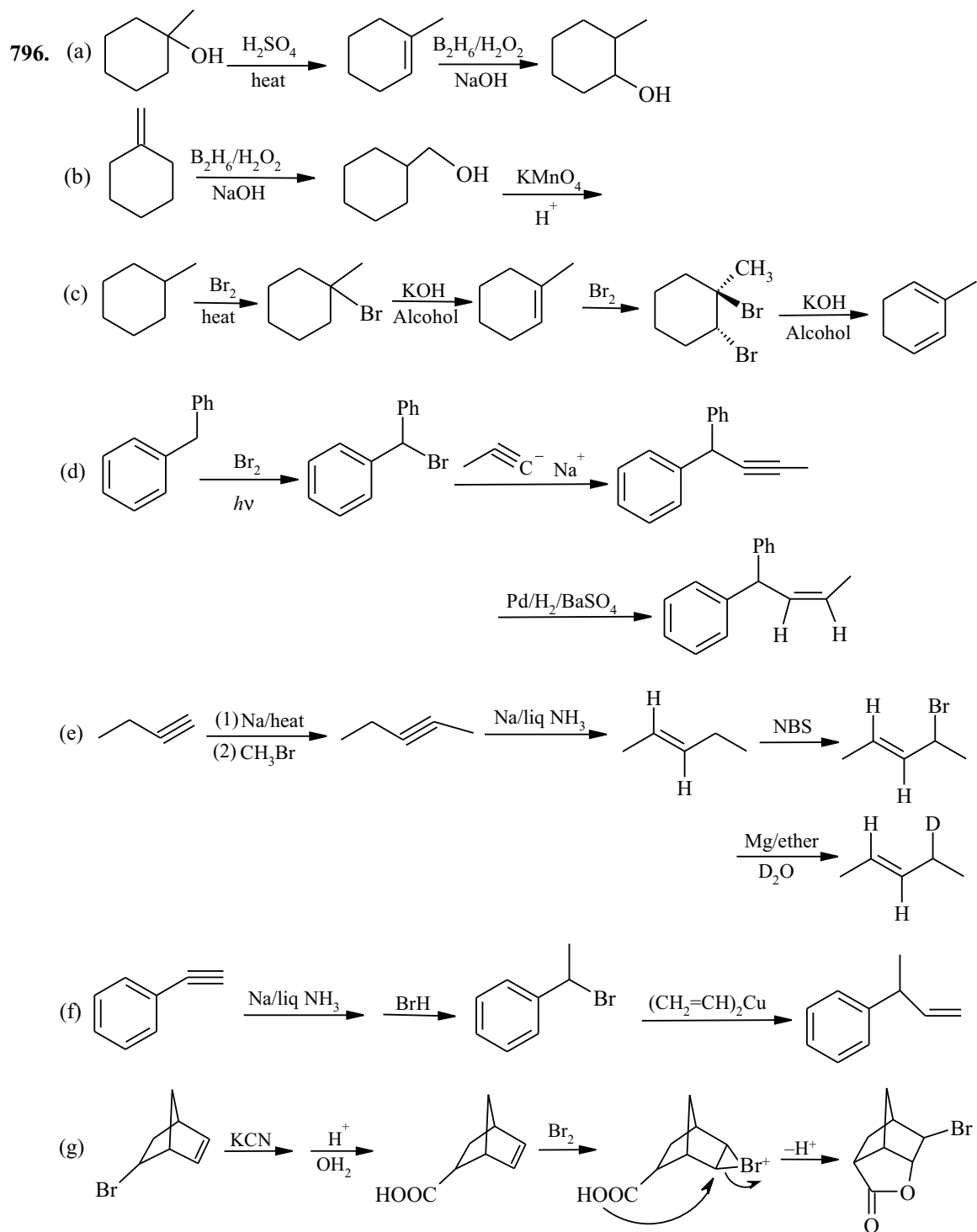
794. Cold, dilute, alkaline KMnO_4 solution adds on $\text{C}=\text{C}$ producing *cis*-diols. One of the stereomer *A* produces meso *cis*-diol therefore it is confirmed that the starting compound is a symmetrical alkene.

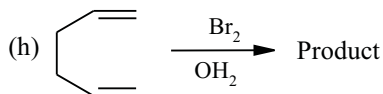
Also oxidative ozonolysis of the starting compound gives no acid as product, it indicates that there is no hydrogen attached to doubly bonded carbon. From these finding it is now concluded that the starting compound has following structural formula-3,4-dimethyl-3-hexene

Also: *A* + Cold, *dil.* $\text{KMnO}_4 \longrightarrow$ *C* (Meso) therefore, *A* is *cis* isomer and *B* is thus *trans* one. Thus the various compounds are: *A*: *cis*-3,4-dimethyl-3-hexene. *B*: *trans*-3,4-dimethyl-3-hexene. *C*: Meso-3,4-dimethyl butan-3,4-diol.

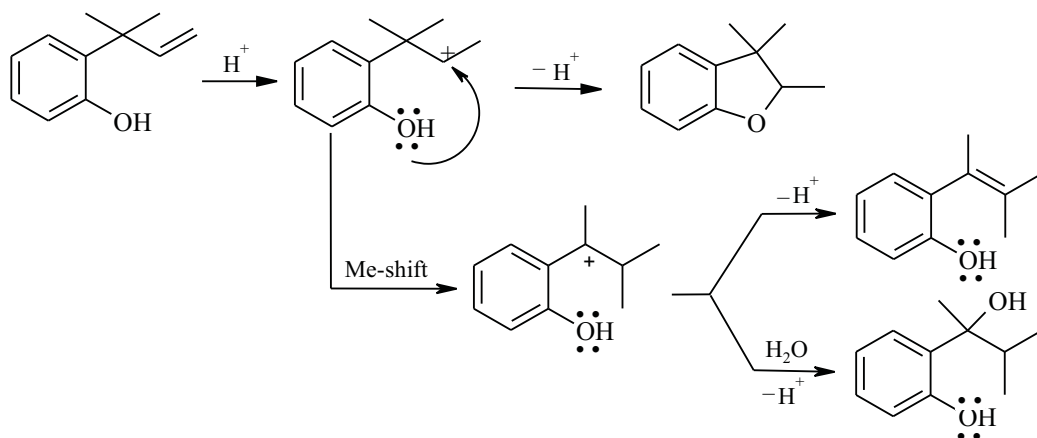
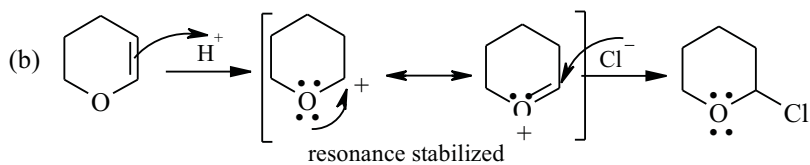
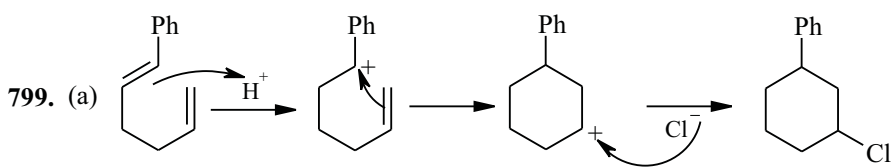
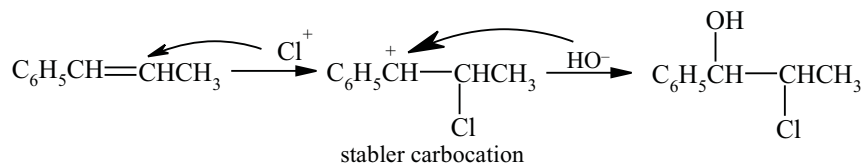
D: 2-Pentanone.

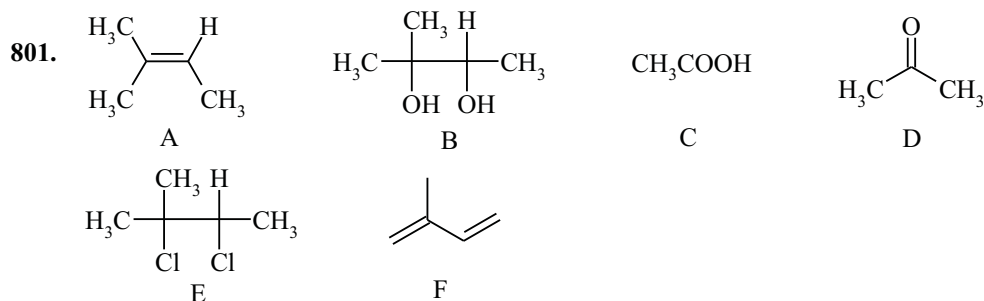
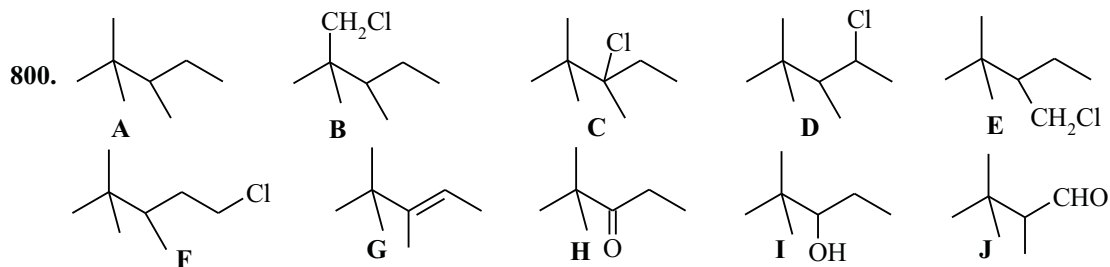






797. (a)

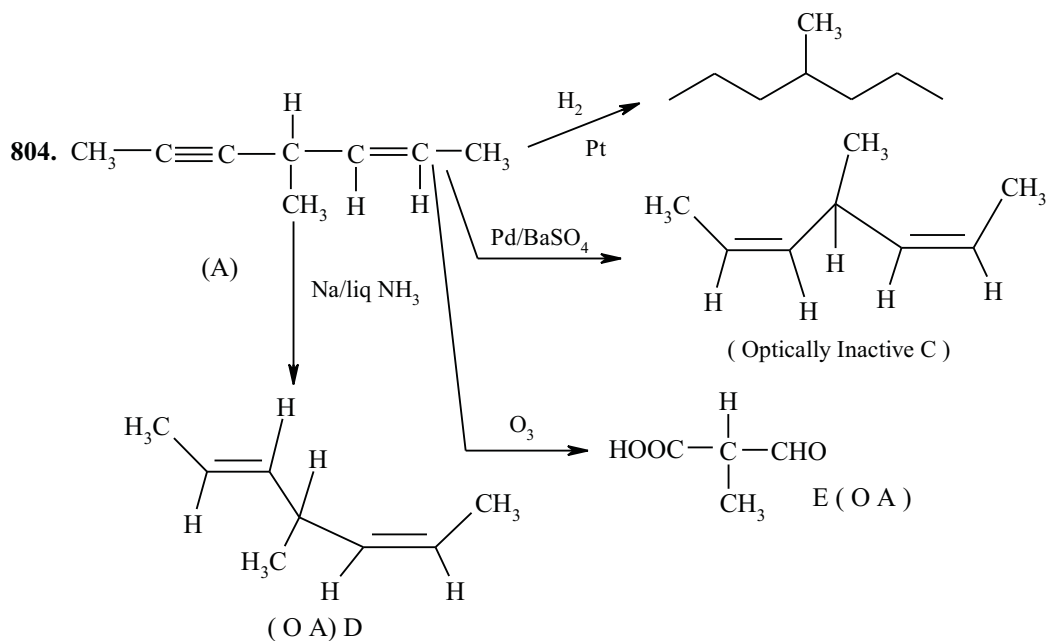
(b) $\text{IV} < \text{II} < \text{III} < \text{V} < \text{I}$ 798. A : $\text{Et}_3\text{N}^+\text{CCl}_2^-$ B : $\text{Et}_2\text{NCHCl}_2$ C : $\text{Et}_2\text{N}-\text{CHO}$ (c) $\text{HOCl} \longrightarrow \text{HO}^- + \text{Cl}^+$ 

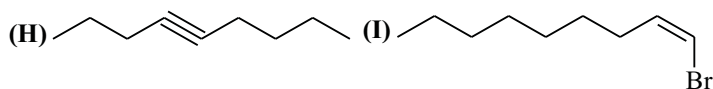
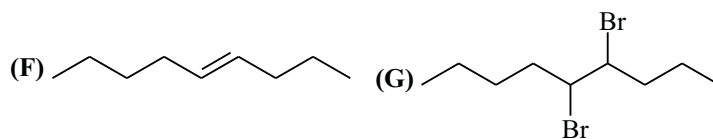
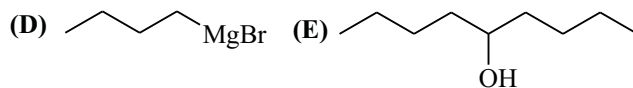
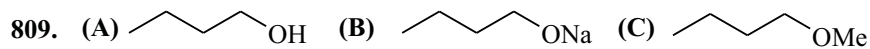
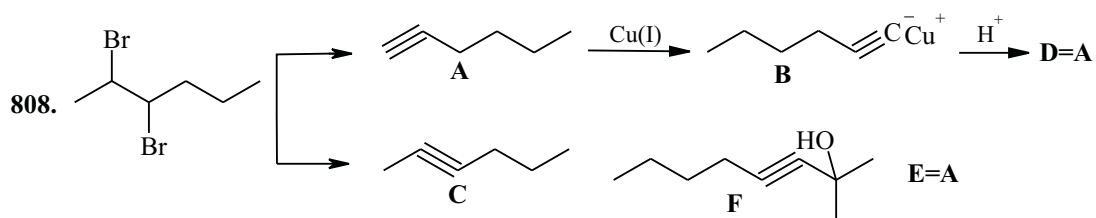
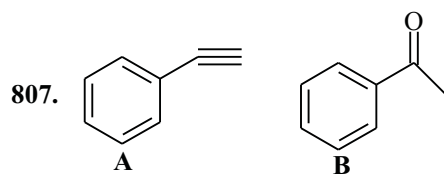
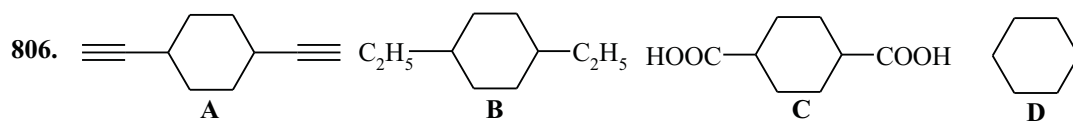
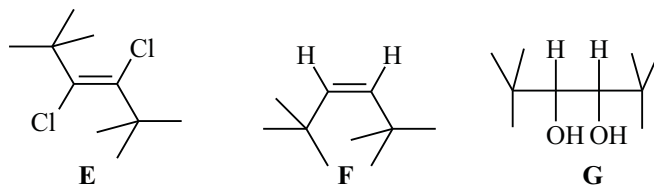
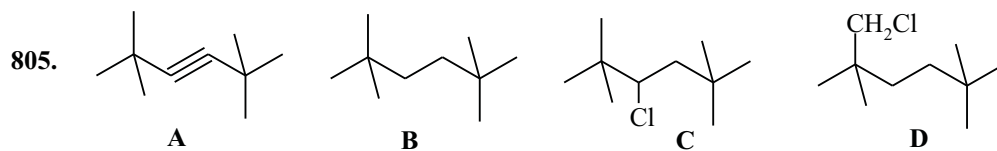


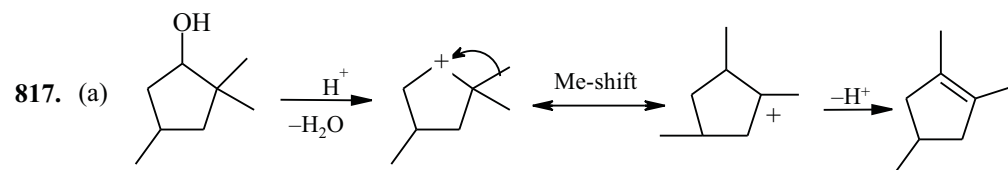
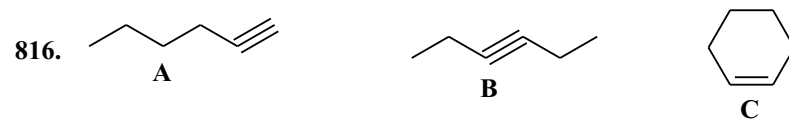
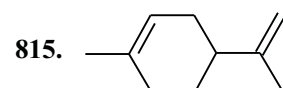
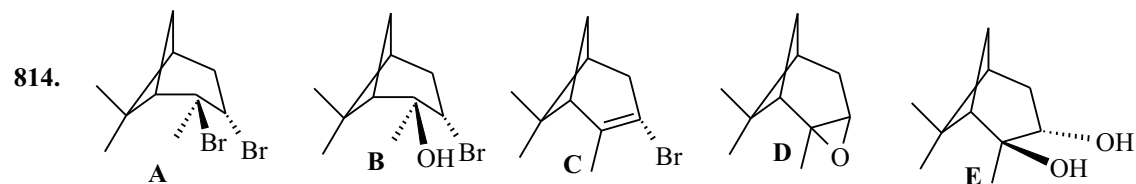
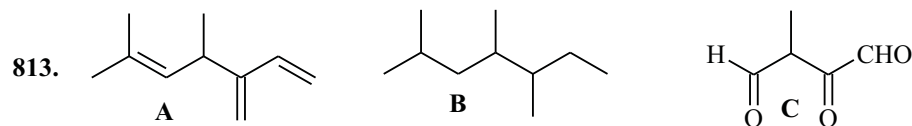
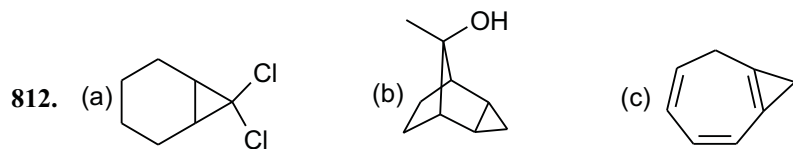
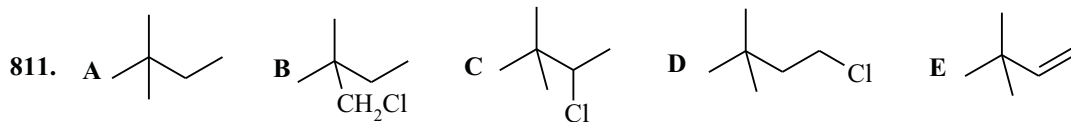
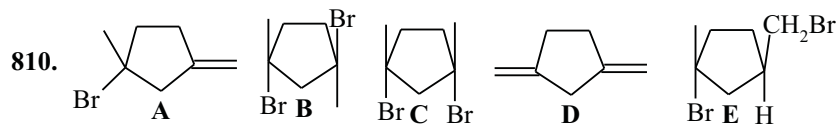
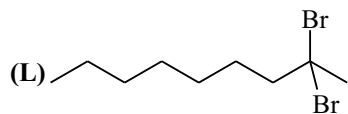
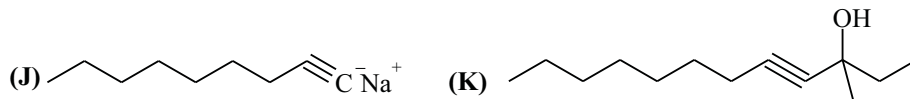
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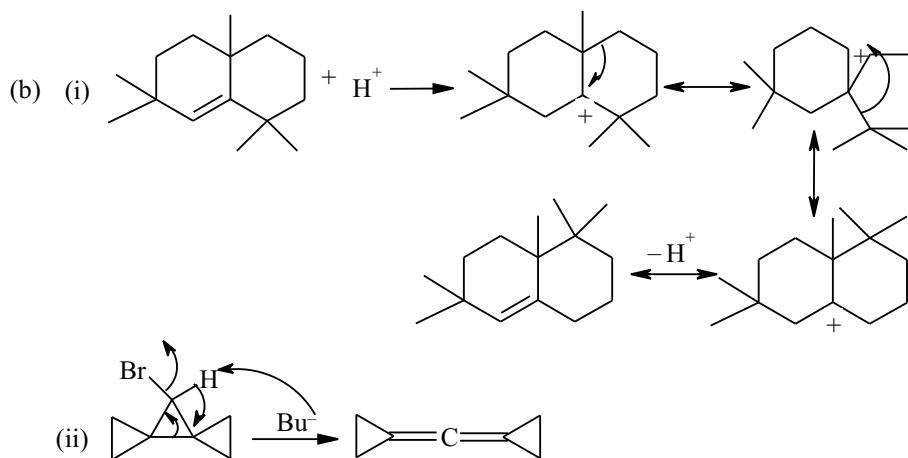
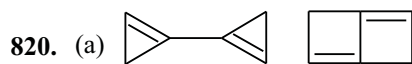
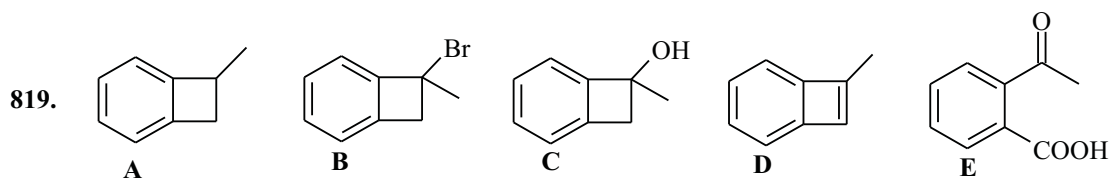
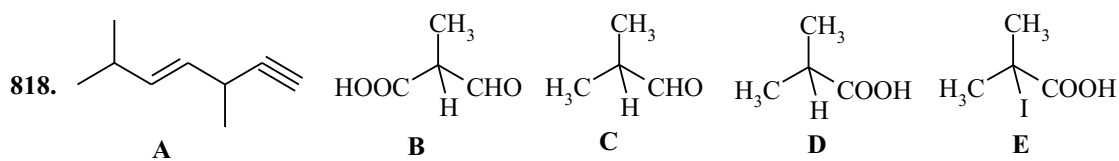
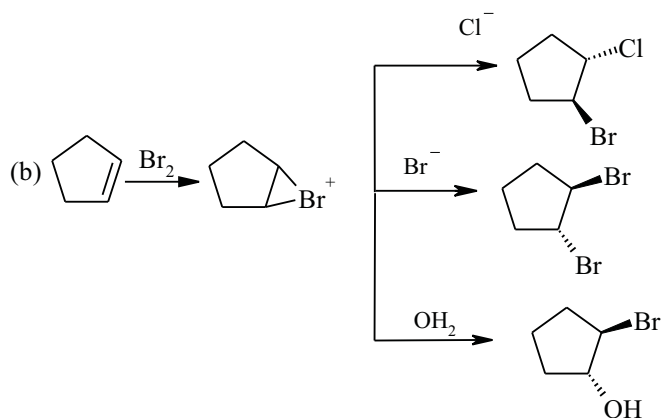
A: 5-methyl-2,4-heptadiene; B: CH_3CHO C: 2-butanone; D: Glyoxal
E: 2-hydroxyethanoic acid.

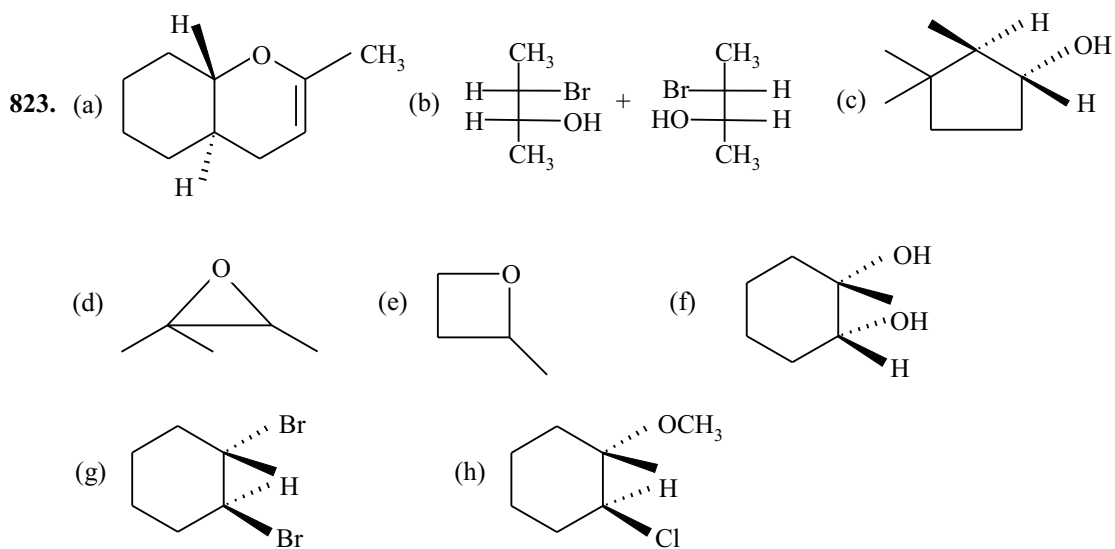
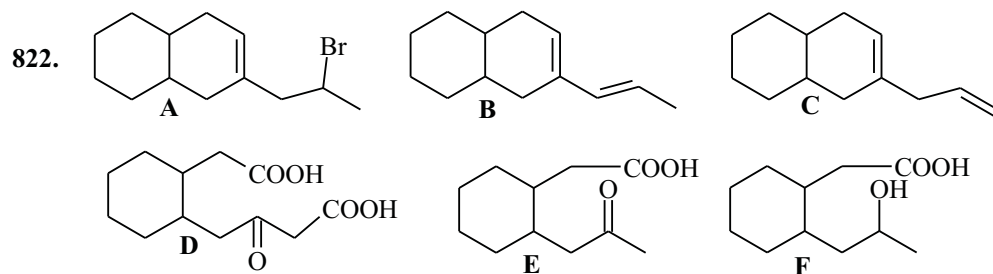
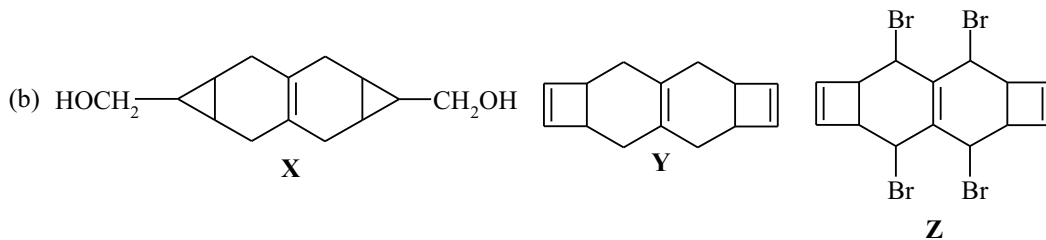
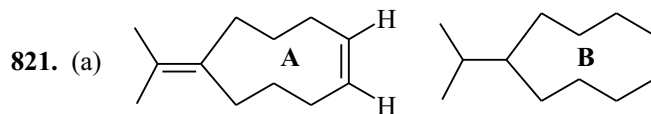
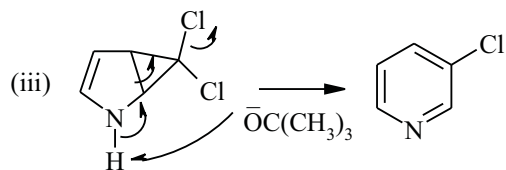
803. A: 3-methyl-1-butene; B: 3-methyl-2-butanol; C: 3-methyl-2-butanone

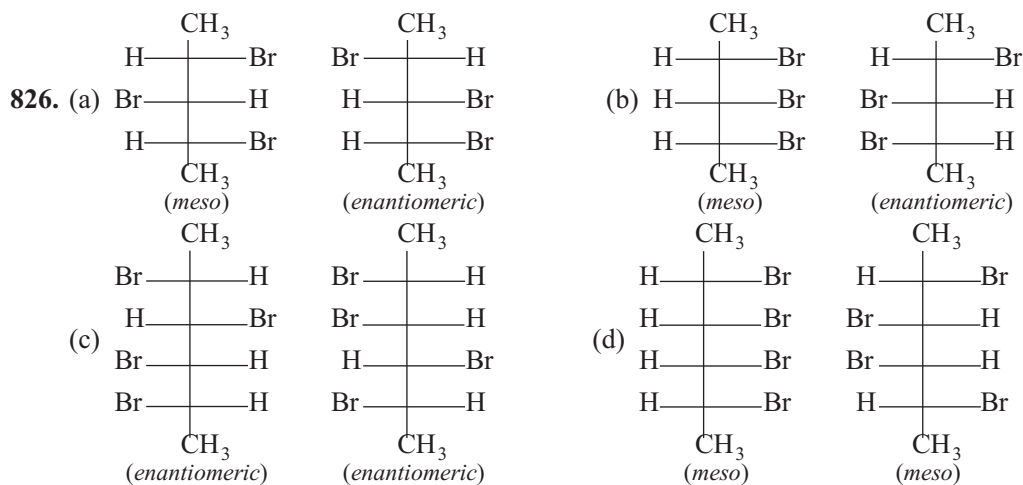
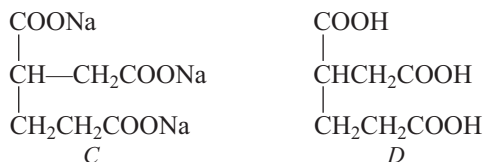
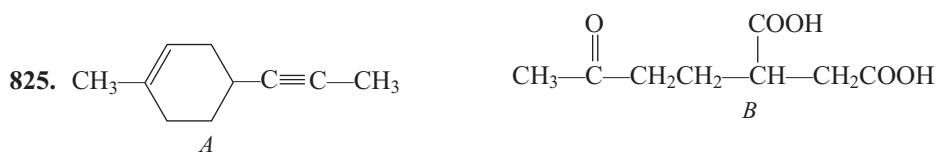
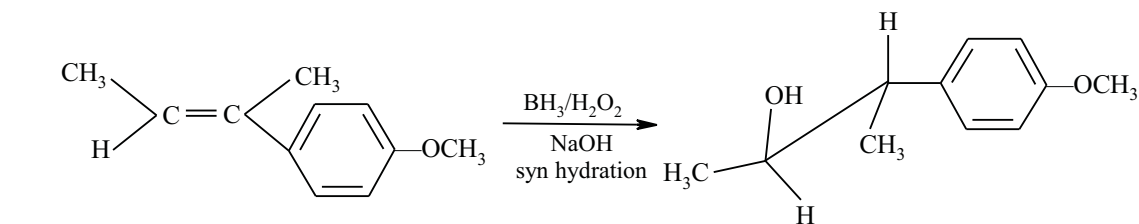
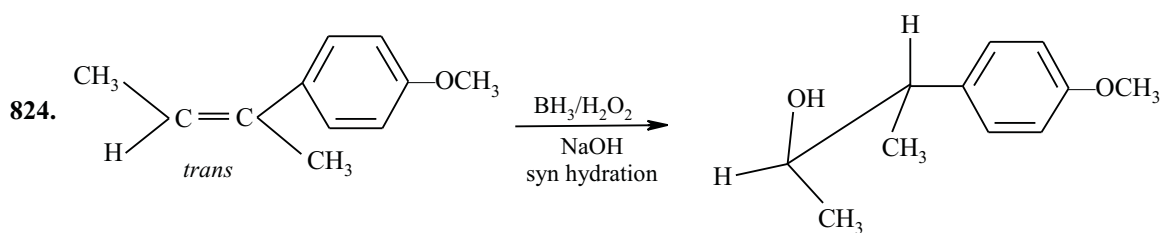


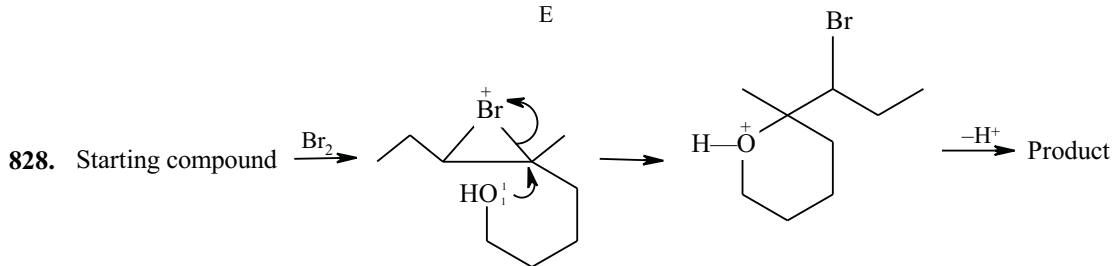
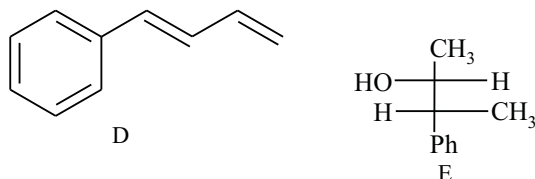
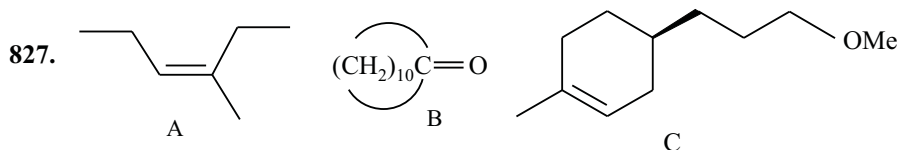




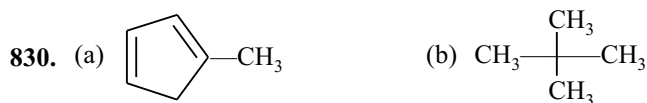




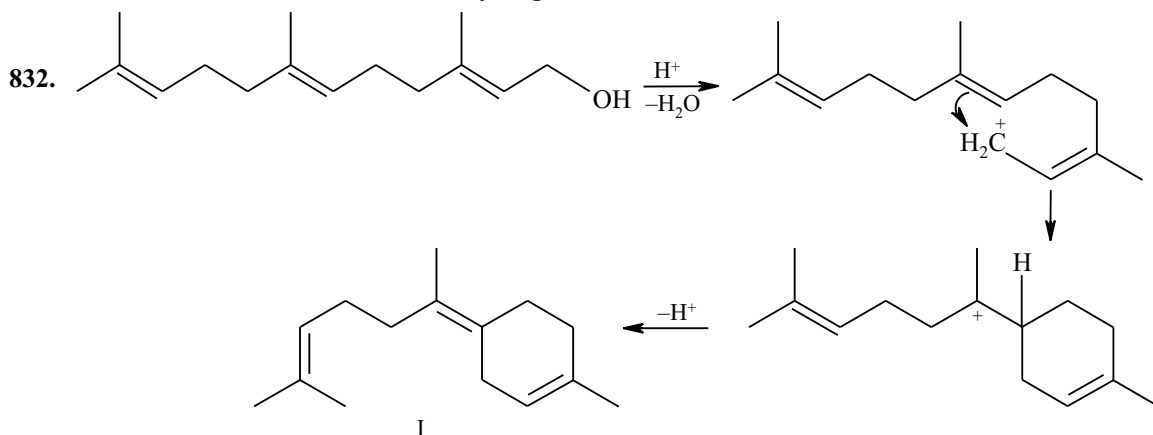


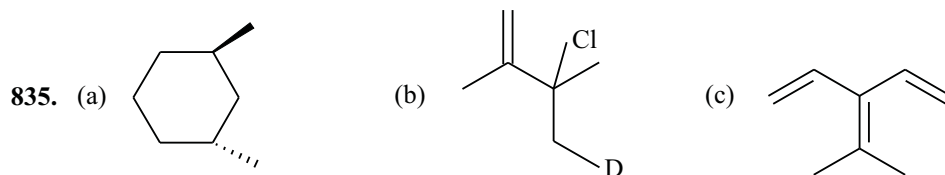
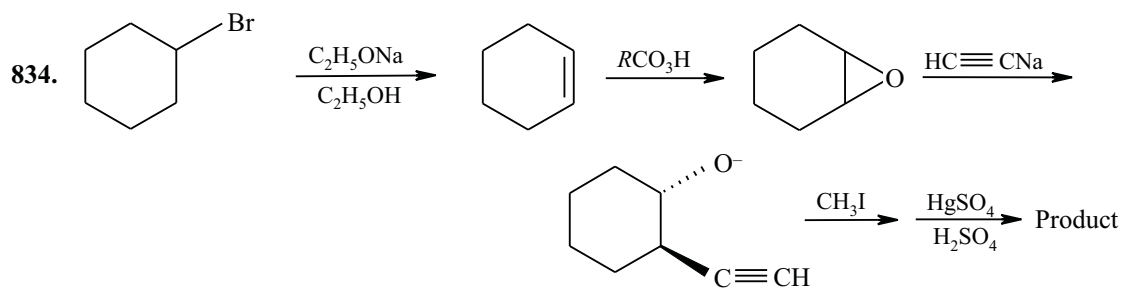
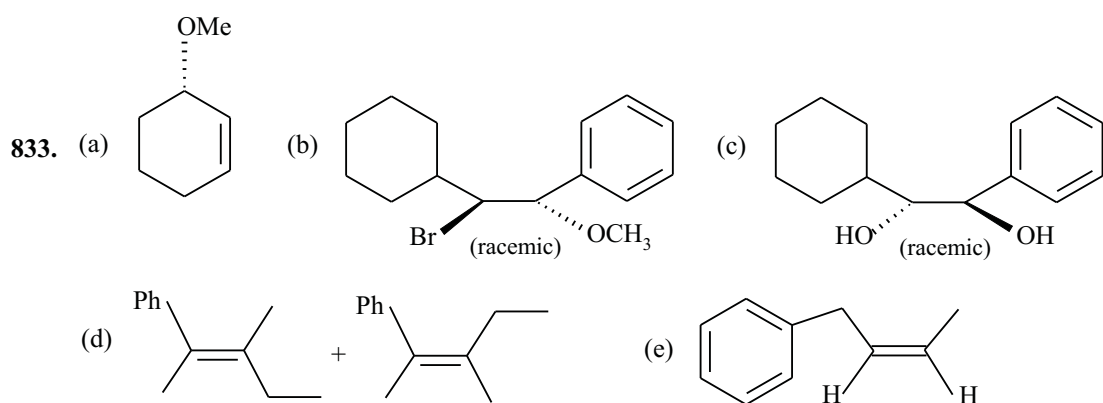
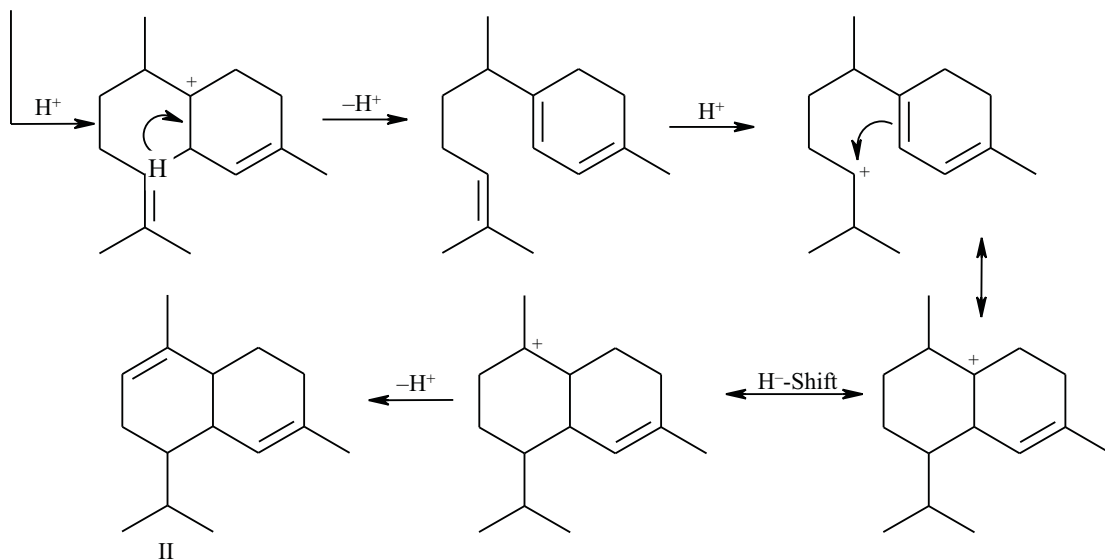


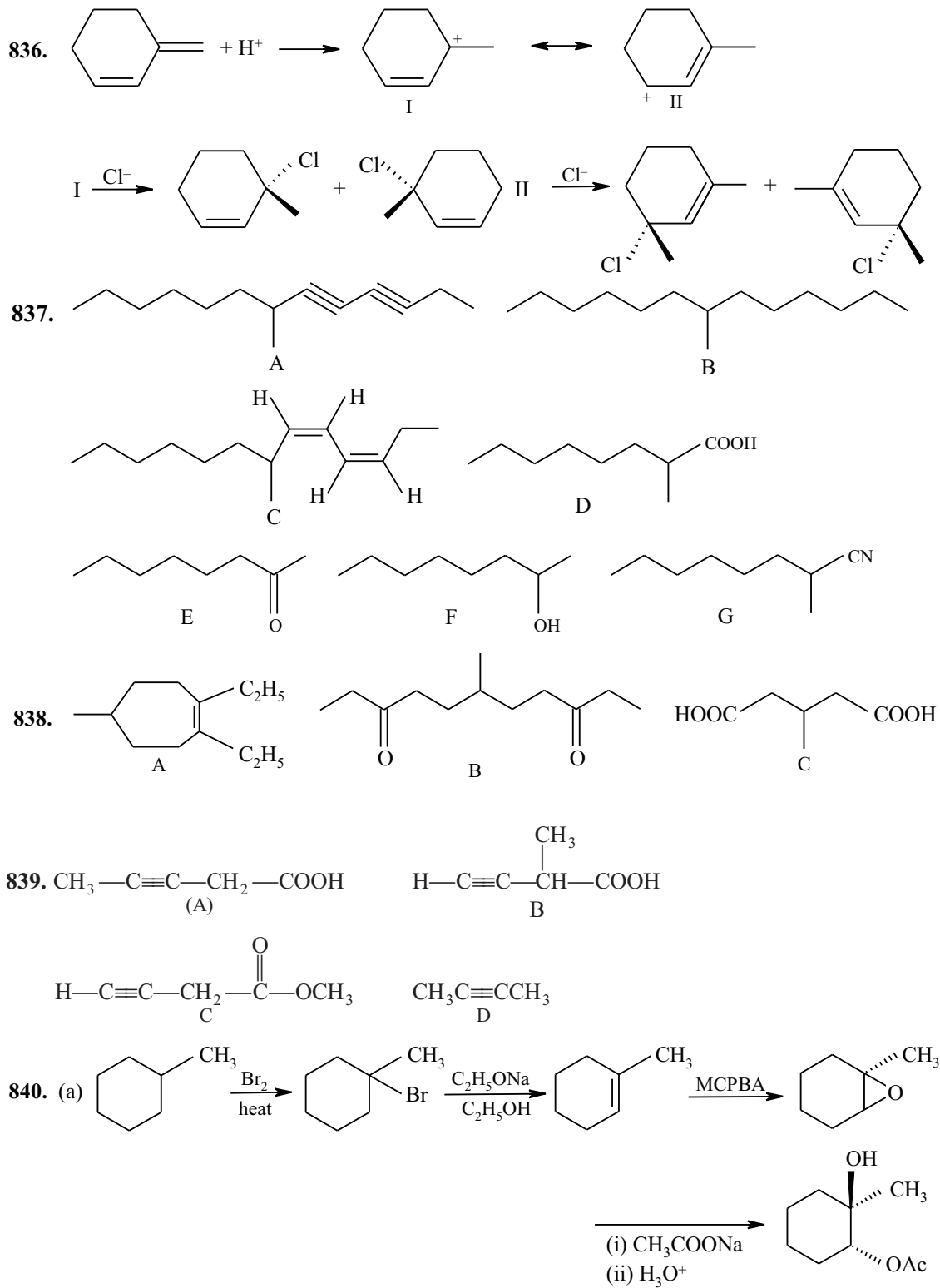
829. (a) (i) $\text{HgSO}_4/\text{H}_2\text{SO}_4$ (ii) NaBH_4
 (b) (i) $\text{H}_2\text{SO}_4/\text{heat}$ (ii) Br_2/MeOH
 (c) (i) $\text{C}_2\text{H}_5\text{ONa}/\text{C}_2\text{H}_5\text{OH}$ (ii) $\text{HOOC}-\text{CH}=\text{CH}-\text{COOH}$

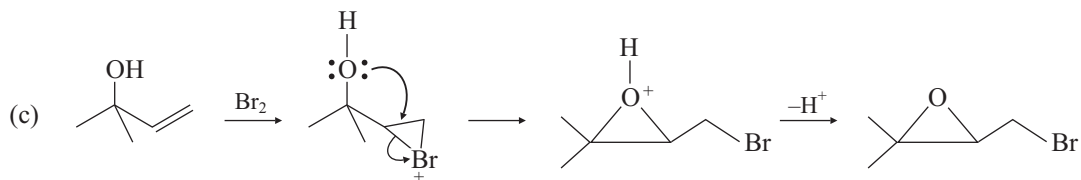
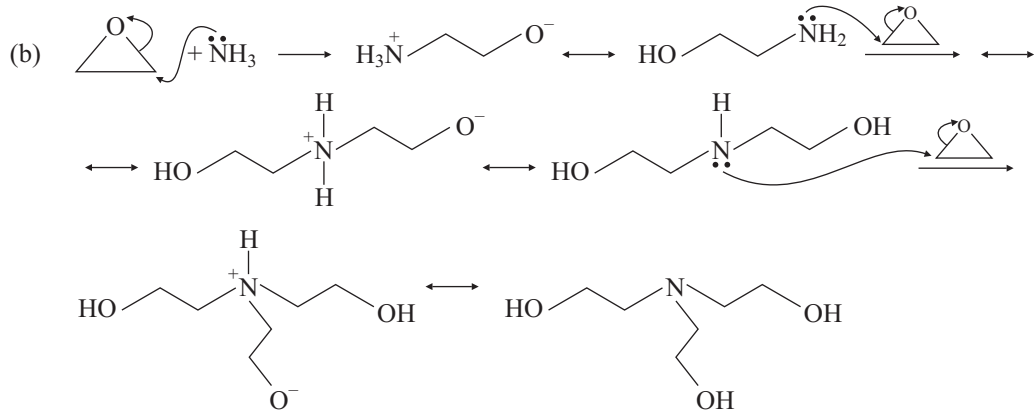
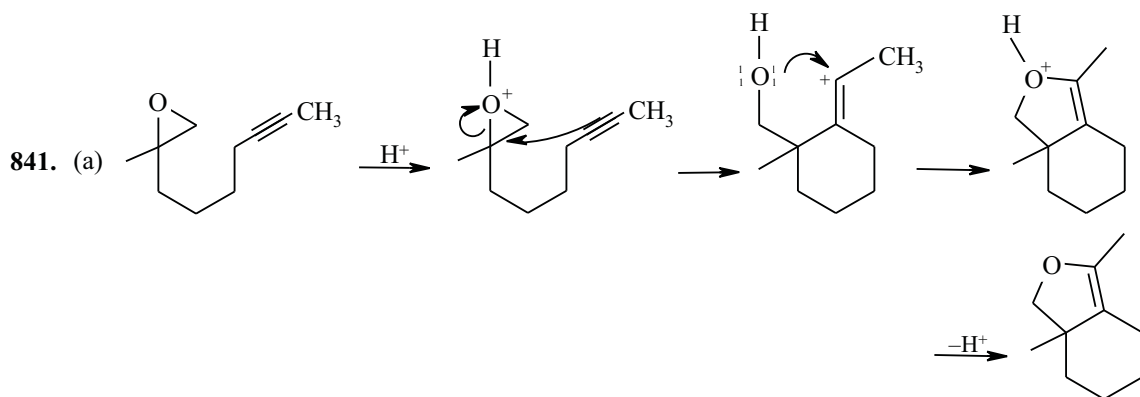
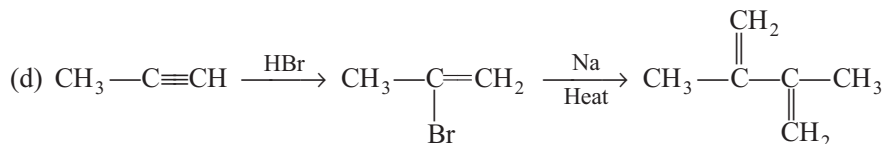
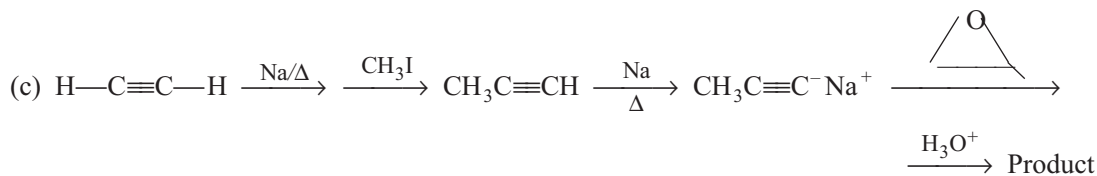
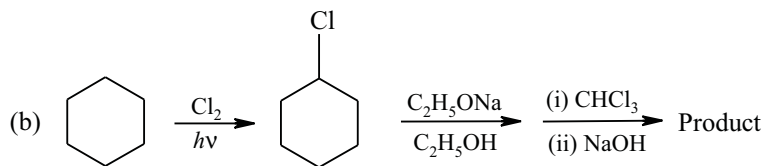


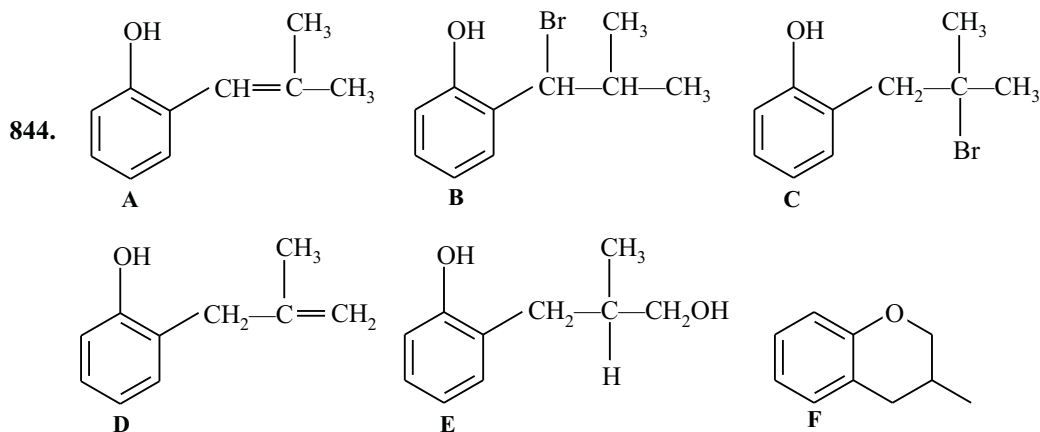
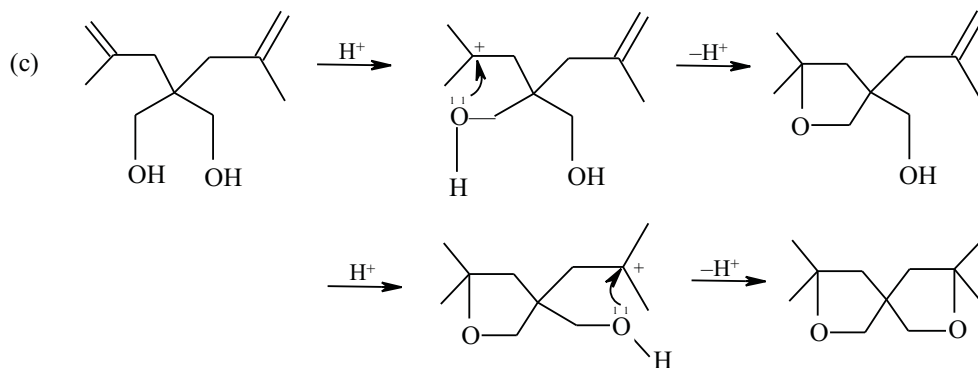
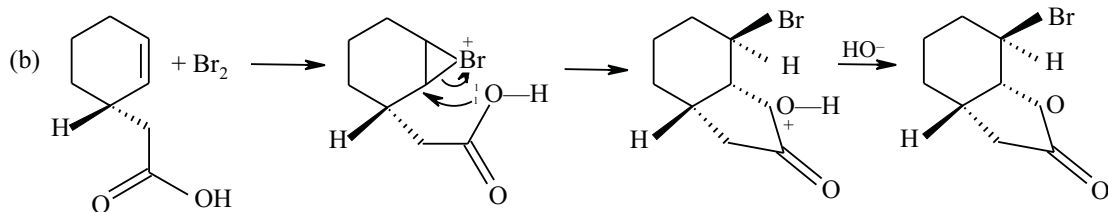
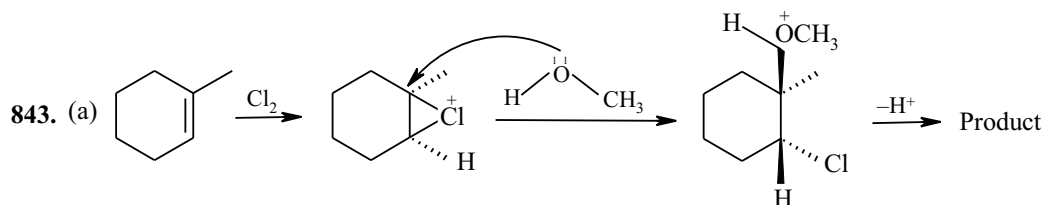
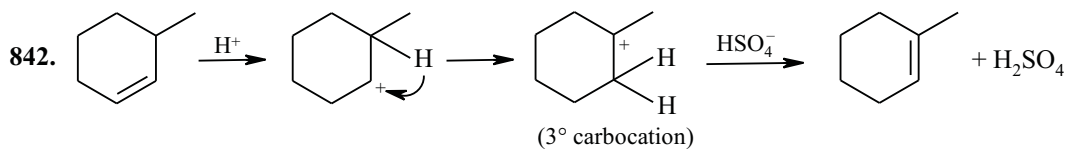
831. If the number of double-bonds are same, heat of hydrogenation depends on degree of substitution at carbon-carbon double bonds. More the number of alkyl substituents at carbon-carbon double bond, more stable will be the alkene towards hydrogenation, hence smaller will be the heat of hydrogenation. On that basis :
 C—least substituted, highest heat of hydrogenation.
 A—most substituted, least heat of hydrogenation.

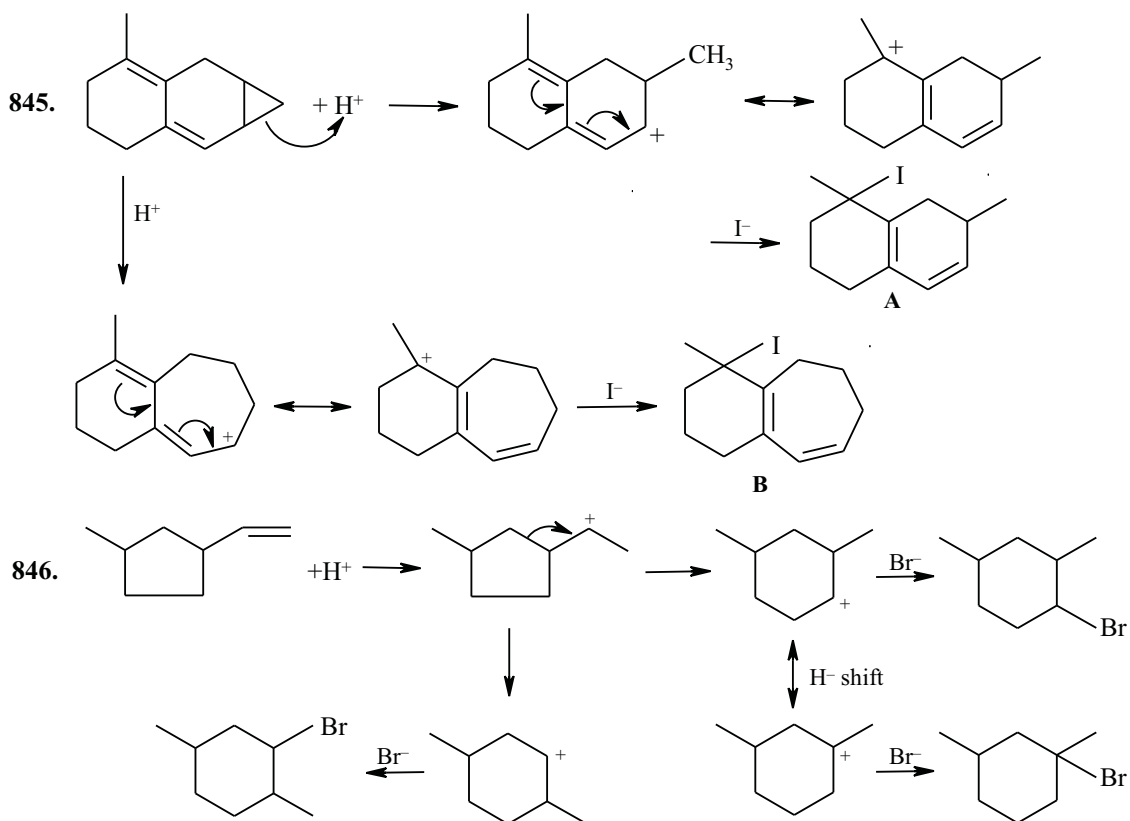




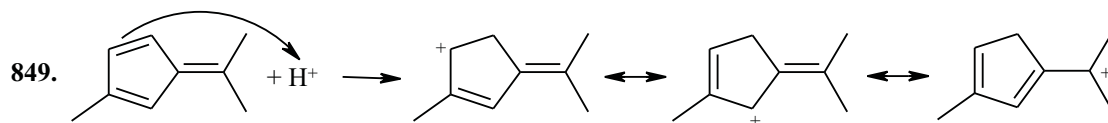
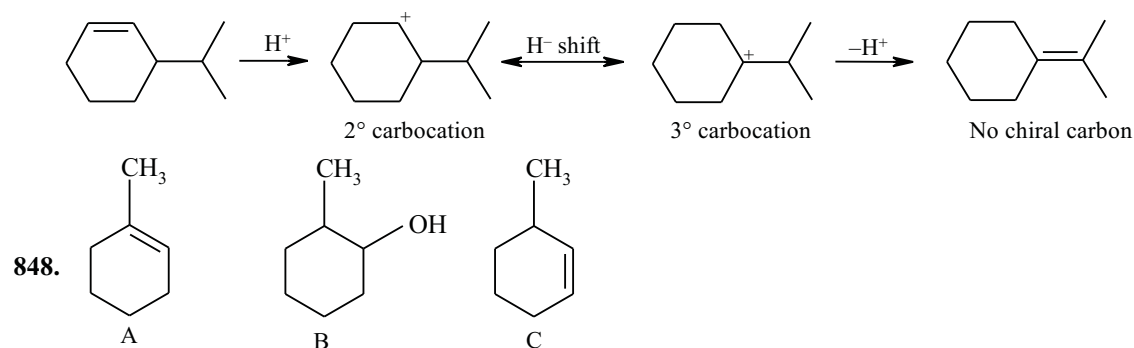








847. This compound has a chiral carbon. Therefore can be resolved into enantiomers. Treatment of this compound with concentrated sulphuric acid bring about isomerization into a more stable compound but without any chiral carbon, hence optical activity is lost as:



Protonation at any other side will produce a less resonance stabilized carbocation.