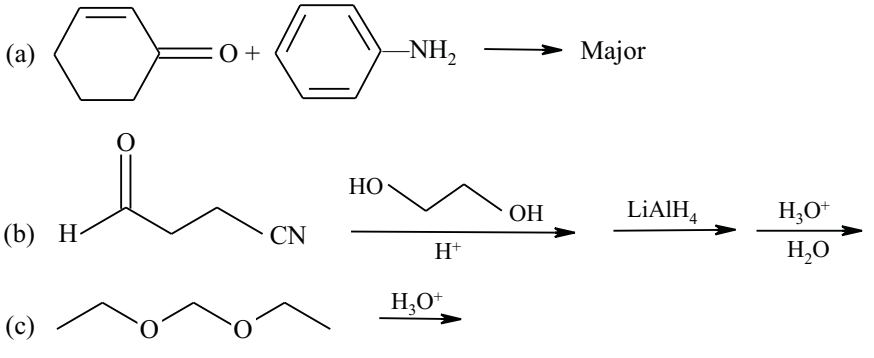
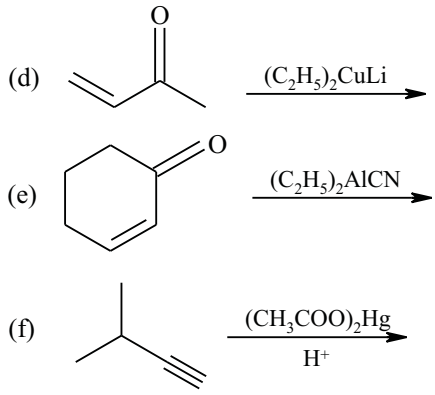
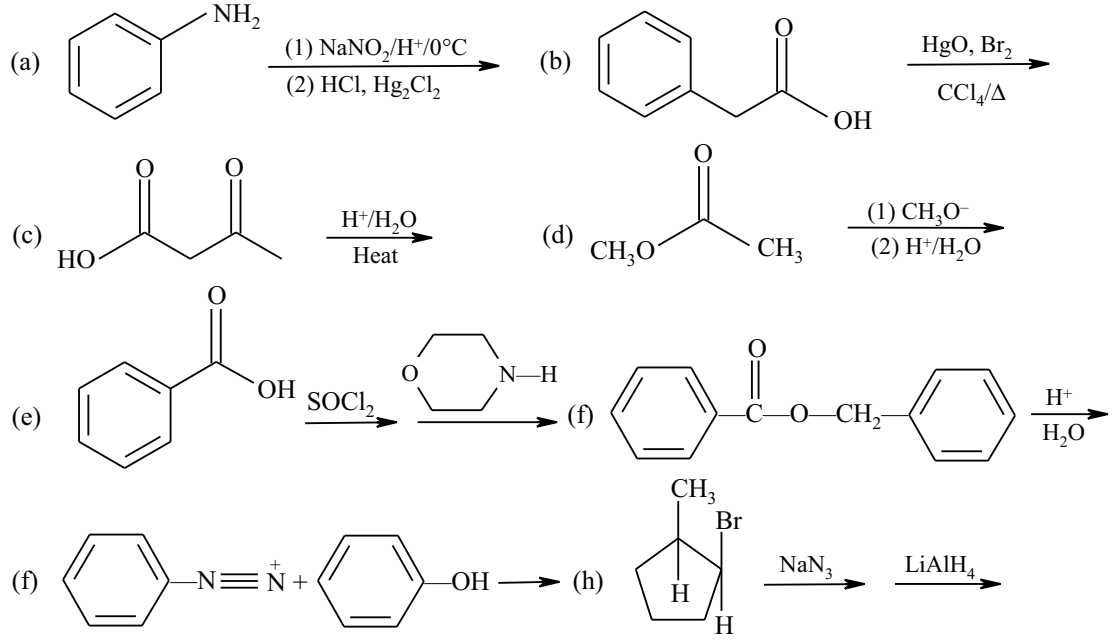
MISCELLANEOUS

PROBLEM 1382 Complete the following reactions:

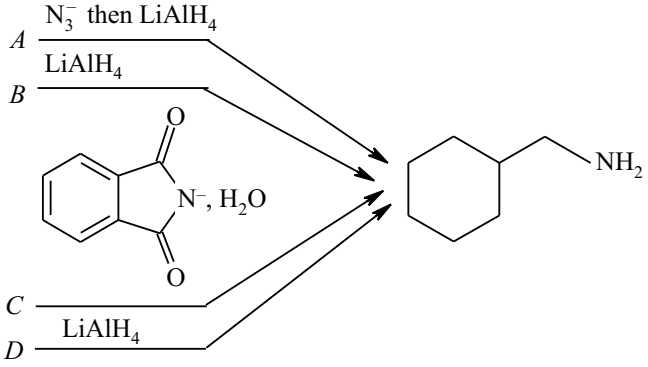




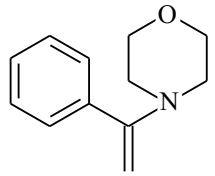
PROBLEM 1383 Write major products of the following reactions:

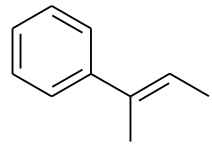


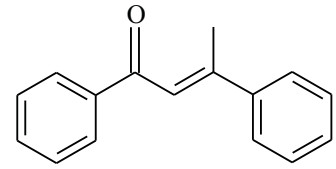
PROBLEM 1384 Aminomethylcyclohexane can be prepared from simple starting materials using the four methods shown below. Provide a suitable starting material for each of the reaction shown:



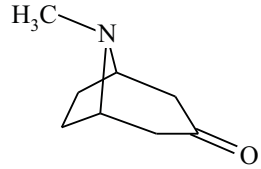
PROBLEM 1385 Starting with acetophenone, suggest a synthesis of each of the following compounds.

(A) 

(B) 

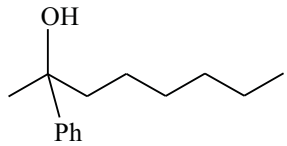
(C) 

PROBLEM 1386 Cocaine (*A*) on alkaline hydrolysis produces benzoic acid, methanol and *B* ($C_9H_{15}NO_3$). *B* on treatment with acidified solution of chromic acid produces "*C*" which on simple heating yields the following compound:

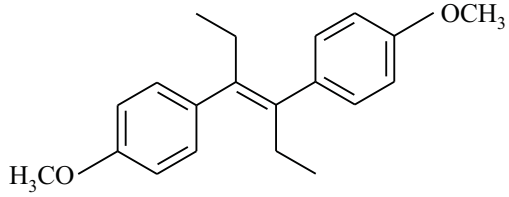


Deduce structures of *A*, *B* and *C*.

PROBLEM 1387 Starting with benzyl alcohol and any alkylhalides containing five or less carbons, propose a step-by-step synthesis of the following compound.



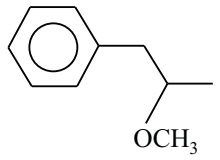
PROBLEM 1388 Propose synthesis of Dimestrol starting from *p*-methoxypropiophenone. Show mechanism of each step.

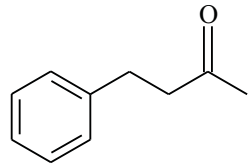


(Dimestrol)

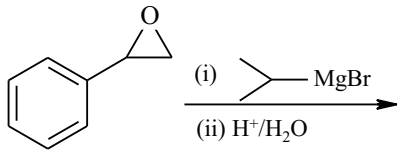
PROBLEM 1389 Compound *A* (C_4H_8O) gives positive iodoform test but does not decolourize bromine water solution or it does not evolve any gas on treatment with NaH. Reaction of *A* with excess of benzaldehyde in alkaline medium gives two products *B* and *C*. These products are unstable and readily dehydrate into stable products *D* and *E*. *D* reacts with I_2 in basic medium to give iodoform; *E* does not. Treatment of *D* with bromine in acetic acid medium yields *F*. *F* can be reduced by $NaBH_4$ to give *G*. Warming *G* in basic solution results in formation of *H*. Ozonolysis of H followed by reductive work-up, gives benzaldehyde and a ketone *I* ($C_4H_6O_2$). Identify *A*–*I*.

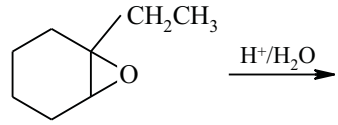
Problem 1390 Beginning with benzyl bromide, suggest a synthesis of the following compounds:

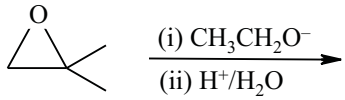
(a) 

and (b) 

Problem 1391 Complete the following reaction indicating stereochemistry of product where appropriate:

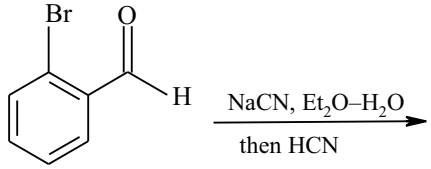
(a) 

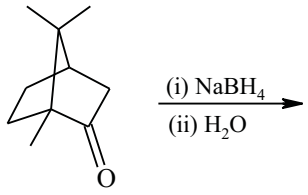
(b) 

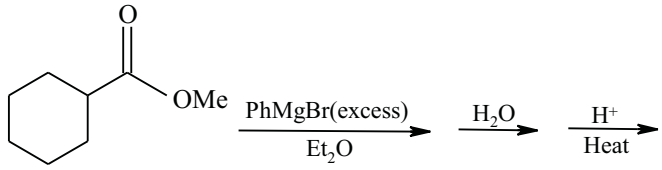
(c) 

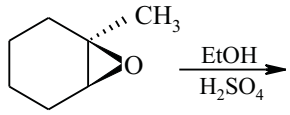
Problem 1392 Compound *A*, on reaction with $CH_3Cl/AlCl_3$ gives compound *B*. The mass spectrum of *B* is dominated by a peak at $m/e = 91$, which is identified as tropylium ion. *B*-undergoes free radical bromination to give *C*. *C* reacts with diethylmalonate in presence of sodium ethoxide to give *D*. Treating *D* with aqueous acid followed by gentle warming gives *E* and CO_2. Identify *A* to *E*.

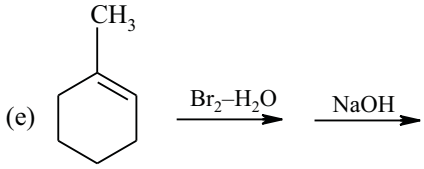
Problem 1393 Draw structures of major organic product in each of the reaction below:

(a) 

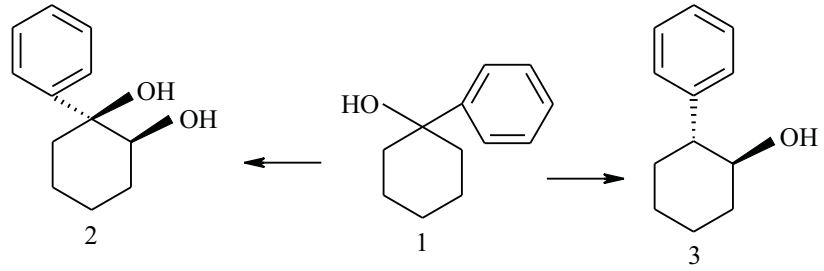
(b) 

(c) 

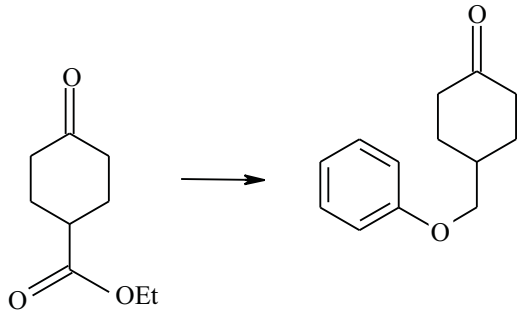
(d) 



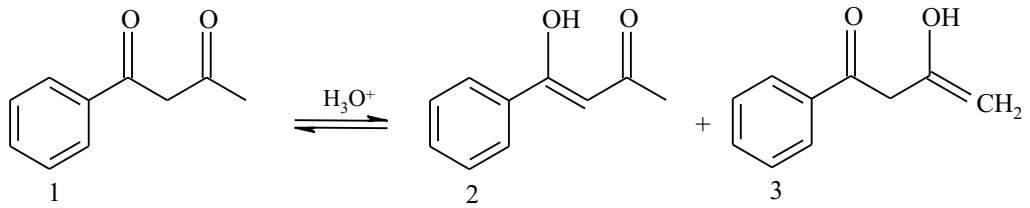
PROBLEM 1394 Suggest reaction sequences, including reagents and conditions, which could be used to effect the transformation of 1 to compound 2 and 3. You may use the indicated starting material and any reagents, which you deem necessary.



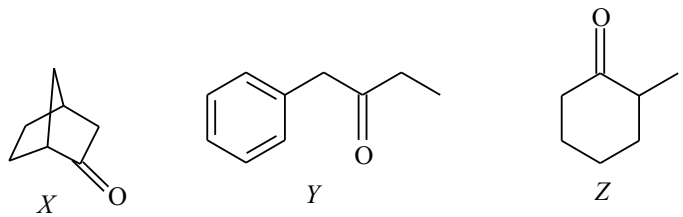
PROBLEM 1395 Bring about the following transformation:



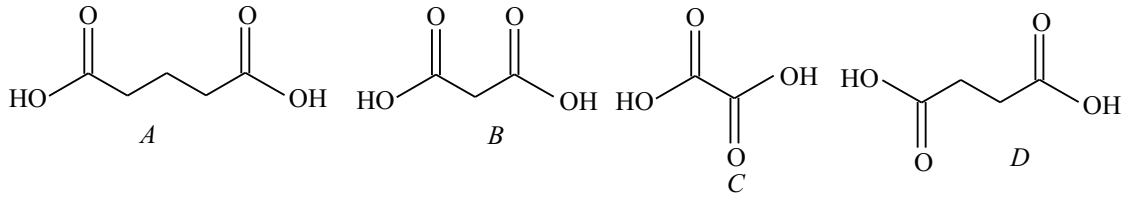
PROBLEM 1396 Exposure of 1,3-diketone 1 to aqueous acid catalyzes the formation of enols 2 and 3. Justifying your answer, indicate, which is thermodynamically more stable enol. Draw a mechanism of formation of most stable tautomer of 1 in presence of an acid catalyst.



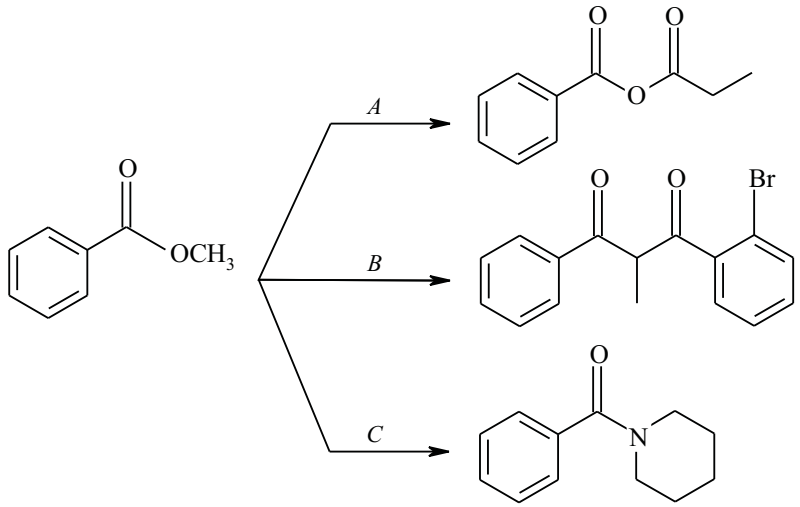
PROBLEM 1397 For the following carbonyl compounds *X*, *Y* and *Z*, draw the structures of thermodynamically most stable enolate anion that could be formed in presence of a strong base:



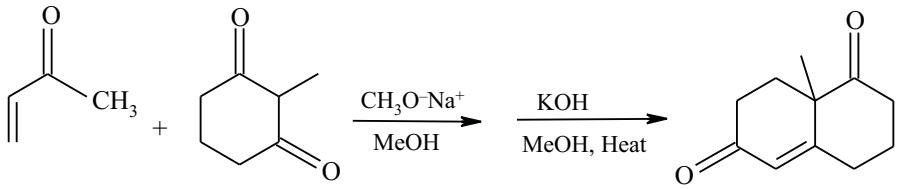
Problem 1398 Place the following dicarboxylic acids in order of increasing acidity.



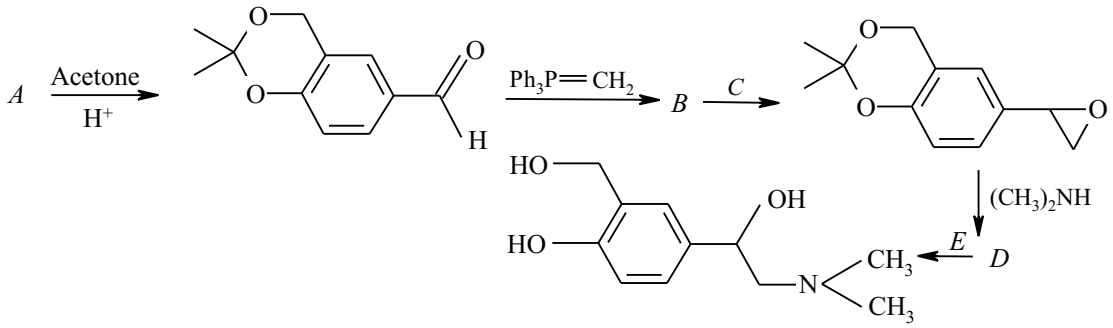
Problem 1399 Suggest reaction sequence, including reagents and conditions, which could be used to bring about the following transformations:



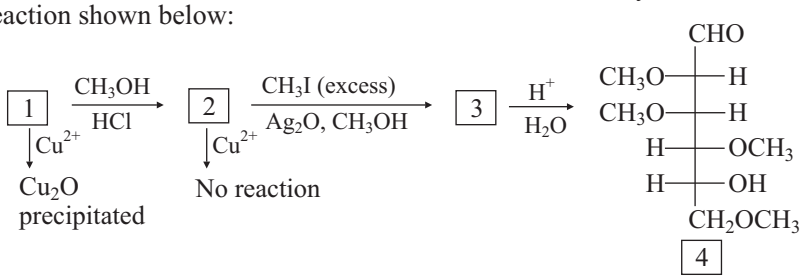
Problem 1400 Propose mechanism of the following reaction:



Problem 1401 Provide structures of missing species:

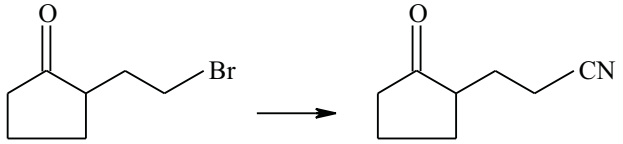


PROBLEM 1402 Unknown monosaccharide 1 was converted to tetramethylated aldohexose 4 through the sequence of reaction shown below:

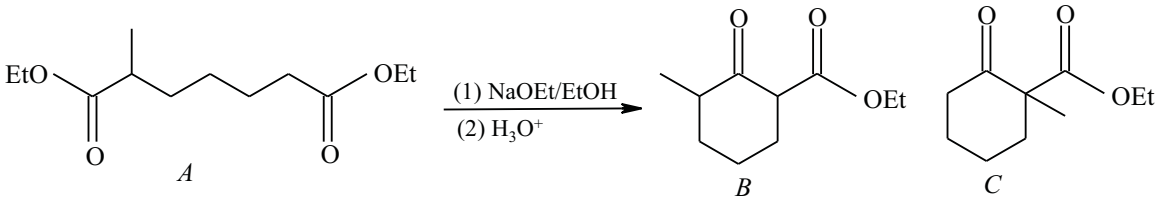


Using the information provided, draw the correct structures of 1, 2 and 3.

PROBLEM 1403 Bring about the following transformations in good yield:



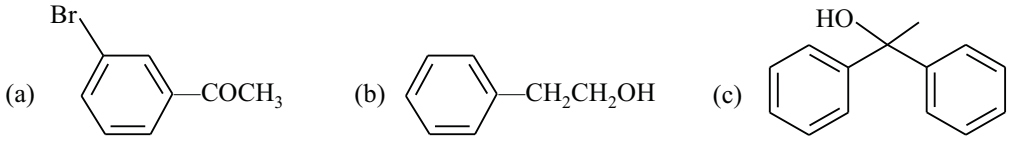
PROBLEM 1404 When the diester (*A*) was treated with a solution of sodium ethoxide in ethanol and the reaction mixture then quenched with aqueous acid, only (*B*) was formed. The alternative product (*C*) was not formed under these reaction conditions. Explain the result.



PROBLEM 1405 Synthesize the following compounds starting from styrene:

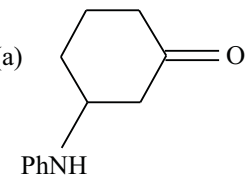
(a) Ph—C(=O)—CH_3 (b) Ph—CH_2—CHO (c) Ph$CH_2CH_2CH_2OH$

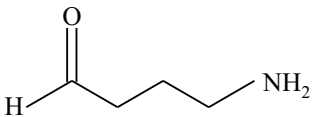
PROBLEM 1406 Bring about the following synthesis starting from phenyl acetylene:

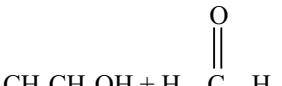


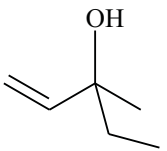
Solutions

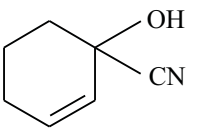
MISCELLANEOUS

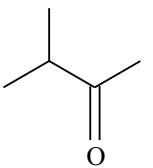
1382. (a) 

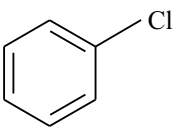
(b) 

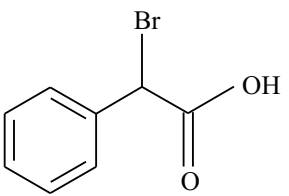
(c) 

(d) 

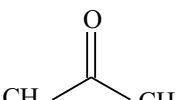
(e) 

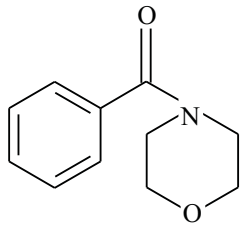
(f) 

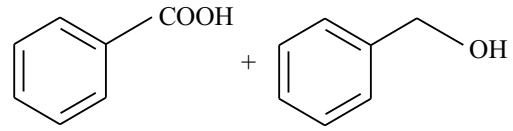
1383. (a) 

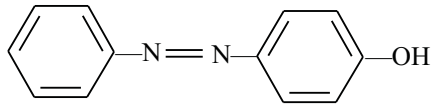
(b) 

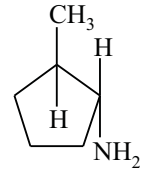
(c) CH_3COCH_3

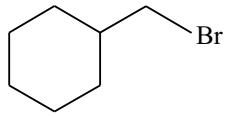
(d) 

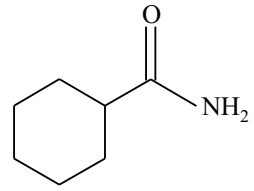
(e) 

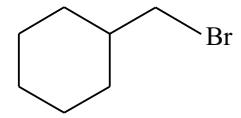
(f) 

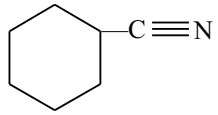
(g) 

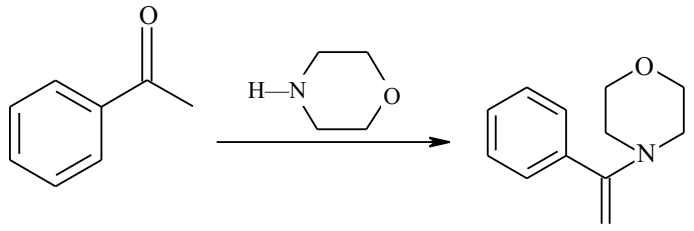
(h) 

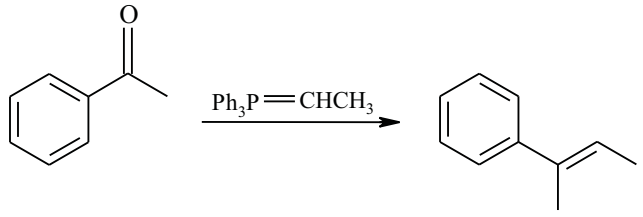
1384. *A* : 

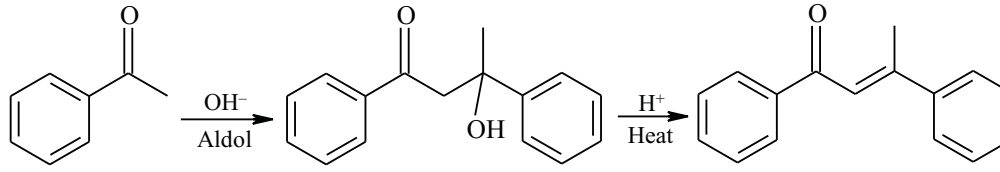
B : 

C : 

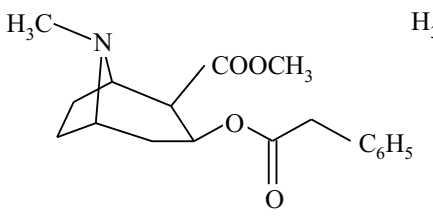
D : 

1385. (A) 

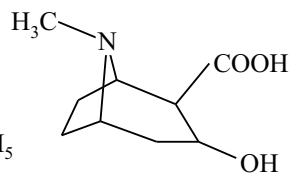
(B) 

(C) 

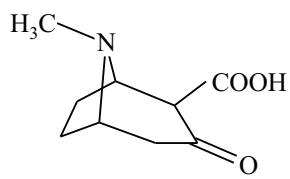
1386.



Cocaine (*A*)

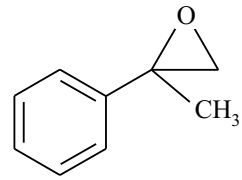


(*B*)



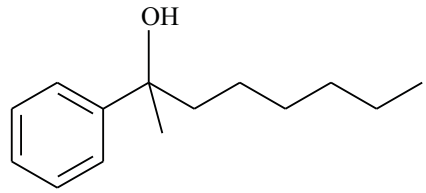
(*C*)

1387. $C_6H_5CH_2OH$ (benzyl alcohol) $\xrightarrow[CCl_4]{PCC}$ C_6H_5CHO $\xrightarrow[(ii)\ H_3O^+]{(i)\ CH_3MgBr}$ $\xrightarrow[CCl_4]{PCC}$ $C_6H_5-\overset{O}{\overset{\|}{C}}-CH_3$ $\xrightarrow[\Delta]{CH_2N_2}$

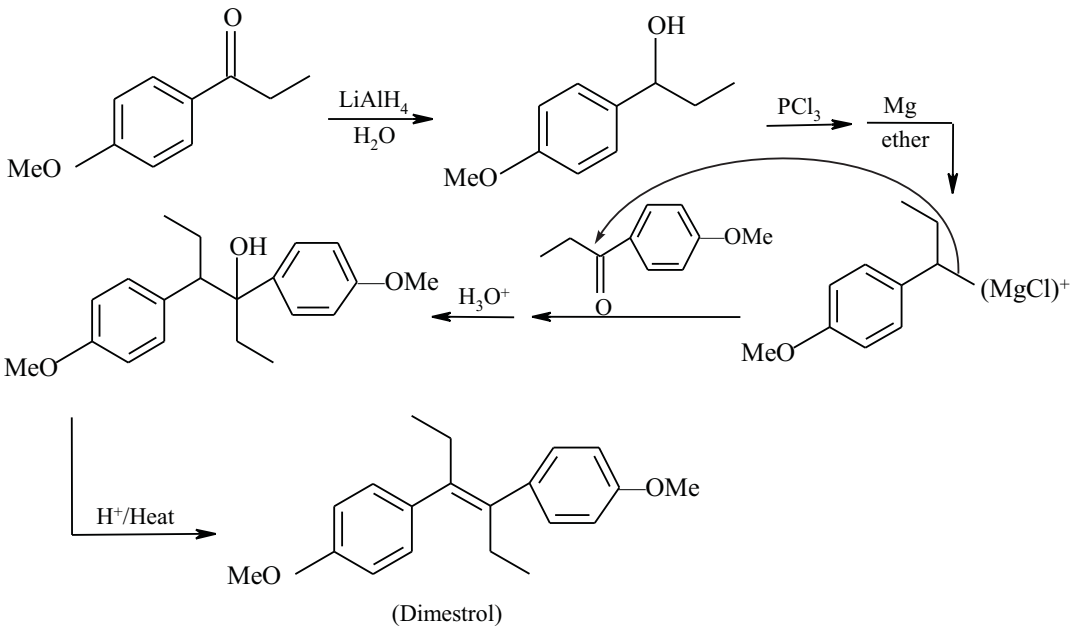


X

X $\xrightarrow{CH_3(CH_2)_3CH_2MgBr}$ $\xrightarrow{H_3O^+}$

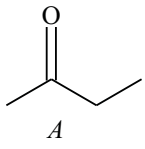


1388.

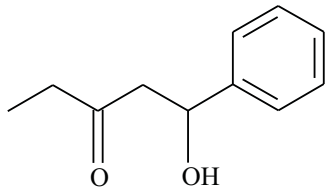


(Dimestrol)

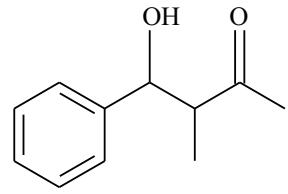
1389.



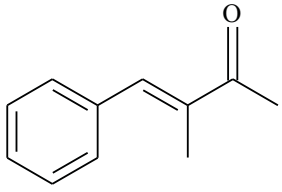
A



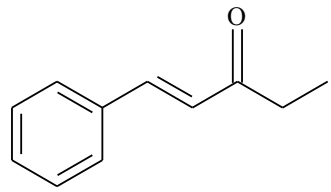
B



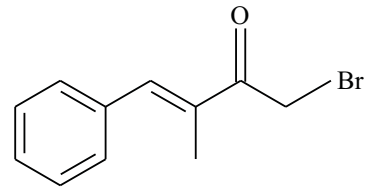
C



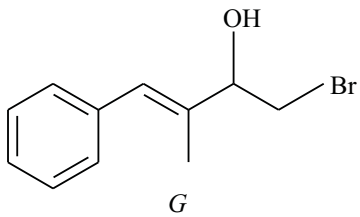
D



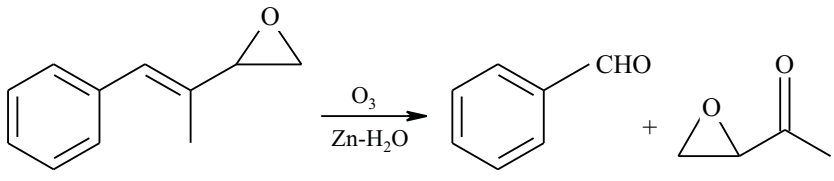
E



F

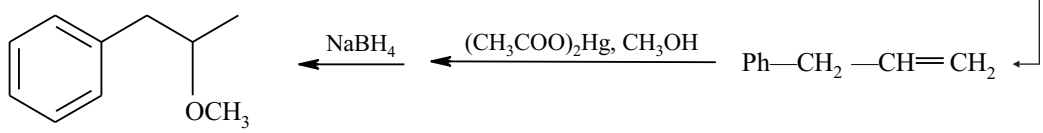


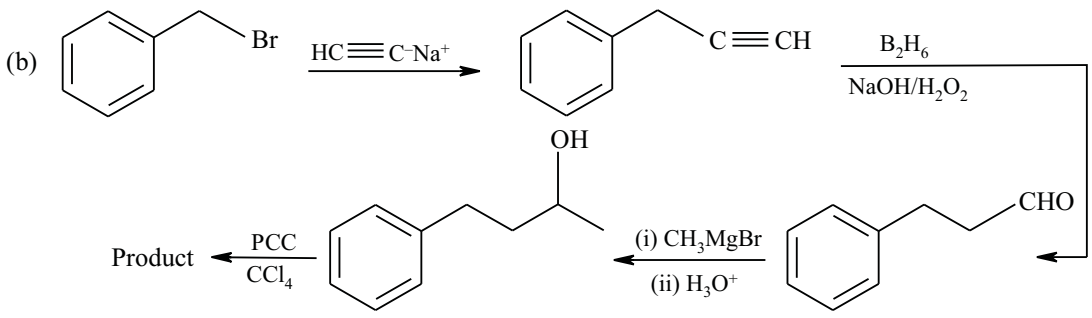
G

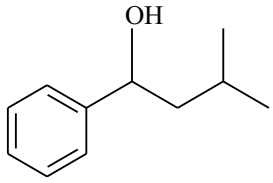


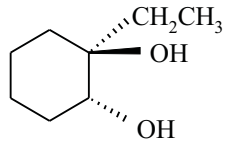
H *I*

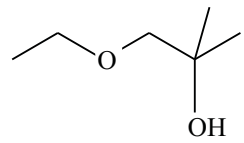
1390. (a) $PhCH_2Br \xrightarrow[ether]{Mg} PhCH_2MgBr \xrightarrow[(ii)\ H_3O^+]{(i)\ \triangle O} Ph{-}CH_2CH_2CH_2OH \xrightarrow{PCl_3} \xrightarrow[C_2H_5OH]{C_2H_5ONa}$

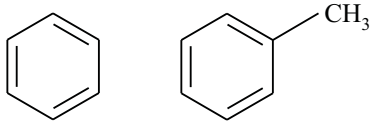


(b) 

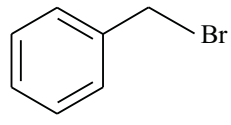
1391. (a) 

(b) 

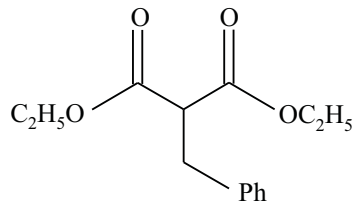
(c) 

1392. 

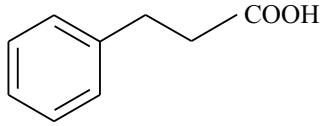
A *B*



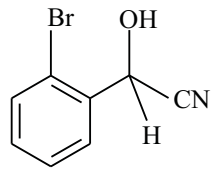
C



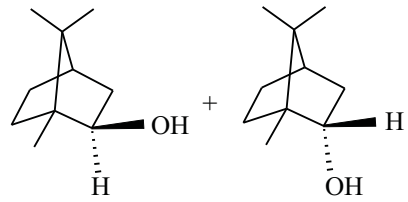
D



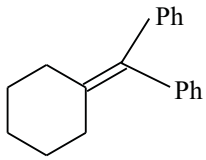
E

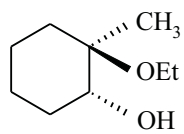
1393. (a) 

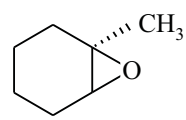
(Enantiomeric)

(b) 

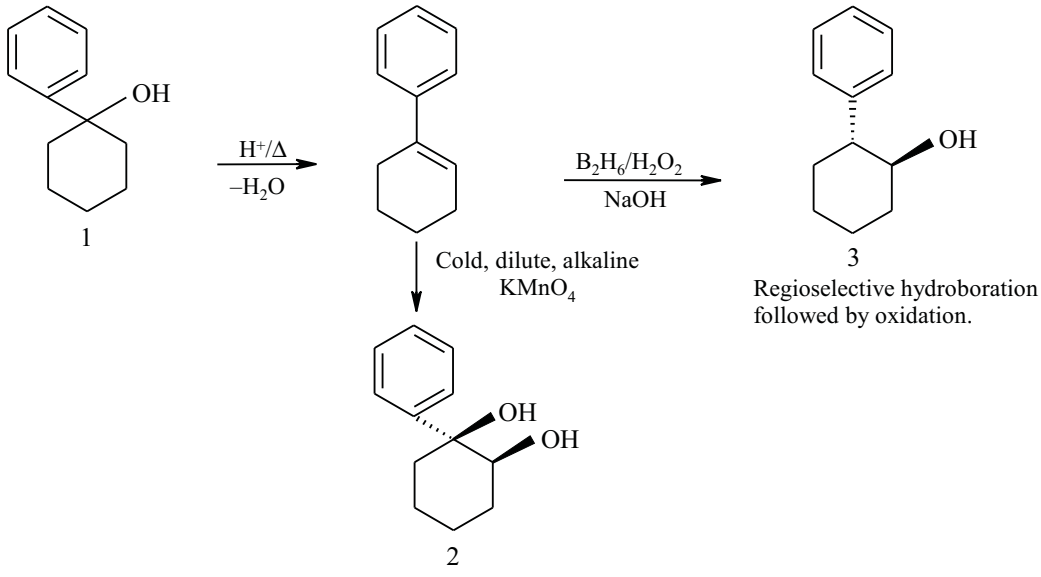
Major Minor

(c) 

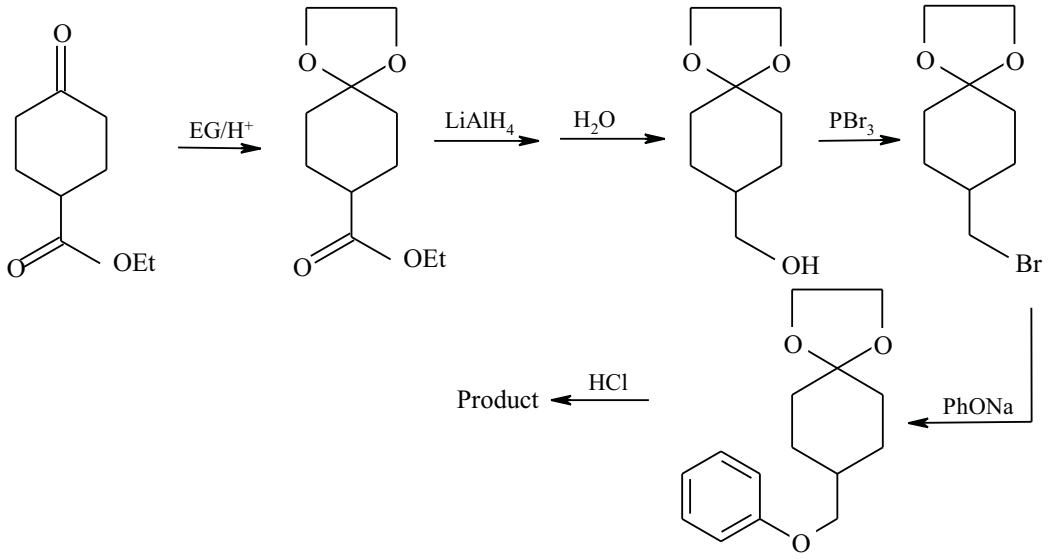
(d) 

(e) 

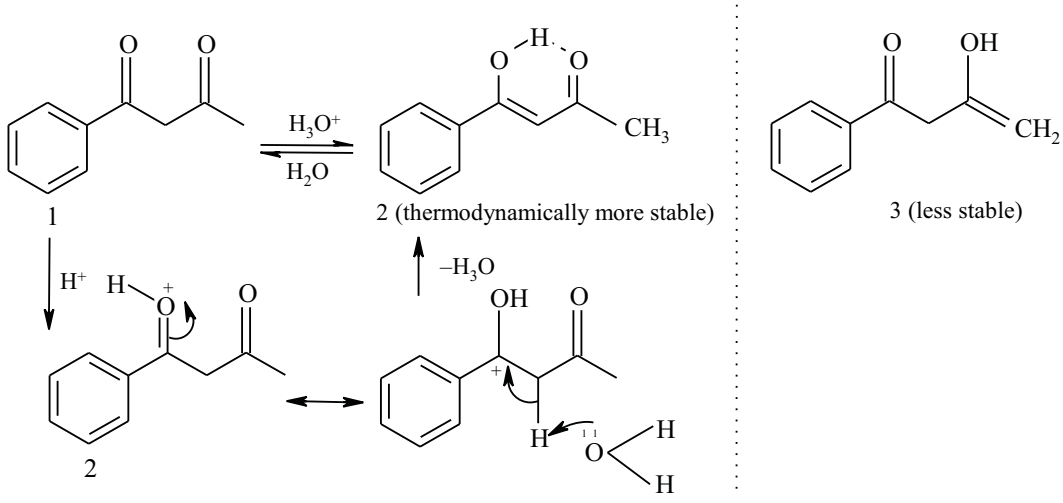
1394.



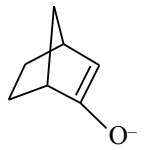
1395.



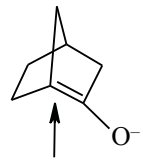
1396. Enol 2 is thermodynamically more stable than 3 because the alkene in this tautomer is conjugated with aromatic ring as well as with carbonyl group. The C═C double bond in enol 3 is isolated and the stability afforded to 2-through resonance is not available to 3.



1397. *X* $\xrightarrow{OH^-}$

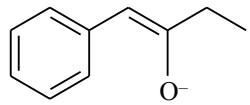


most stable



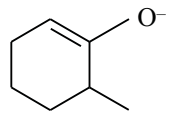
This enol is highly disfavoured-the individual $2p_z$ orbital of the double bond are orthogonal and consequently, the $p\pi$-bond can't form (Berdt's rule)

Y $\xrightarrow{OH^-}$

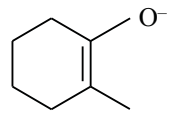


most stable enolate anion because the double bond is in conjugation with aromatic ring.

Z $\xrightarrow{OH^-}$



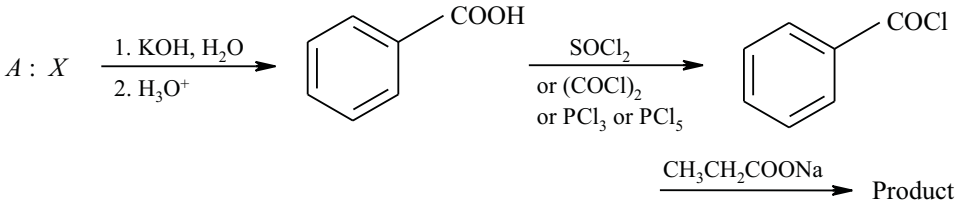
Less stable

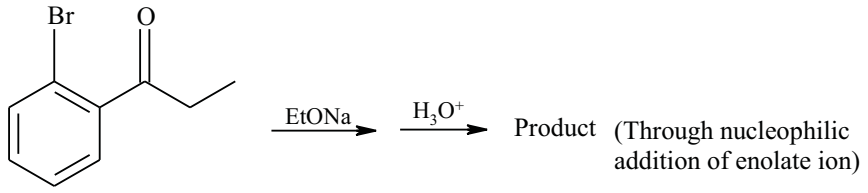


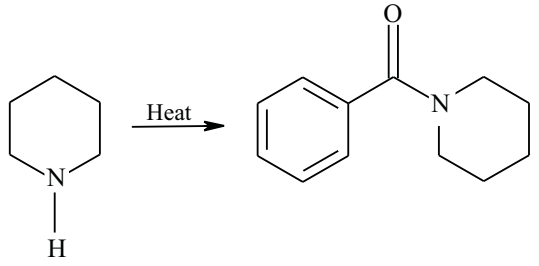
Most stable, because the double bond is tetrasubstituted and consequently thermodynamically more stable than the alternative, trisubstituted enolate anion.

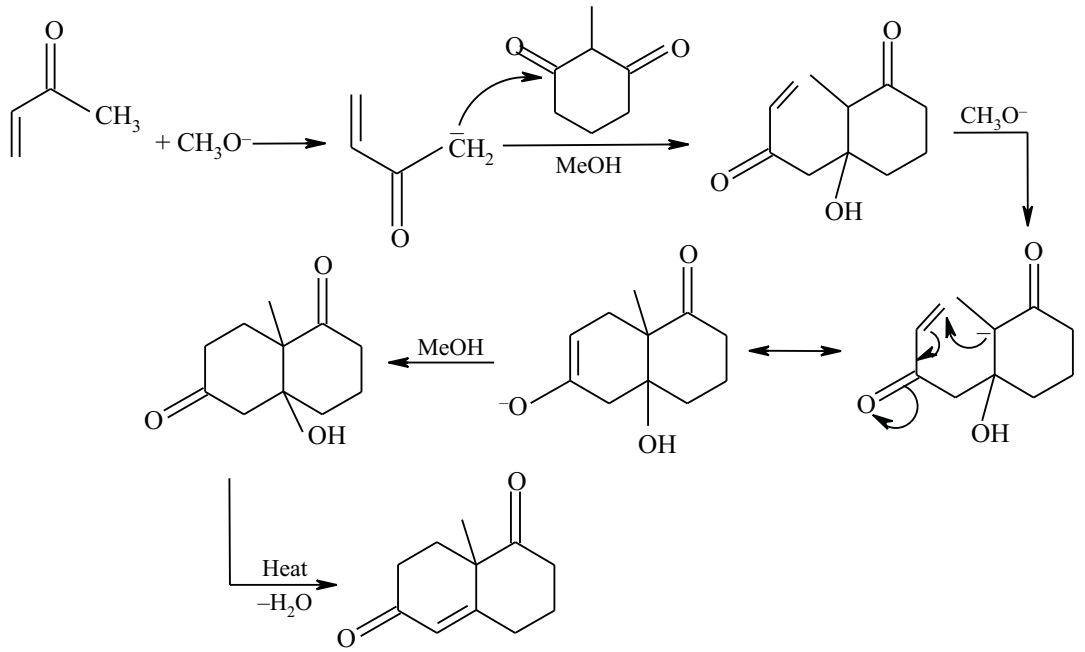
1398. Here, the acidity is due to —COOH groups and not due to α—H. Also, —COOH is a strong electron withdrawing functional group, distance of one —COOH group from other determine acidic strength. Larger the distance, weaker is the acid. Thus, the order of acid strength is:

$$C > B > D > A$$

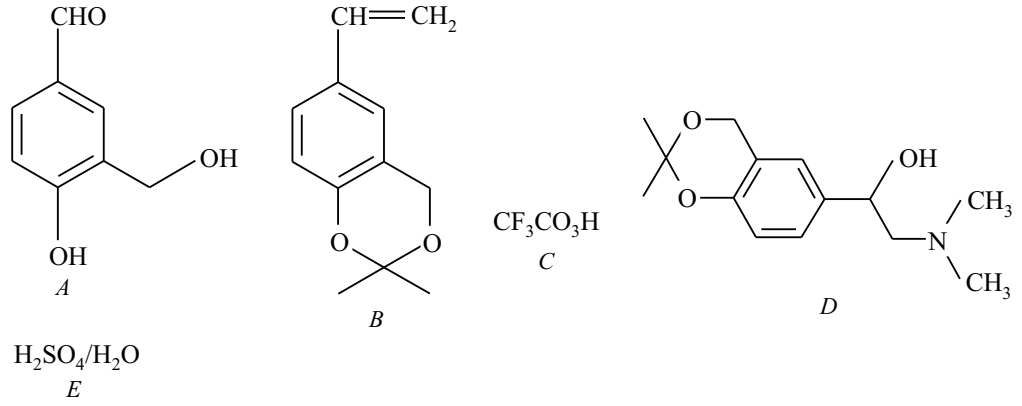
1399. *A* : *X* 

B : *X* + 

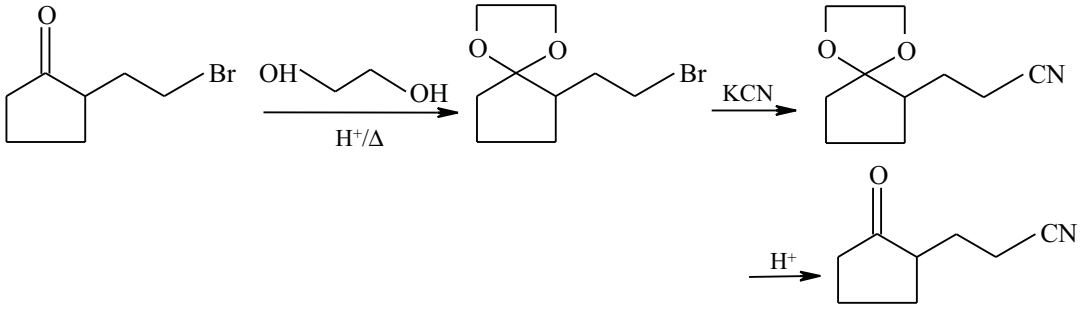
C : *X* + 

1400. 

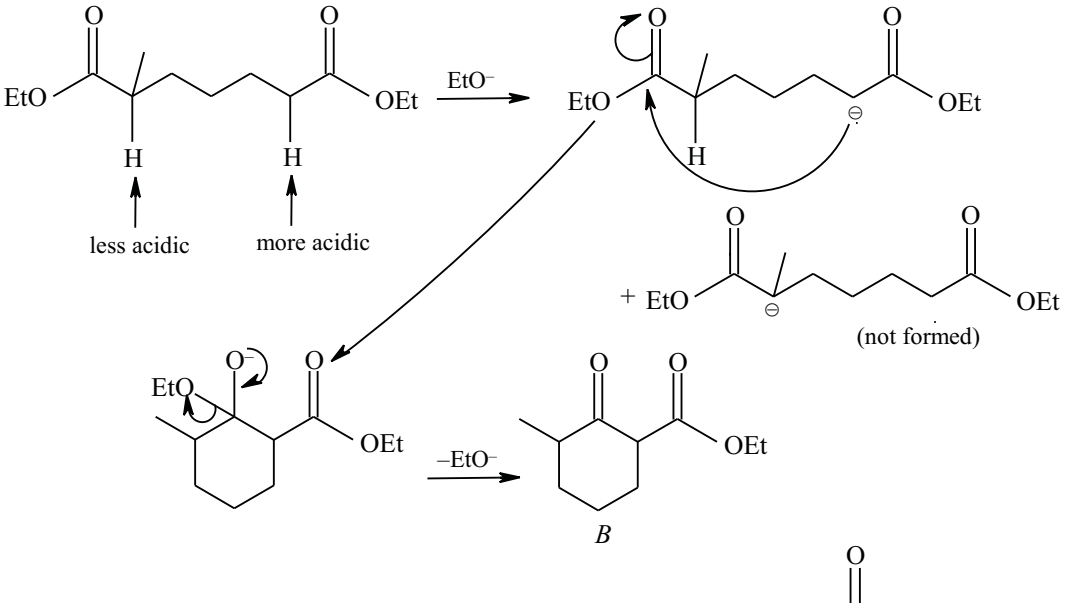
1401.



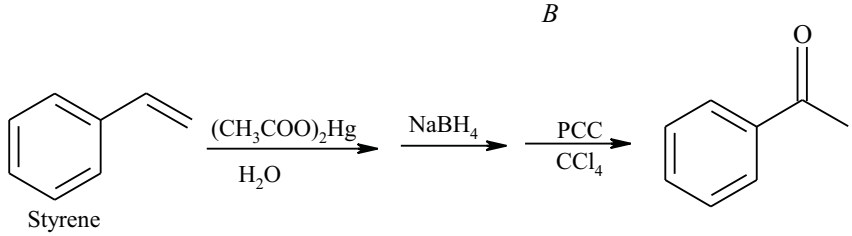
1403.

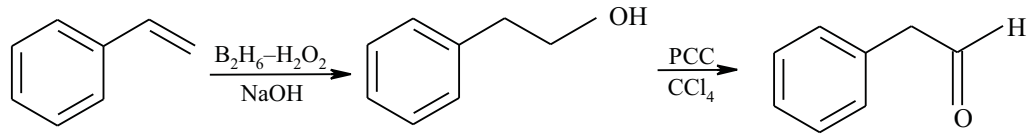


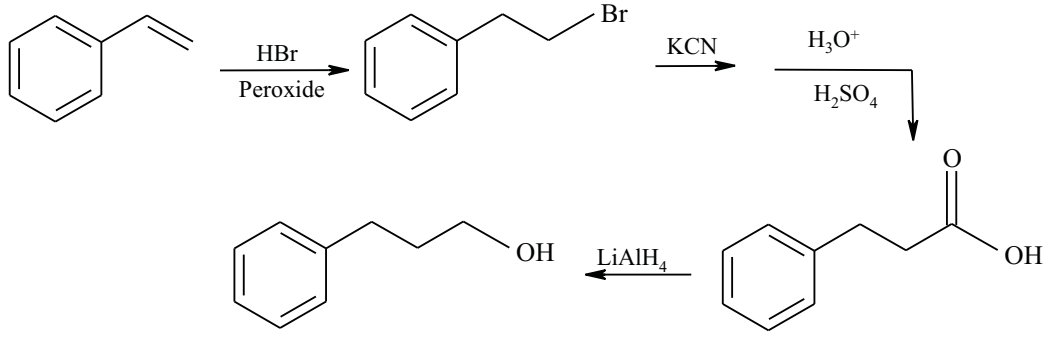
1404.

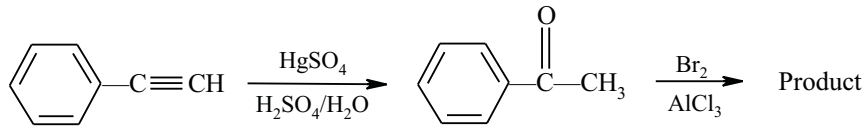


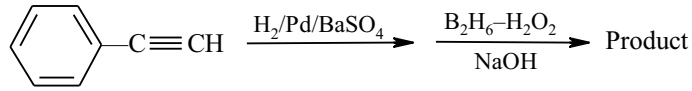
1405. (a)

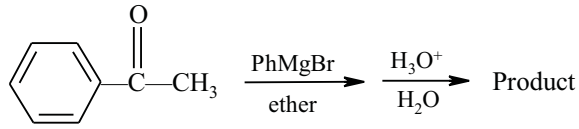


(b) 

(c) 

1406. (a) 

(b) 

(c) 

(from a)