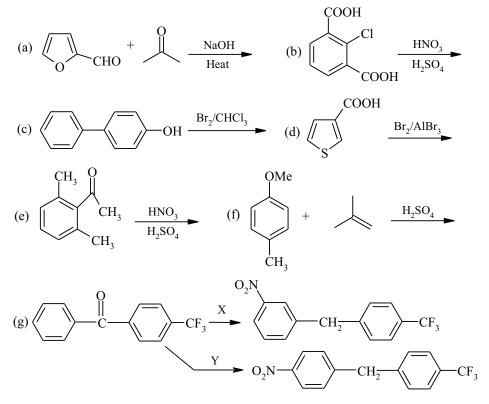
# **AROMATIC COMPOUNDS**

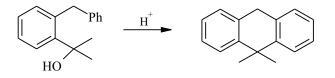
**PROBLEM 1226** A resolvable organic compound *A* has molecular formula  $C_{10}H_{14}O$ . *A* does not forms any salt with NaOH but evolve a colourless gas on heating with sodium metal. *A* gives an yellow precipitate with NaOH/I<sub>2</sub> but does not decolourise Br<sub>2</sub>-water solution. *A* on treatment with CrO<sub>3</sub>/HCl/pyridine produces  $B(C_{10}H_{12}O)$  which is non-resolvable but gives iodoform test. *B* on

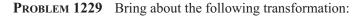
treatment with  $Cl_2/AlCl_3$  gives  $C(C_{10}H_{11}OCl)$  as the only possible isomer. Also A on heating with alkaline KMnO<sub>4</sub> solution yields  $C_8H_6O_4(D)$  as one of the product which evolves a gas with NaHCO<sub>3</sub>. D on heating with ethan-1,2-diol in presence of an acid catalyst forms a polyester E. Deduce structures of A to D and write the formula of repeat unit of E.

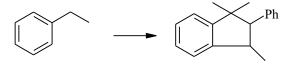
PROBLEM 1227 Predict products/reagents:







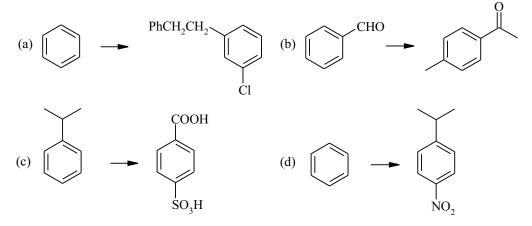




**PROBLEM 1230** An organic compound  $A(C_{11}H_{14}O)$  exist in two stereo-isomeric forms, none of which is resolvable. A does not evolve any gas with sodium metal but decolourise bromine water solution. A on

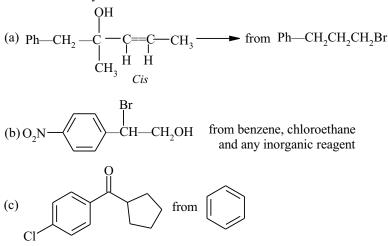
treatment with ozone followed by work-up with  $(CH_3)_2S$  yields  $B(C_9H_{10}O_2)$  as one of the product. *B* neither forms any salt with NaOH nor does it evolve any gas with sodium metal. Also *B* does not react with Tollen's reagent. *B* on treatment with concentrated solution of HI forms  $C(C_8H_8O_2)$  as one of the product which forms salt with NaOH but does not evolve any gas with NaHCO<sub>3</sub>. *B* on treatment with AlCl<sub>3</sub>/Cl<sub>2</sub> gives  $D(C_9H_9O_2Cl)$  as the only possible product. *C* can also be obtained by treatment of an ester  $E(C_8H_8O_2)$  with AlCl<sub>3</sub>. Deduce structures of *A* to *E* and explain the formation of *C* from *E*.

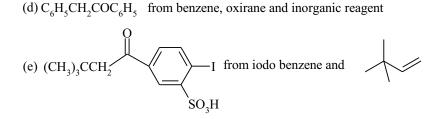
**PROBLEM 1231** Bring about the following transformation:



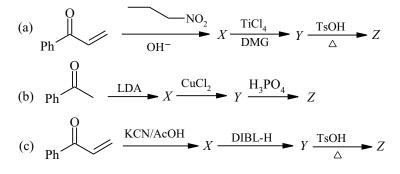
**PROBLEM 1232** An optically active organic compound *A* has molecular formula  $C_{11}H_{16}O_2$  and it does not forms salt with NaOH as well as it does not decolourise  $Br_2$ — $H_2O$  solution, but evolve a gas on treatment with MeMgBr. *A* on treatment with HI gives another optically active compound  $B(C_9H_{10}O_2)$ . *B* on treatment with aqueous KOH yields another optically active compound  $C(C_9H_{12}O_2)$ . *C* on treatment with PCC yields  $D(C_9H_8O_2)$  which gives positive iodoform test as well as positive Tollen's test. *D* is optically inactive and on treatment with  $Cl_2/AlCl_3$  gives one and only one possible monochloro derivative  $E(C_9H_7O_2Cl)$ . Deduce structures of *A* to *E*.

**PROBLEM 1233** Synthesize:

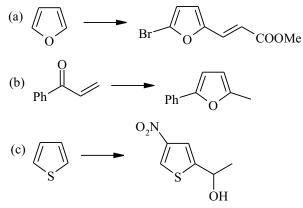




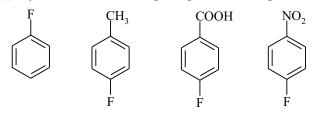




**PROBLEM 1235** Bring about the following transformation:

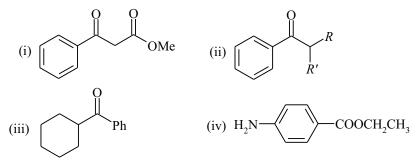




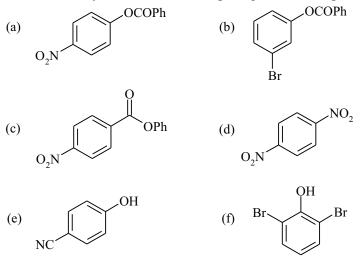


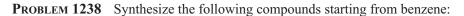
(b) Write mechanism of the reaction of *p*-nitrofluoro benzene with  $(C_2H_5)_2$ NH. Explain why *m*-nitro fluoro benzene does not react with diethyl amine under identical conditions.

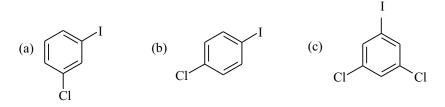
(c) Synthesize the following compounds starting from benzene and any other reagents needed:



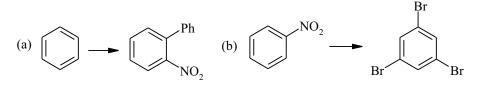
**PROBLEM 1237** Synthesize the following compounds starting from benzene:

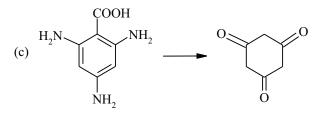


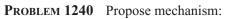


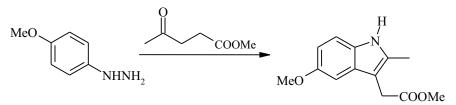


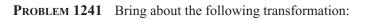
## **PROBLEM 1239** Bring about the following transformation:

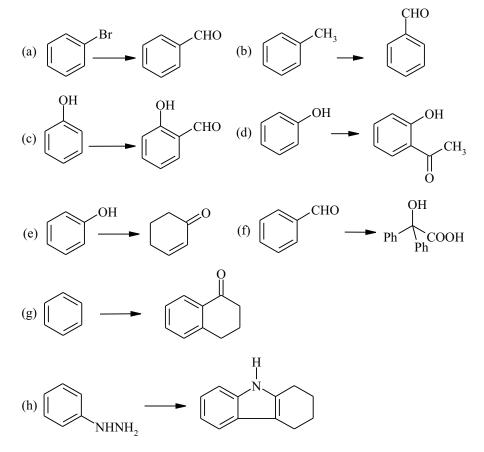




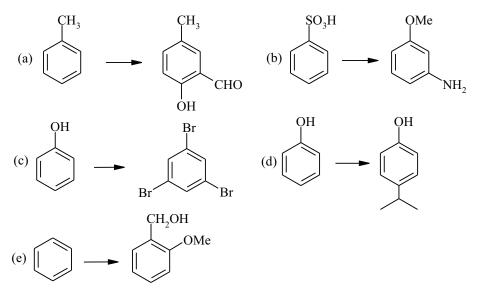


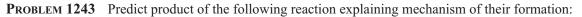






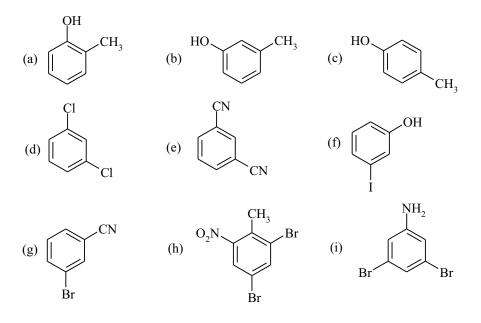
**PROBLEM 1242** Bring about the following conversions:

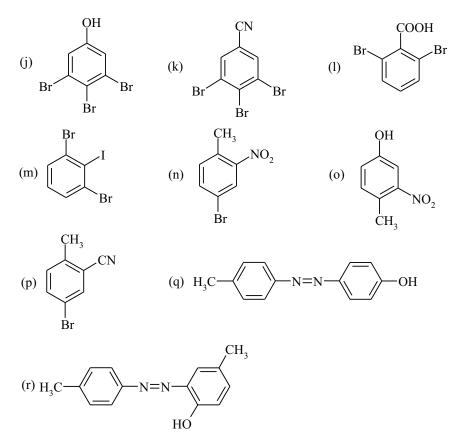


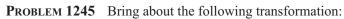


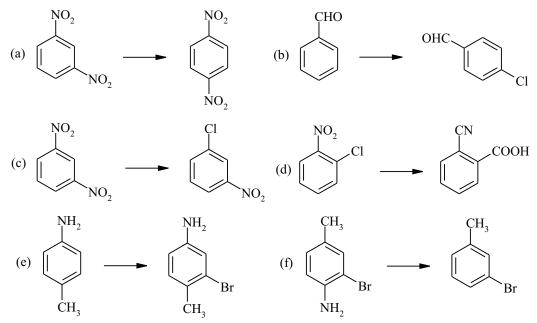


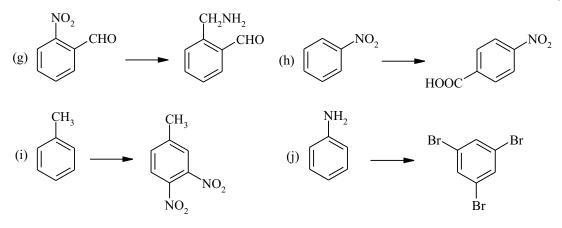
**PROBLEM 1244** Prepare the following compounds starting with either benzene or toluene:



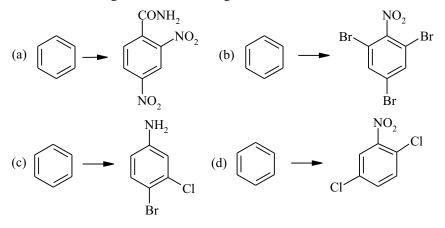






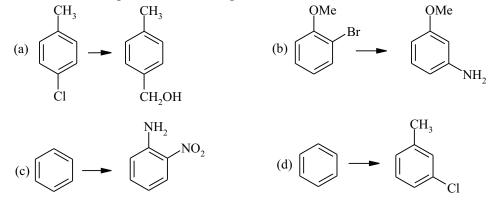


**PROBLEM 1246** Bring about the following transformation:

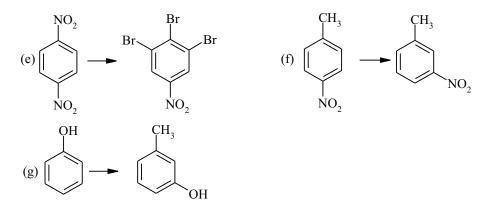


**PROBLEM 1247** An organic compound  $A(C_8H_{10})$  on treatment with fuming sulphuric acid yields two isomeric products *B* and *C*. *B* on fusion with KCN gives  $D(C_9H_9N)$  which on hydrolysis yields  $E(C_9H_{10}O_2)$ . *E* on treatment with hot alkaline KMnO<sub>4</sub> yields  $F(C_8H_6O_4)$ . *F* on heating with P<sub>2</sub>O<sub>5</sub> undergo intramolecular dehydration to yield  $G(C_8H_4O_3)$ . Identify *A* to *G*.

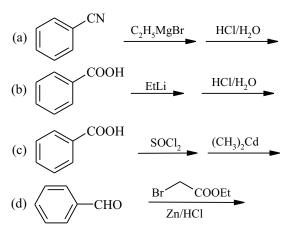
**PROBLEM 1248** Bring about the following transformation:

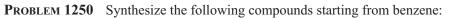


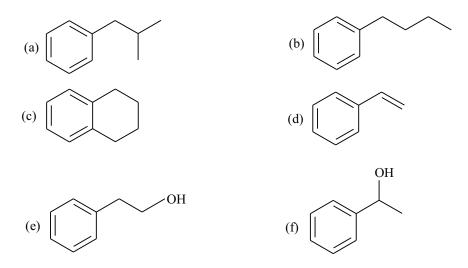
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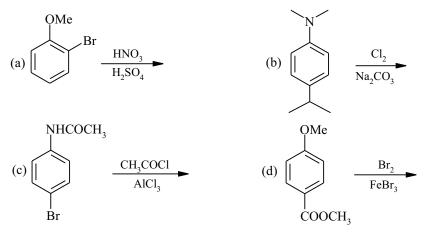
**PROBLEM 1249** Identify the aromatic product formed in the following reaction:

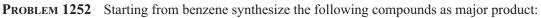


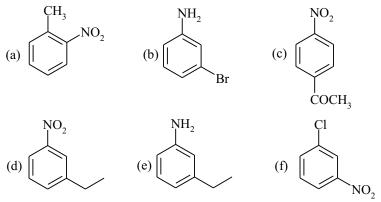




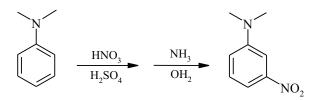
**PROBLEM 1251** Predict major substitution product in the following reactions:



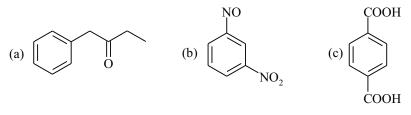




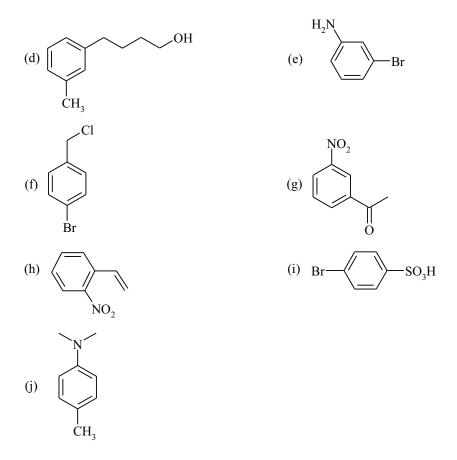
**PROBLEM 1253** How would you rationalize the following experimental result:



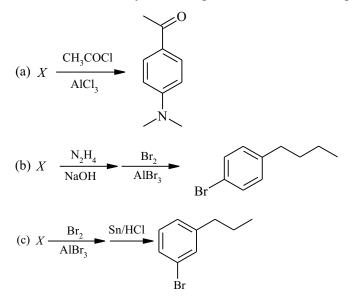
**PROBLEM 1254** Propose synthesis of the following compounds starting from benzene:

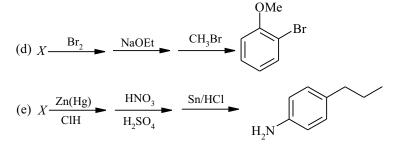


Problems

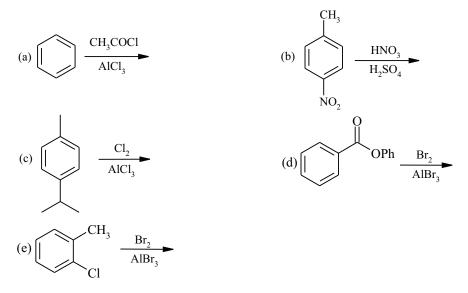


**PROBLEM 1255** Identify the starting material in the following sequence of reaction:



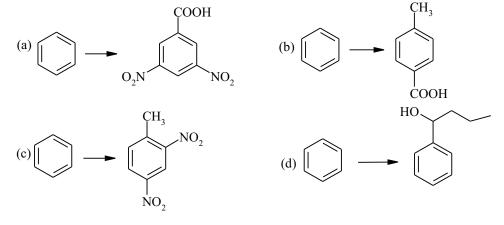


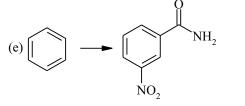
**PROBLEM 1256** Predict the major product in the following reaction:

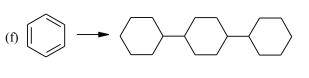


**PROBLEM 1257** *p*-nitro phenol is shaken with one equivalent of  $D_2O$  in the presence of a strong acid (perchloric acid) at 100°C for a long time. The product has two deuterium atom in it. One of these is lost instantly when the product is treated with ordinary water. Propose a structure for the original product and explain the difference in the ease with which the two deuterium atoms can be removed from the molecule.

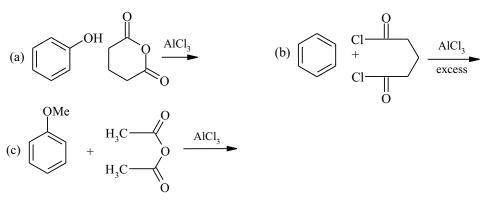
**PROBLEM 1258** Bring about the following transformation:



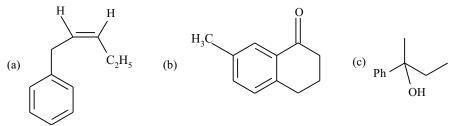




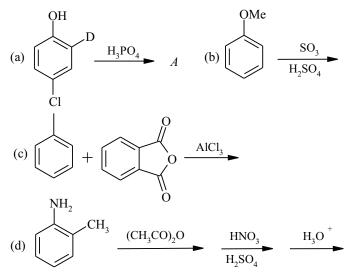
**PROBLEM 1259** Complete the following reactions:



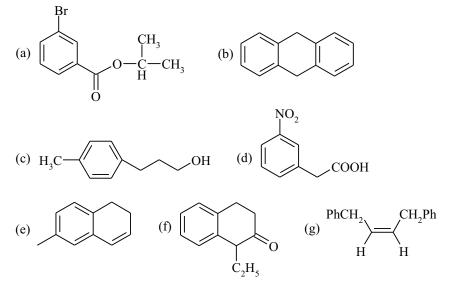








**PROBLEM 1262** Predict synthesis of the following products starting from benzene:

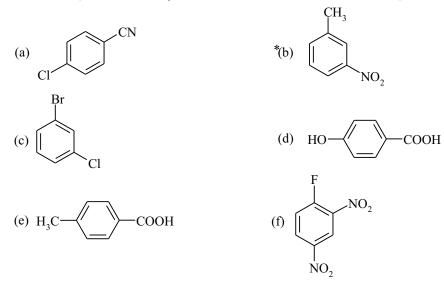


**PROBLEM 1263** 1,3,5-trimethyl benzene undergoes electrophilic aromatic substitution with iodine monochloride (ICl). Write mechanism for this reaction showing major product.

**PROBLEM 1264** When allyl alcohol is treated with HF in presence of benzene, two products are formed: 3-phenyl-1-propene and 1,2-diphenyl propane. Write equations showing the mechanism for the formation for these products.

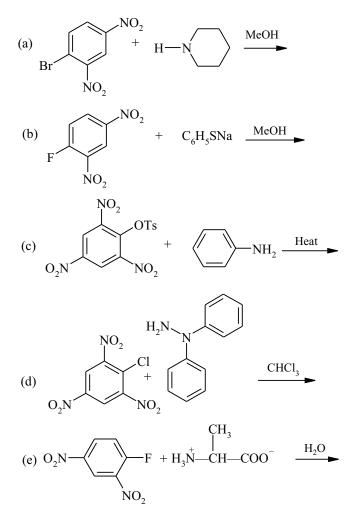
**PROBLEM 1265** When 2-hydroxy benzoic acid is heated with isobutyl alcohol in presence of sulphuric acid, compound A is formed. The same product is formed if tertiary butyl alcohol and sulphuric acid is used. What is the structure of compound A? Write mechanism of formation of this product.

**PROBLEM 1266** Bring about the following synthesis starting from benzene: (\*direct F.C. alkylation of nitro benzene does not succeed)

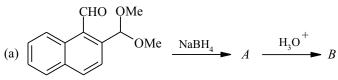


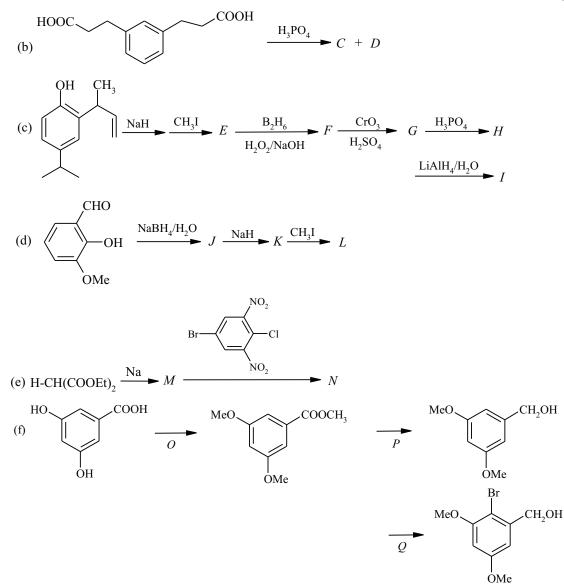




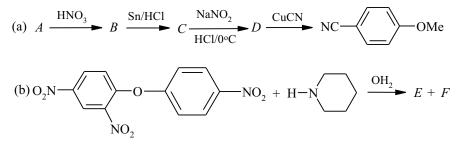


**PROBLEM 1268** Give structural formula for all reagents, intermediates and products designated by letters in the following equations:

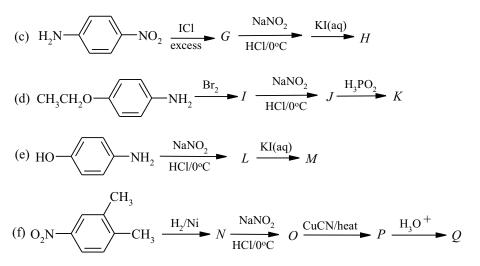




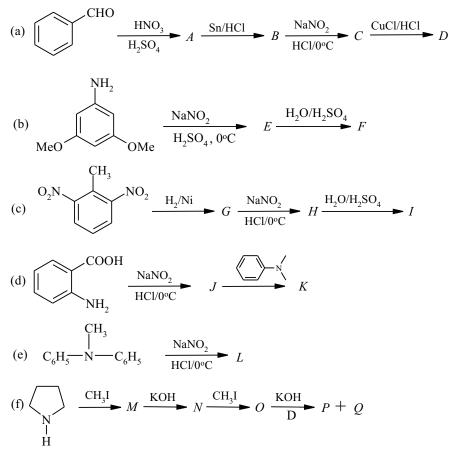
**PROBLEM 1269** Identify the missing reagents/reactants/products in the following sequence of reactions:



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**PROBLEM 1270** Write structural formula for all the products in the following sequence of reaction:



**PROBLEM 1271** An organic compound  $A(C_8H_{10})$  does not decolourise aqueous solution of Br<sub>2</sub> and on treatment with Br<sub>2</sub>/FeBr<sub>3</sub> in dark yields two product in principle, *B* and *C* but due to steric reason, *B* predominates. *A* on refluxing with alkaline solution of KMnO<sub>4</sub> yields  $D(C_8H_6O_4)$  which gives off gas on treatment with NaHCO<sub>3</sub>. *D* on treatment with Br<sub>2</sub>/FeBr<sub>3</sub> reacts very slowly to produce  $E(C_8H_5O_4Br)$  as the only isomer. Also *D* on treatment with excess of SOCl<sub>2</sub> followed by work-up with benzene solution of AlCl<sub>3</sub> produces  $F(C_{14}H_8O_2)$  which does not yields any gas with NaHCO<sub>3</sub>. *F* on heating with N<sub>2</sub>H<sub>4</sub> produces  $G(C_{14}H_8N_2)$ . Deduce structures of *A* to *G*.

**PROBLEM 1272** An organic compound A (C<sub>9</sub>H<sub>10</sub>O<sub>2</sub>) does not change colour of Br<sub>2</sub>-H<sub>2</sub>O and produces no gas with NaH. A on treatment with Br<sub>2</sub> in presence of FeBr<sub>3</sub> yields B(C<sub>9</sub>H<sub>9</sub>O<sub>2</sub>Br) as only isomer. Also A gives orange precipitate with 2,4-dinitro phenyl hydrazine and produces a resolvable compound C(C<sub>9</sub>H<sub>12</sub>O<sub>2</sub>) on reduction with NaBH<sub>4</sub>. Deduce structures of A, B and C.

**PROBLEM 1273** An organic compound  $A(C_9H_8O_2)$  does not decolourise bromine water solution and evolves no gas with CH<sub>3</sub>MgBr but gives orange precipitate with 2,4-dinitro phenyl hydrazine. *A* on refluxing with dilute H<sub>2</sub>SO<sub>4</sub> produces  $B(C_9H_{10}O_3)$  which forms salt with NaOH and on treatment with excess of CH<sub>3</sub>COCl yields C<sub>13</sub>H<sub>14</sub>O<sub>5</sub>. *B* is a non-resolvable compound which on heating with N<sub>2</sub>H<sub>4</sub>/NaOH yields C(C<sub>9</sub>H<sub>12</sub>O<sub>2</sub>). *C* on dehydrating with concentrated H<sub>3</sub>PO<sub>4</sub> yields  $D(C_9H_{10}O)$  as major product. *D* on ozonolysis followed by work-up with (CH<sub>3</sub>)<sub>2</sub>S yields  $E(C_7H_6O_2)$  which can also be obtained by the action of phenol with alkaline solution of chloroform followed by acidification of product. Identify *A* to *E*.

**PROBLEM 1274** An oily liquid *A* is insoluble in water, but on heating with aqueous solution of sodium hydroxide for one hour, it dissolves. From the reaction mixture, a liquid *B* can be distilled, which gives a yellow precipitate with NaOH/I<sub>2</sub> as well as it is resolvable. *B* on treatment with acidic dichromate solution yields *C* which also gives positive iodoform test. If sulphuric acid is added to solution obtained on heating with NaOH, a white precipitate *D* is obtained. *D* gives effervescence with NaHCO<sub>3</sub> and heating *D* with soda lime converts it into toluene. Also *A* on treatment with Br<sub>2</sub>/FeCl<sub>3</sub> in dark yield single mono bromo derivative as a substitution product. Compound *B* on heating with concentrated H<sub>2</sub>SO<sub>4</sub> yields stereomeric alkene, one of which on treatment with cold, dilute and alkaline KMnO<sub>4</sub> yields a meso diol. Deduce structures of *A* to *D*.

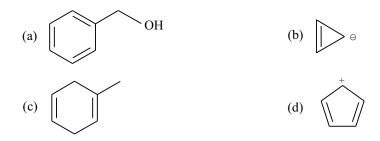
**PROBLEM 1275** An organic compound *A* has molecular formula  $C_{10}H_{14}$  and it does not decolourize bromine water solution. *A* on treatment with  $Br_2/Fe$  yields three products in principle but in actual practice, only two of these are produced as mono-bromo derivative. *A* on heating with  $Br_2$  yields *B* ( $C_{10}H_{13}Br$ ) as the mono-bromo derivative which is optically inactive. *A* on heating with alkaline KMnO<sub>4</sub> yields C( $C_8H_6O_4$ ) which does not forms anhydride on heating. Deduce structures of *A* to *C*.

**PROBLEM 1276** An organic compound  $A(C_8H_8O_3)$  evolves a gas with NaHCO<sub>3</sub> as well as forms salt with NaOH. *A* on treatment with HI yields  $B(C_7H_6O_3)$  which when treated with excess of acetyl chloride (CH<sub>3</sub>COCl) yields  $C(C_{11}H_{10}O_5)$ . *B* on treatment with Br<sub>2</sub>/FeBr<sub>3</sub> in CCl<sub>4</sub> should yield three products *D*, *E* and *F* in principle but only two products *E* and *F* are produced in reality and *E* is the major product. Deduce structures of *A* to *F*.

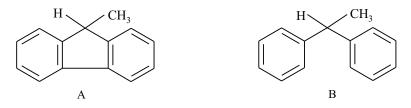
**PROBLEM 1277** An oily liquid is insoluble in water, but on heating with aqueous solution of sodium hydroxide for one hour, it dissolves. From the reaction mixture, a liquid *B* can be distilled, which gives a yellow precipitate with iodine and NaOH solution. On careful oxidation, *B* gives an aldehyde *C*, which also gives positive iodoform test. If sulphuric acid solution is added to the solution obtained from heating

A with NaOH, a white crystal D is obtained. D liberates a gas with NaHCO<sub>3</sub>. Heating D with NaOH/CaO, converts it into  $C_6H_6$ . Identify A to D.

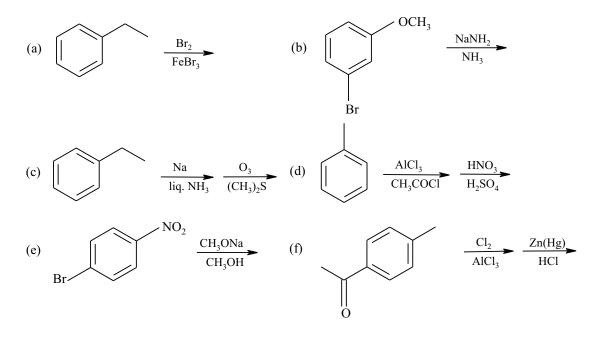
**PROBLEM 1278** Identify the followings as aromatic, antiaromatic or non-aromatic, supporting your answer with brief explanations.

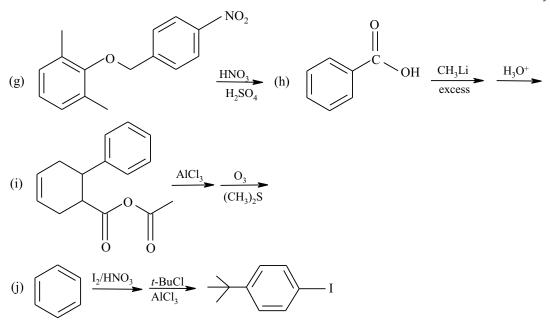


**PROBLEM 1279** The p $K_a$  of benzylic hydrogen in A is ~ 16, whereas the p $K_a$  of benzylic H in B is ~ 25. Explain the difference.



**PROBLEM 1280** Predict products in the following reactions and show stereochemistry where appropriate:

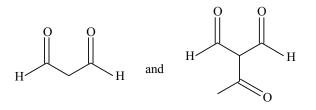




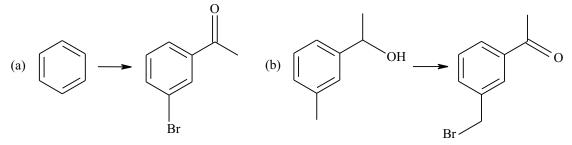
**PROBLEM 1281** Provide a mechanism for the nitration of benzene using concentrated nitric acid-sulphuric acid mixture. Draw an energy diagram for the reaction. Will the rate of reaction change if benzene is replaced by hexadeutrobenzene? Why?

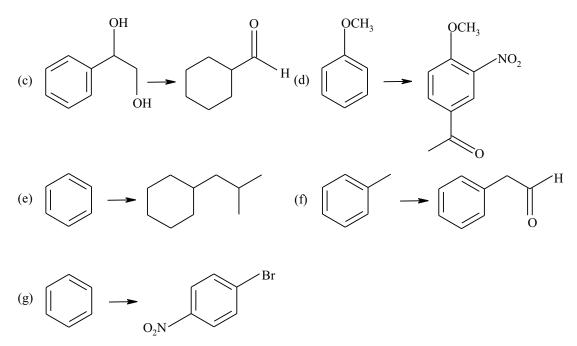
**PROBLEM 1282** A by product of sulphonation of benzene is diphenyl sulphone. Propose a mechanism by which diphenyl sulphone is produced during sulphonation reaction.

**PROBLEM 1283** Synthesize the following compounds starting from benzene:



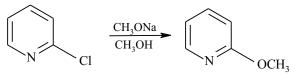
**PROBLEM 1284** Provide reagents that will accomplish the following transformations:



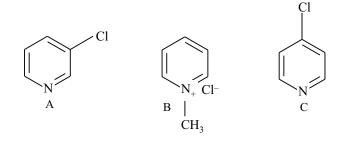


**PROBLEM 1285** Reaction of acetophenone with  $Br_2/FeBr_3$  yield meta-bromo acetophenone. Does this reaction occur at faster rate or slower rate than the treatment of benzene with bromine under similar conditions? Why?

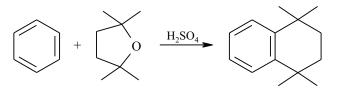
**PROBLEM 1286** Chloropyridines undergo nucleophilic substitution with sodium methoxide to give methoxy pyridine as:



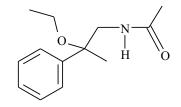
Order the following derivatives from high to low in term of their reactivity towards nucleophilic aromatic substitution.



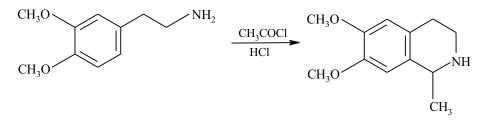
**PROBLEM 1287** Propose a mechanism for the following reaction:



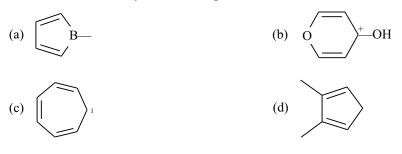
**PROBLEM 1288** Devise synthesis of indicated compound starting from benzene:



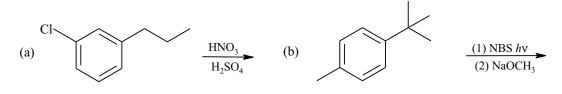
**PROBLEM 1289** Provide a mechanism for the following reaction:

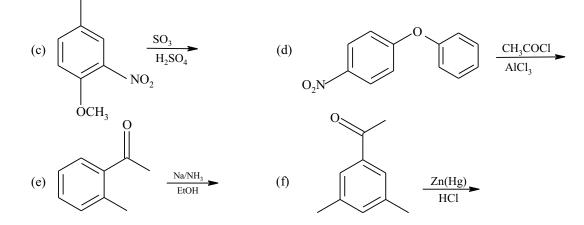


**PROBLEM 1290** Identify the followings as aromatic, antiaromatic or nonaromatic:

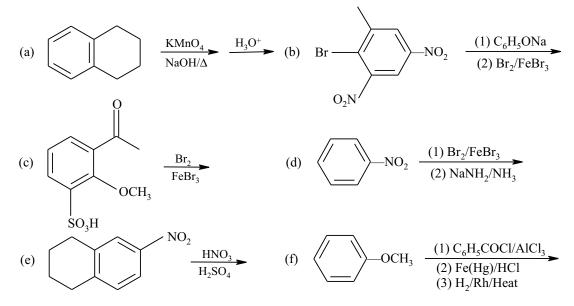


## **PROBLEM 1291** Predict major products in the following reactions:



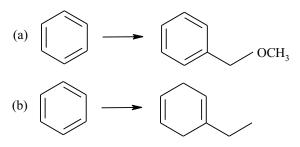


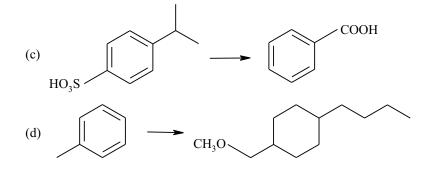
**PROBLEM 1292** Predict major products in the following reactions:



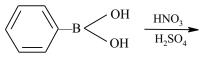
**PROBLEM 1293** Nitration of toluene gives exclusively the ortho and para substitution products. Using mechanism, explain the reason for regioselectivity.

**PROBLEM 1294** Provide reagents that will effect the following transformations. More than one steps may be required:

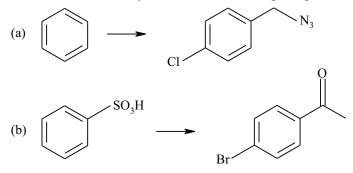




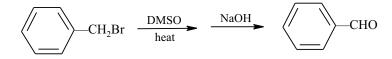
**PROBLEM 1295** Will the following reaction give mostly ortho/para products or mostly meta product. Explain.



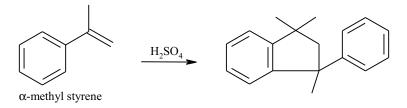
**PROBLEM 1296** Devise synthesis of the following compounds from the indicated starting materials:



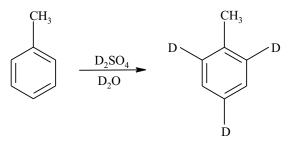
**PROBLEM 1297** Propose mechanism for the following reaction:



**PROBLEM 1298** When treated with  $H_2SO_4$ ,  $\alpha$ -methyl styrene gives the indicated dimeric product. Propose mechanism of its formation:

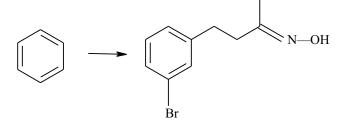


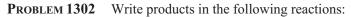
**PROBLEM 1299** Propose a mechanism of the following reaction:

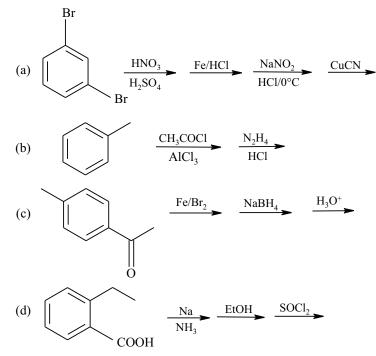


**PROBLEM 1300** Would you expect Birch reduction (Na/liq.  $NH_3$ /EtOH) of benzoic acid or anisole to proceed more quickly, explain.

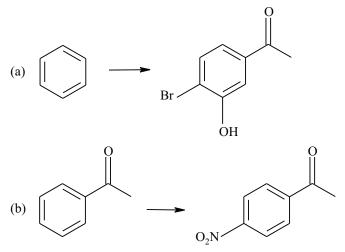
**PROBLEM 1301** Devise a synthesis of the indicated compound starting from benzene:







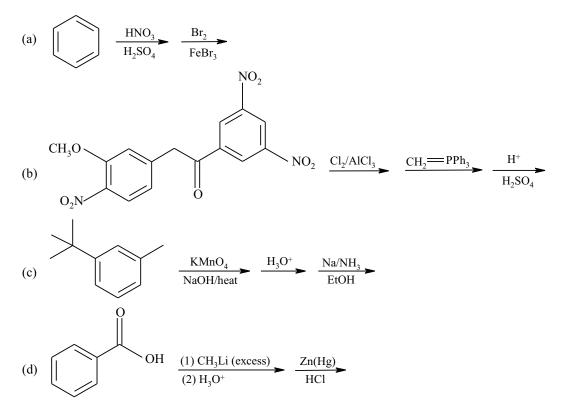
**PROBLEM 1303** Bring about the following transformation:



**PROBLEM 1304** Provide structure of one example of the following species:

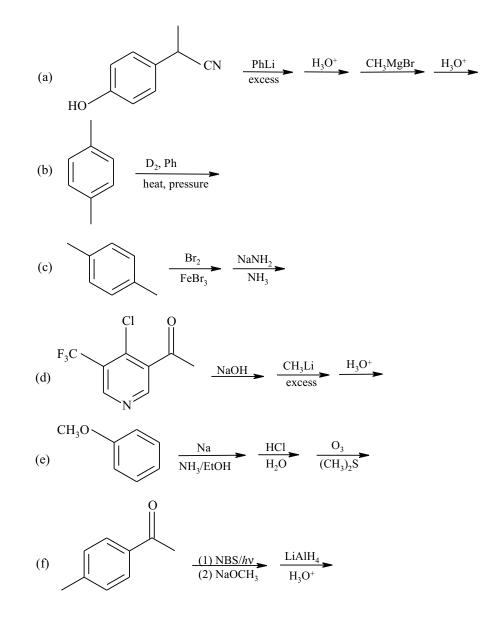
(a) An antiaromatic, (b) An aromatic cation, (c) A cyclic non-aromatic compound containing  $6\pi$  electrons, (d) A neutral, aromatic heterocyclic compound.

**PROBLEM 1305** Predict products in the following reactions:

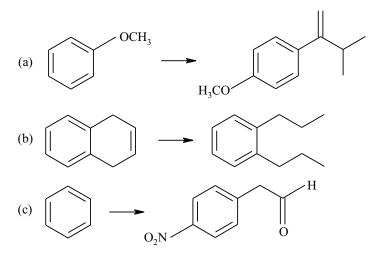




# **PROBLEM 1306** Predict products of the following reactions:



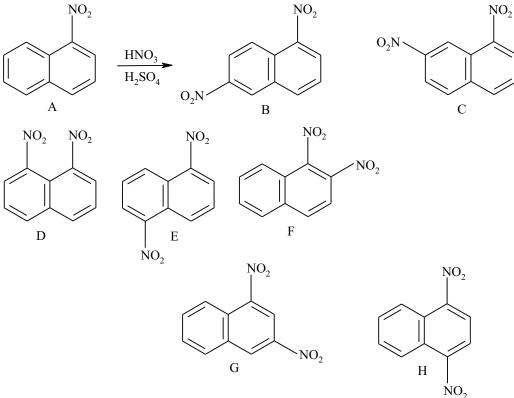
**PROBLEM 1307** Provide reagents that can be used to carryout the following transformations:

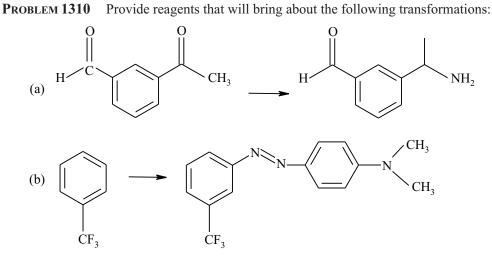


**PROBLEM 1308** Identify *A*, *B* and *C* in the following sequence of reaction:

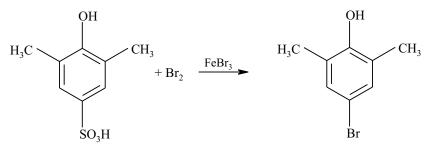
 $CH_{3}OCH_{2}I \xrightarrow{Ph_{3}P} A \xrightarrow{C_{6}H_{5}CHO} B \xrightarrow{HCl} C$ 

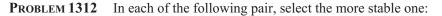
**PROBLEM 1309** Nitration of *A* can give rise to seven possible products in principle (B—H). However, only three are produced. Indicate, which are formed and explain with the of aid of mechanism.

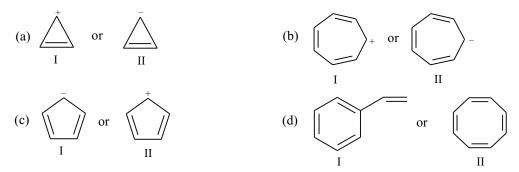




**PROBLEM 1311** Propose mechanism of the following reaction:





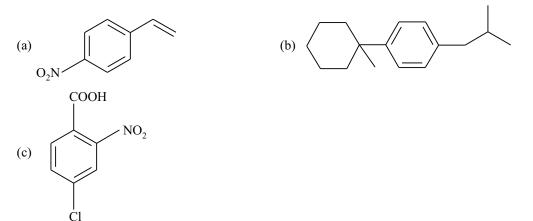


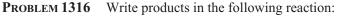
**PROBLEM 1313** Rank the compounds in each group in increasing order of their reactivity towards electrophilic aromatic substitution reaction:

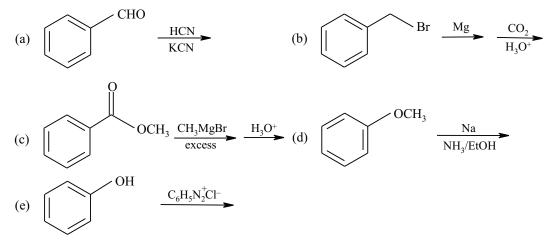
- (a) Chlorobenzene (I), fluorobenzene (II), cyanobenzene (III),
- (b) o-dichlorobenzene (I), benzaldehyde (II), methoxybenzene (III),
- (c) methoxybenzene (I), o-xylene (II), benzene (III).

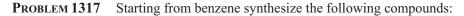
**PROBLEM 1314** Discuss the orienting effect of nitroso group (—NO) in aromatic electrophilic substitution reaction.

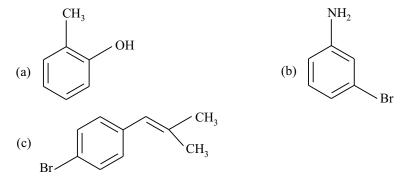
**PROBLEM 1315** Provide synthesis of the following compounds starting from benzene:



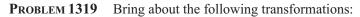


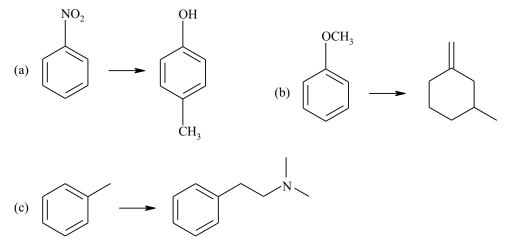




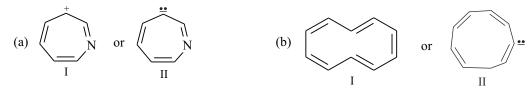


**PROBLEM 1318** Furan undergo electrophilic aromatic substitution. With the help of mechanism, explain the most probable site for the attack of electrophile on furan ring.





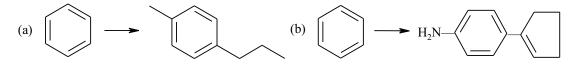
**PROBLEM 1320** Which of the following pairs is more stable:



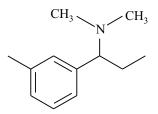
**PROBLEM 1321** Arrange the following compounds in increasing order of reactivity towards electrophilic aromatic substitution reaction:

- (a) Chlorobenzene (I), benzene (II), nitrobenzene (III),
- (b) *m*-chloroanisole (I), *p*-chloroanisole (II), anisole (III),
- (c) Cyanobenzene (I), *p*-cyanotoluene (II), *p*-cyanoanisole (III).

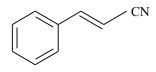
**PROBLEM 1322** Bring about the following transformations:



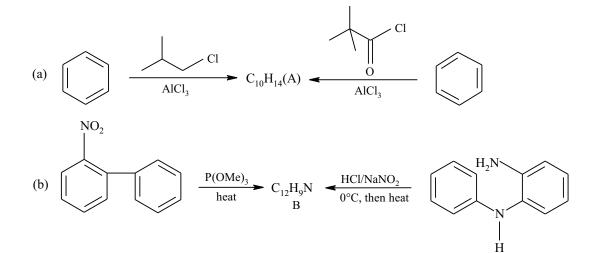
**PROBLEM 1323** Starting from toluene, synthesize:



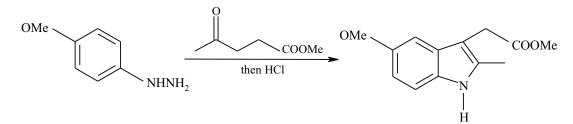
**PROBLEM 1324** Predict the direction of electrophilic attack on the following compound:



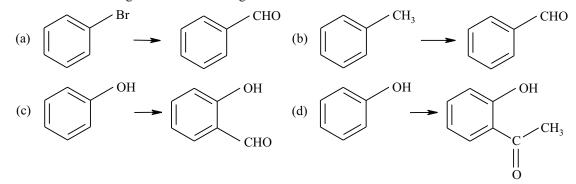
**PROBLEM 1325** Provide structures of *A* and *B* and suggest mechanism of their formation:

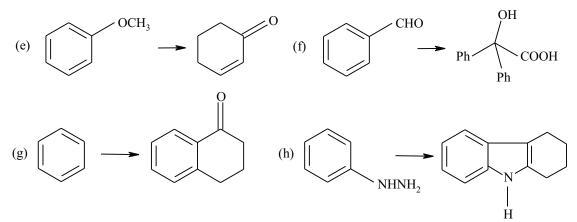


**PROBLEM 1326** Propose mechanism:

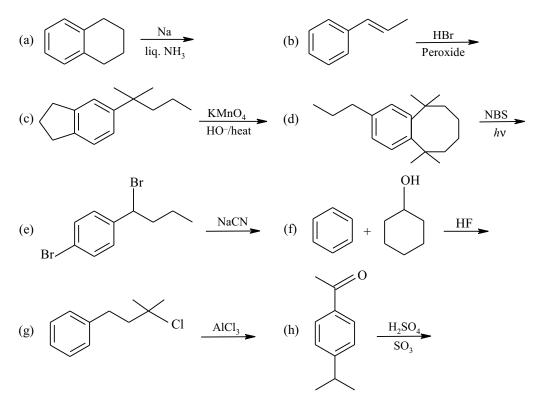


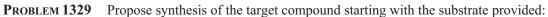
**PROBLEM 1327** Bring about the following transformations:

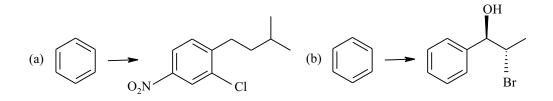




**PROBLEM 1328** Provide missing species in the following reactions:

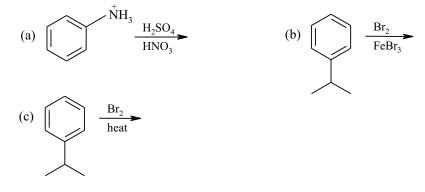


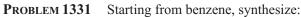




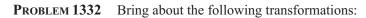
249

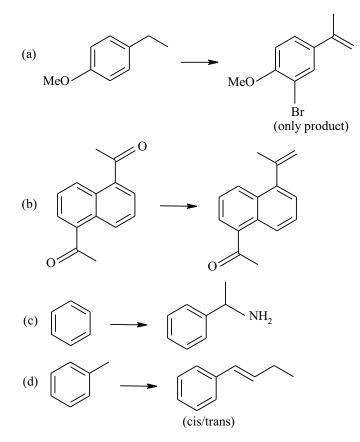
**PROBLEM 1330** Complete the following reaction:



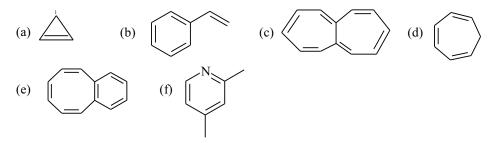


O<sub>2</sub>N-N=N-OH

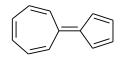




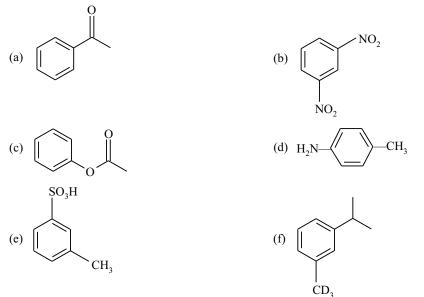
**PROBLEM 1333** Classify each of the followings as aromatic, antiaromatic or nonaromatic:



**PROBLEM 1334** Ordinarily barrier to rotation about carbon-carbon double bond is quite high ( $\approx 40 \text{ kcal/mol}$ ) but the compound shown below was observed to have a rotational barrier of about only 20 kcal/mol, explain.

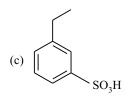


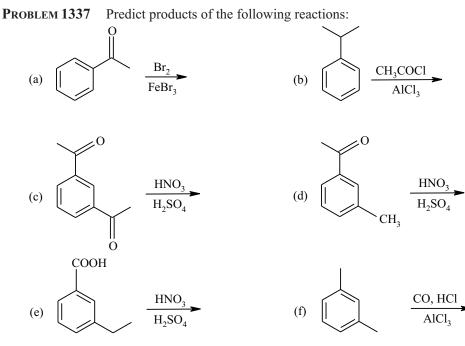
**PROBLEM 1335** Specify whether you expect the benzene ring in the following compounds to be activated/deactivated for electrophilic aromatic substitution reaction:



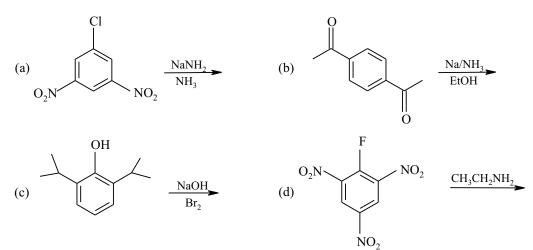
**PROBLEM 1336** Propose a reasonable synthesis of each of the following multiply substituted arenes from benzene:



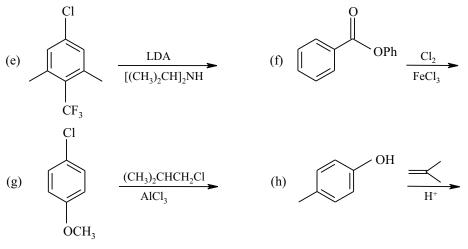




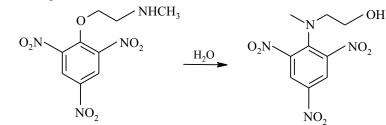
**PROBLEM 1338** Predict product of the following reactions:



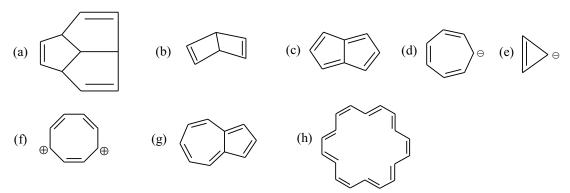
Problems



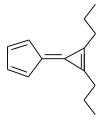


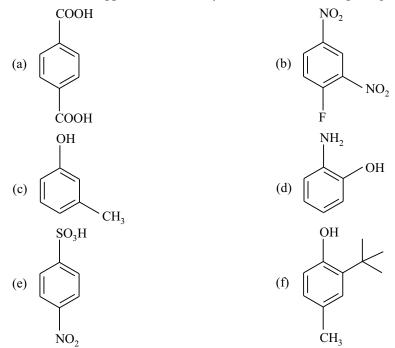


**PROBLEM 1340** Classify each of the following species as either antiaromatic, aromatic or non aromatic.

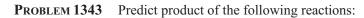


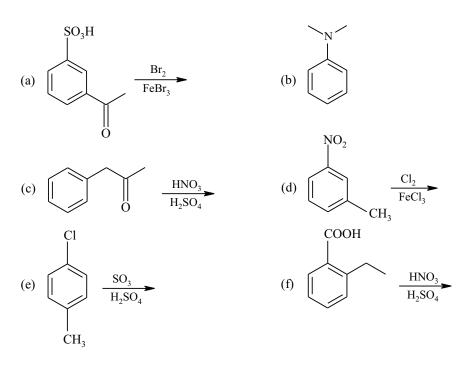
**PROBLEM 1341** Discuss the reasons for low energy barrier to rotation about the double bond connecting the two rings, as compared to normal double bond.

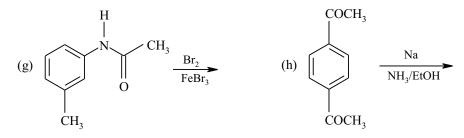


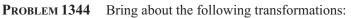


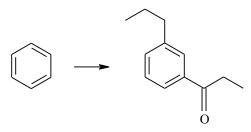
**PROBLEM 1342** Suggest a method of synthesis of the following compounds starting from benzene:







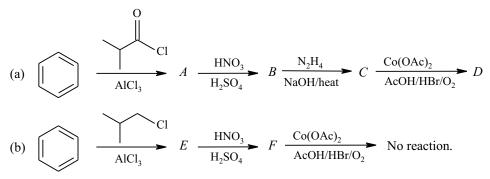




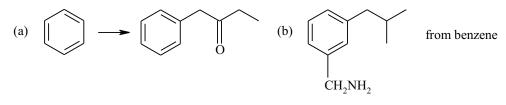
**PROBLEM 1345** Synthesize following compounds starting from benzene:

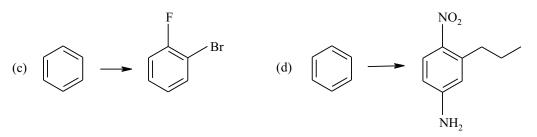


**PROBLEM 1346** Identify *A* to *F* in the following reaction:

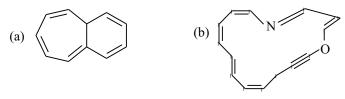


**PROBLEM 1347** Bring about the following transformations:

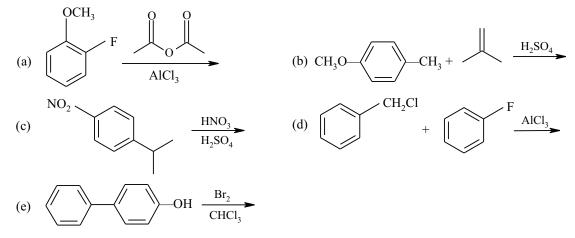




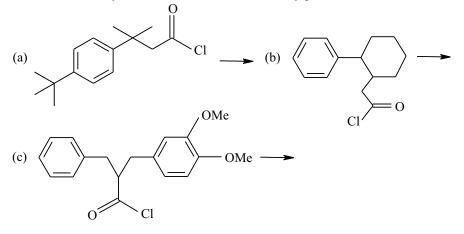
**PROBLEM 1348** On the basis of Huckel rule, discuss the aromaticity of the followings:



**PROBLEM 1349** Give formula of the major organic product in each of the followings:



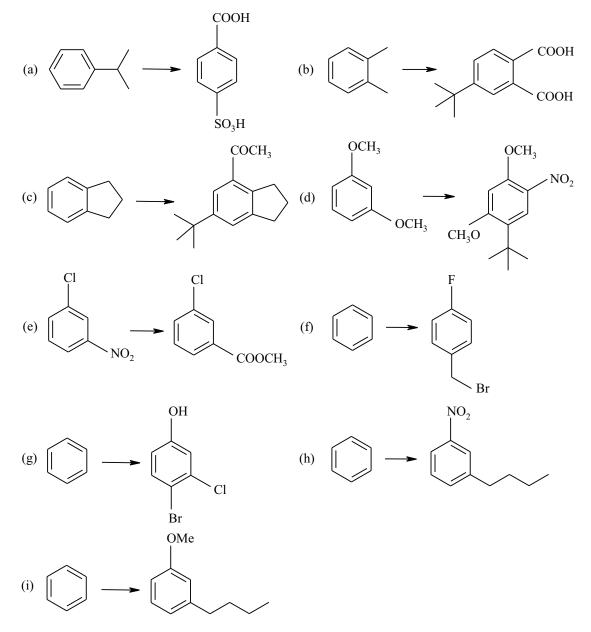
**PROBLEM 1350** The following compounds undergo intramolecular Friedel-Craft reaction in presence of a Lewis acid catalyst. Give structures of most likely product in each case.



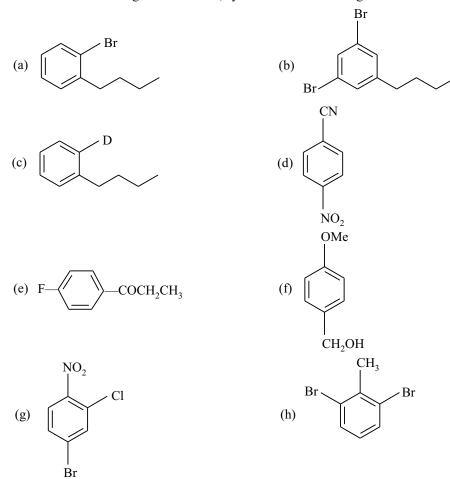
**PROBLEM 1351** Synthesize the following compounds starting from benzene:

(a) 2-bromo-4-nitro toluene, (b) *p*-bromoanisole, (c) *p*-nitrobenzene sulphonic acid.

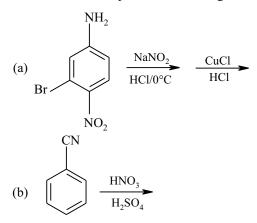
**PROBLEM 1352** Bring about the following transformations:



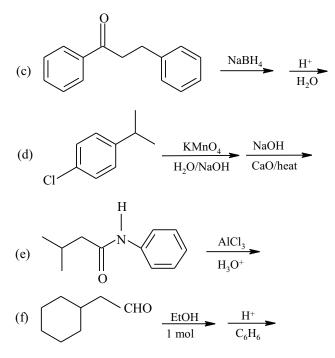
## **PROBLEM 1353** Starting from benzene, synthesize the following:



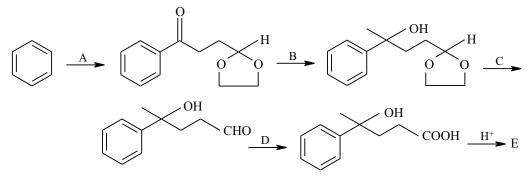
**PROBLEM 1354** Complete the following reactions:



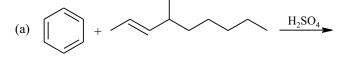
Problems



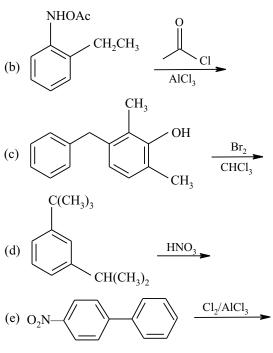
**PROBLEM 1355** A sequence of reaction has been carried out on benzene as described below. Provide reagents which are needed for each observed transformations and give a structure of product E which results.

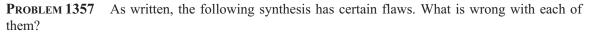


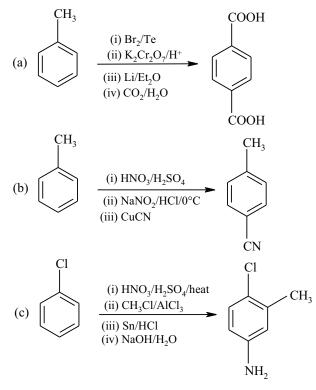
**PROBLEM 1356** Each of the following reaction is reported to yield single predominant product. Write structural formula for one of them.



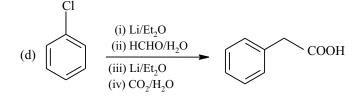




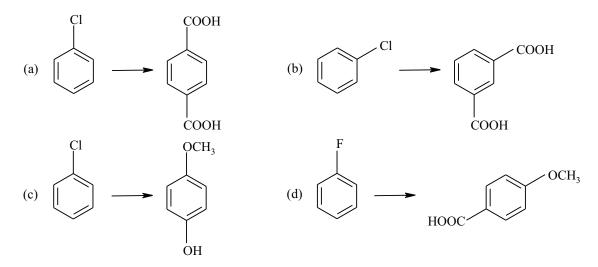




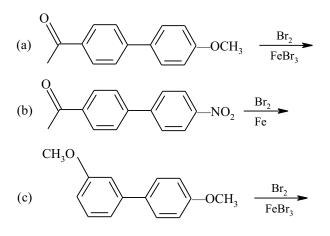
Problems



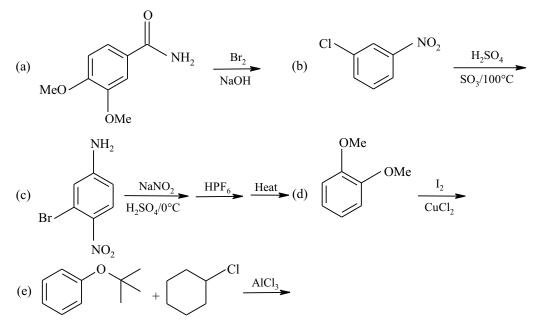
**PROBLEM 1358** Bring about the following transformations:



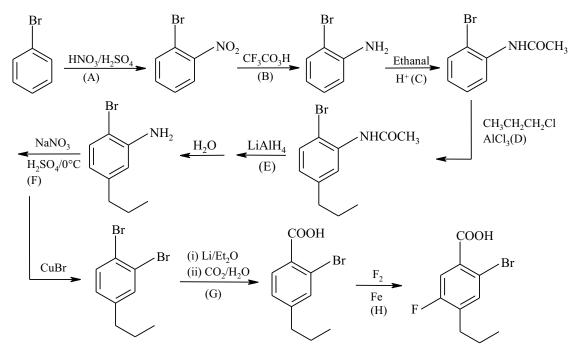
**PROBLEM 1359** If we do the electrophilic bromination on the compound below, only one product (major) will be formed. Predict structure of the predominant product in each case:



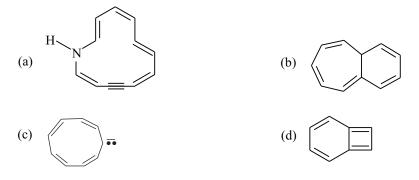
**PROBLEM 1360** Write product (major) in the following reactions:



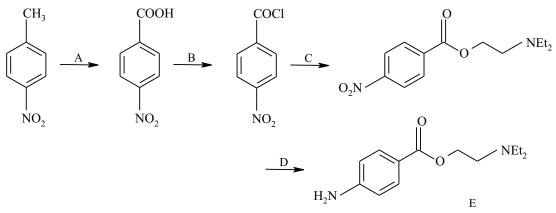
**PROBLEM 1361** In the following sequence of reaction, every steps has certain flaws. Correct them by providing appropriate reagents:



**PROBLEM 1362** On the basis of Huckel rule, decide whether the following species are aromatic or not:

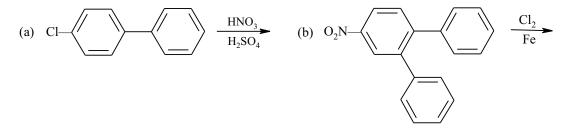


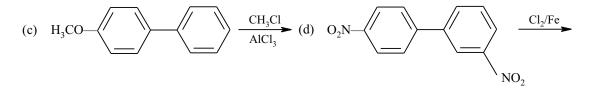
**PROBLEM 1363** The following series of reaction was performed during synthesis of E. Provide appropriate reagents needed to perform the indicated transformations:



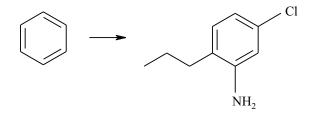
**PROBLEM 1364** Two, isomeric, aromatic lactones *A* and *B* have molecular formula  $C_9H_8O_4$ . Both *A* and *B* dissolves in dilute NaOH solution but none gives gas with NaHCO<sub>3</sub>. Both *A* and *B* gave violet colouration with FeCl<sub>3</sub>. Reaction of *A* with NaOH followed by work-up with CH<sub>3</sub>I yields  $C(C_{10}H_{10}O_4)$ . Selective demethylation of C with BCl<sub>3</sub> followed by aqueous work-up yields *D* which is also an isomer of *A*. *D* showed presence of an intramolecularly hydrogen bonded hydroxyl group. Complete hydrolysis of either *A* or *C* with dilute H<sub>2</sub>SO<sub>4</sub> produced the same compound  $E(C_8H_8O_5)$ . Oxidising E with alkaline permanganate followed by acidification of product yields  $F(C_8H_6O_6)$ . Heating *F* with sodalime followed by acidification of product yields 1,3-dihydroxy benzene. Identify *A* to *F*.

**PROBLEM 1365** Write the major product in the following reactions:

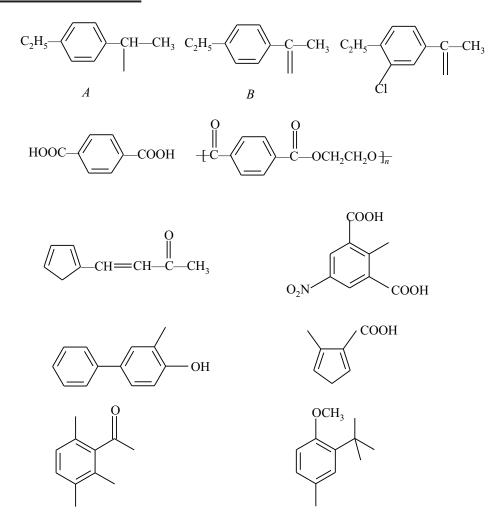




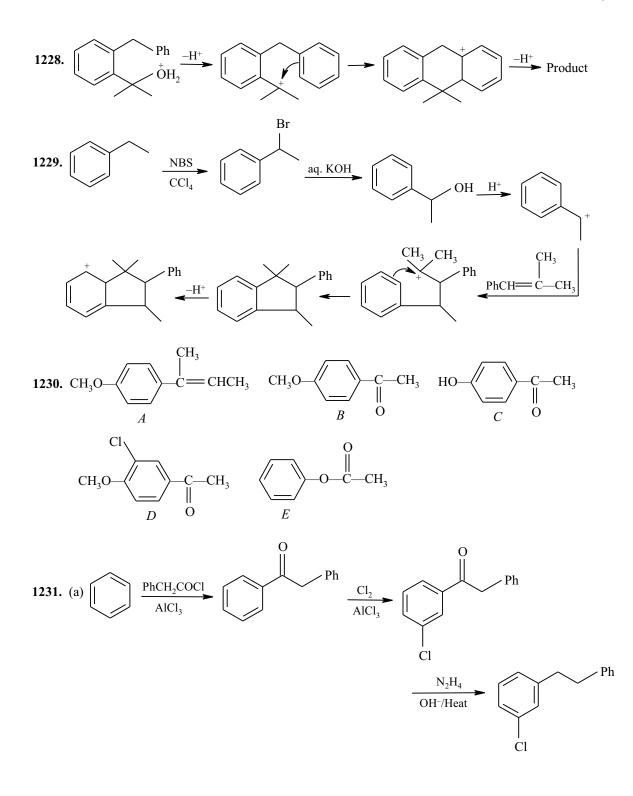
**PROBLEM 1366** Bring about the following transformation in good yield.

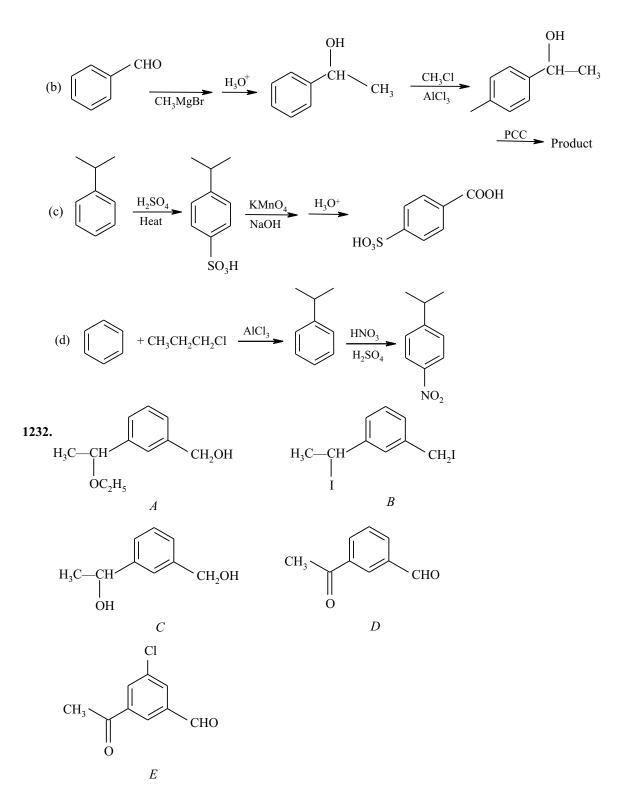


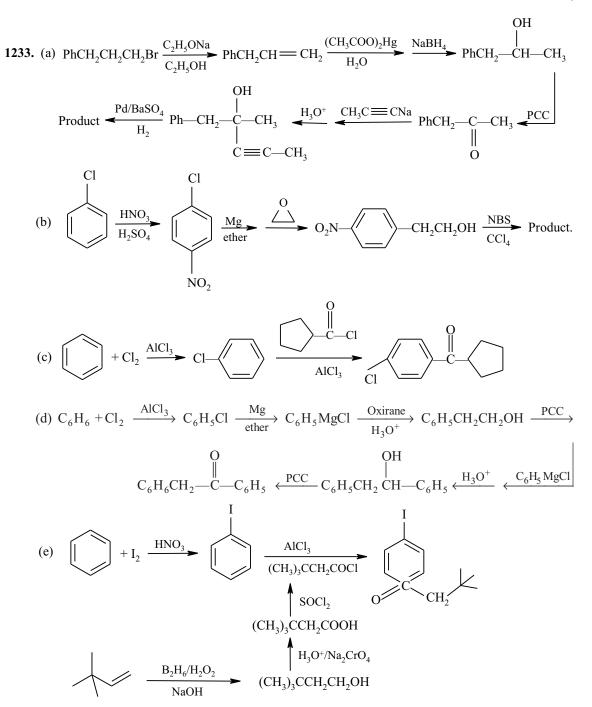
**AROMATIC COMPOUNDS** 

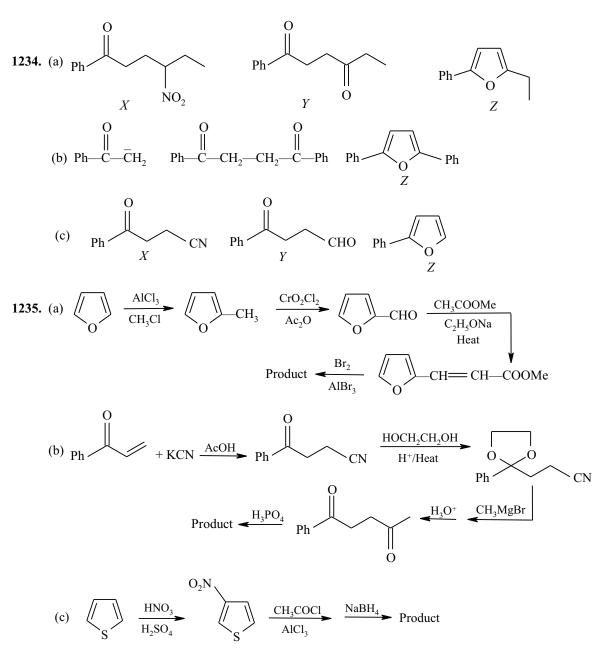


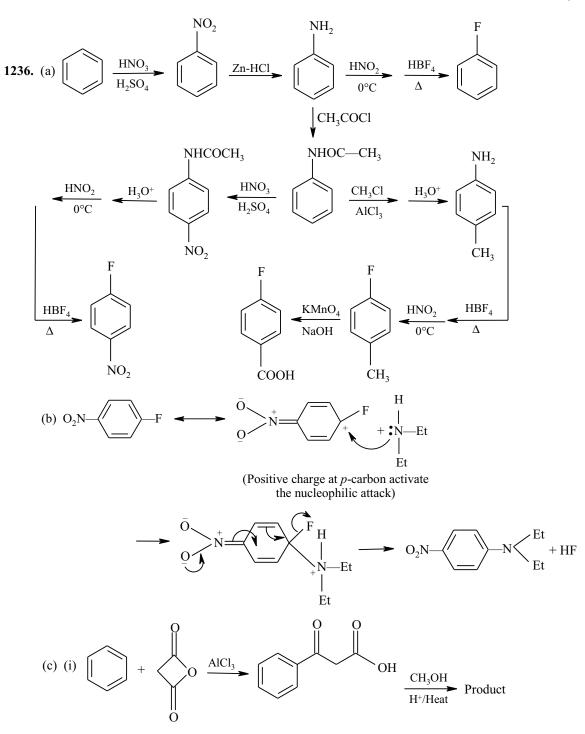
(g)  $X: HNO_3/H_2SO_4$  followed by reduction with  $N_2H_4/OH^-/Heat$ . Y: Reduction with  $N_2H_4/OH^-/Heat$  followed by nitration.

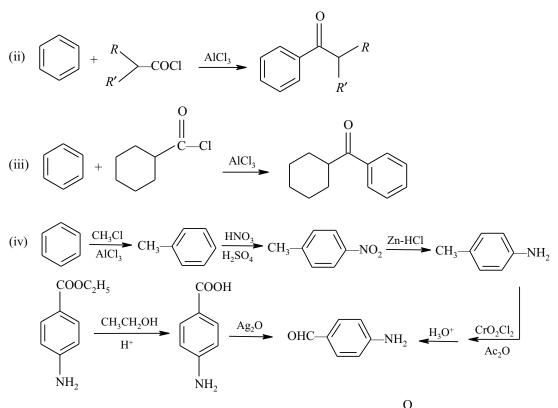


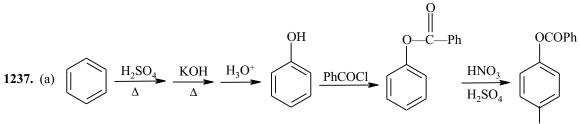


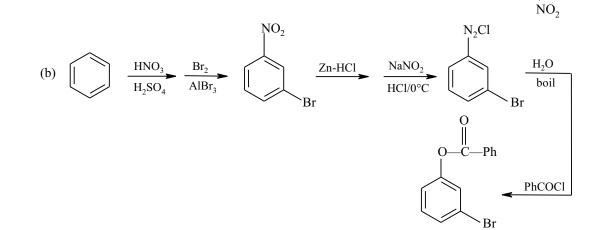


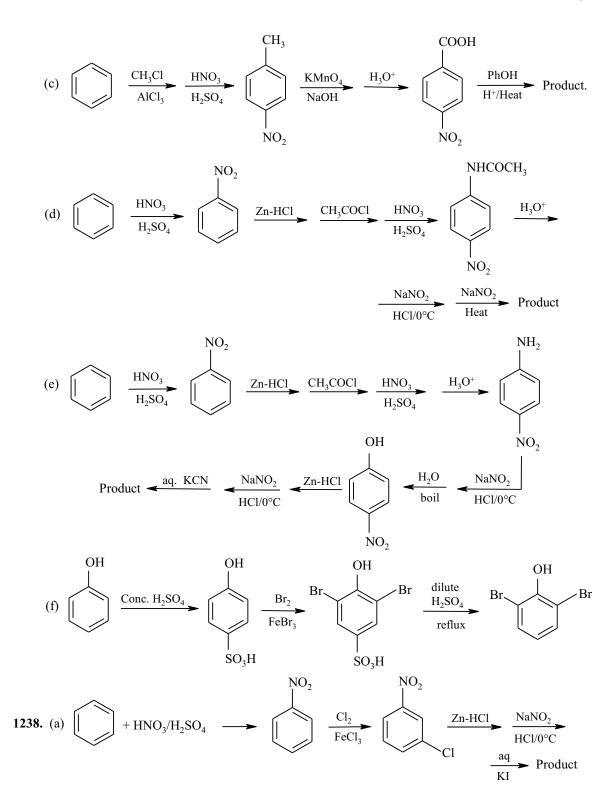


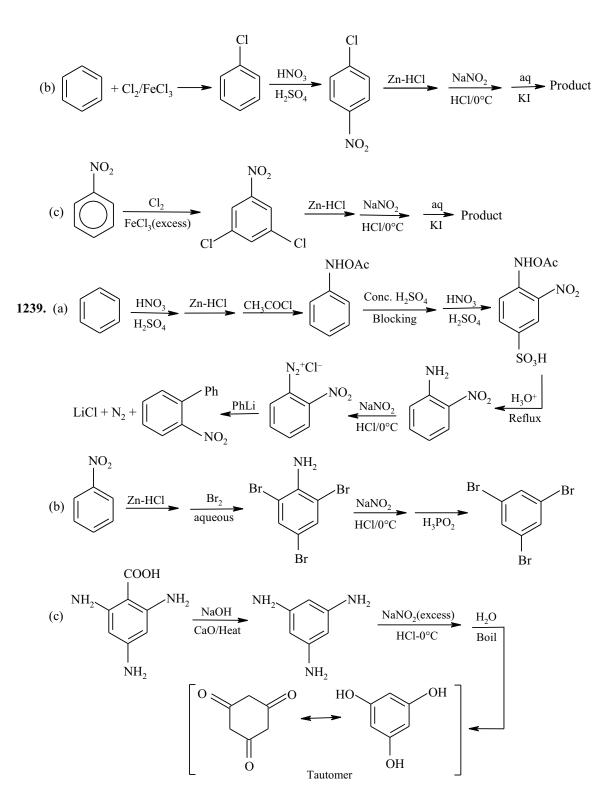


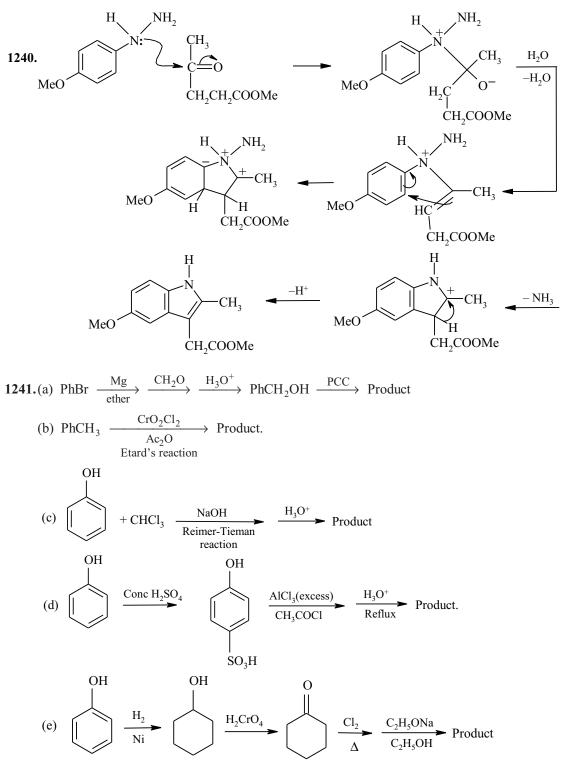


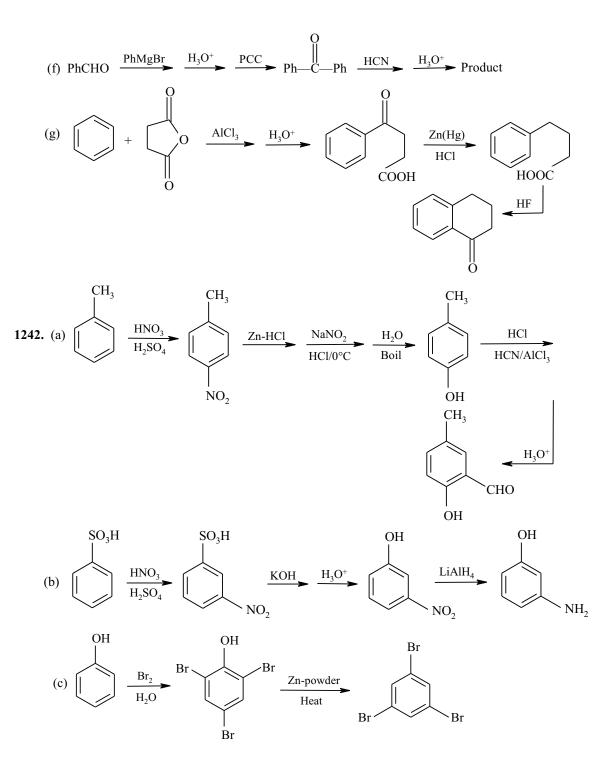


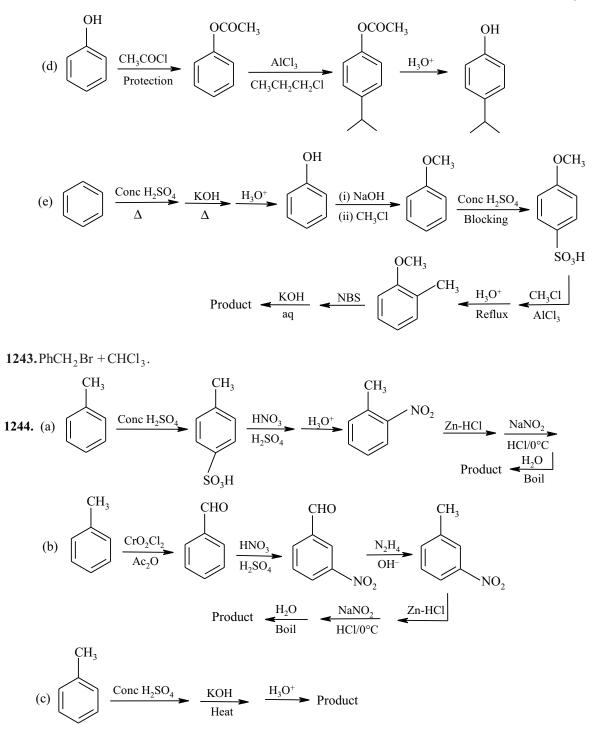


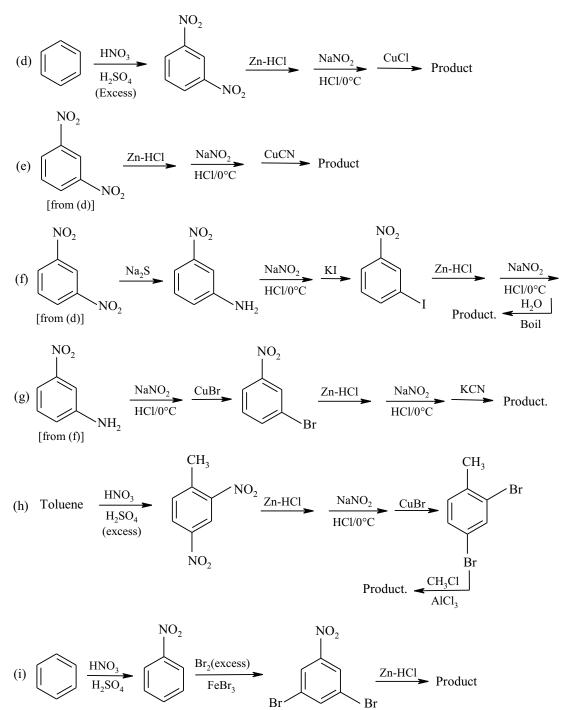


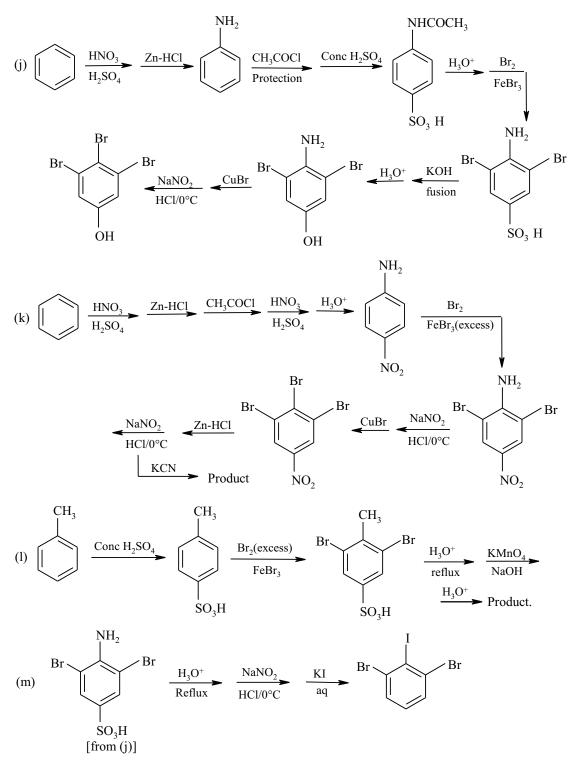


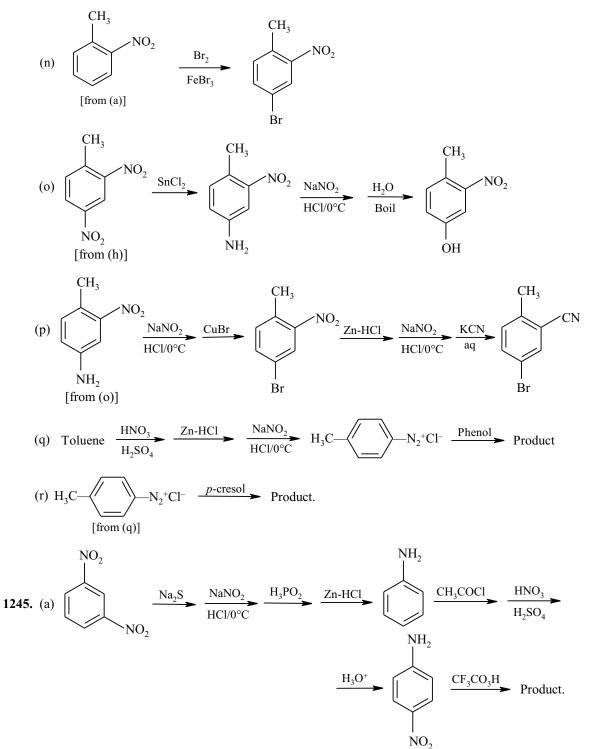




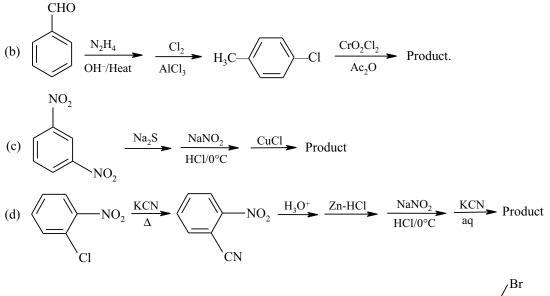


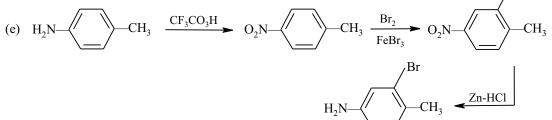


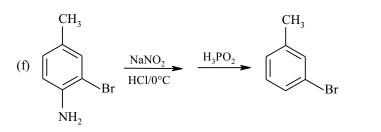


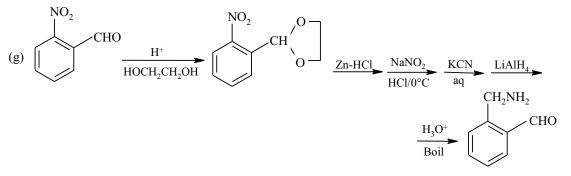


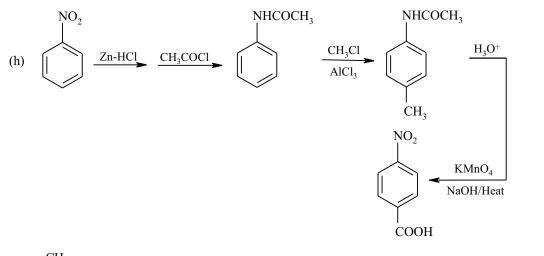
## Problems in Chemistry

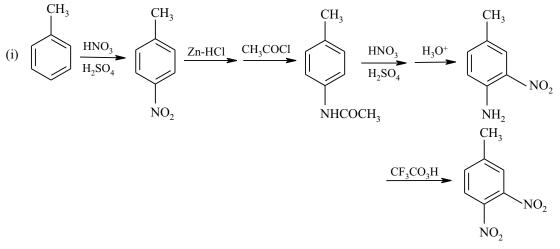


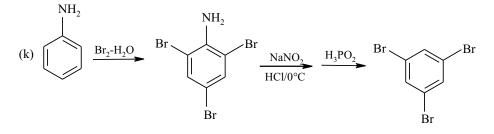




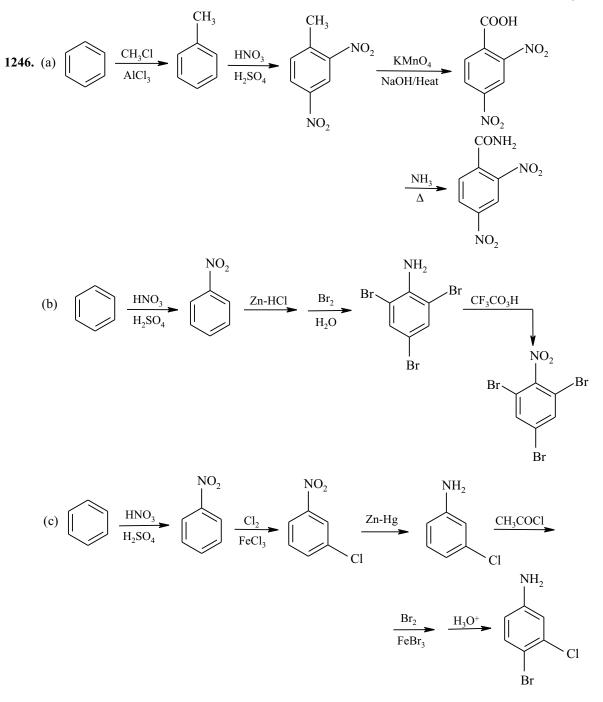


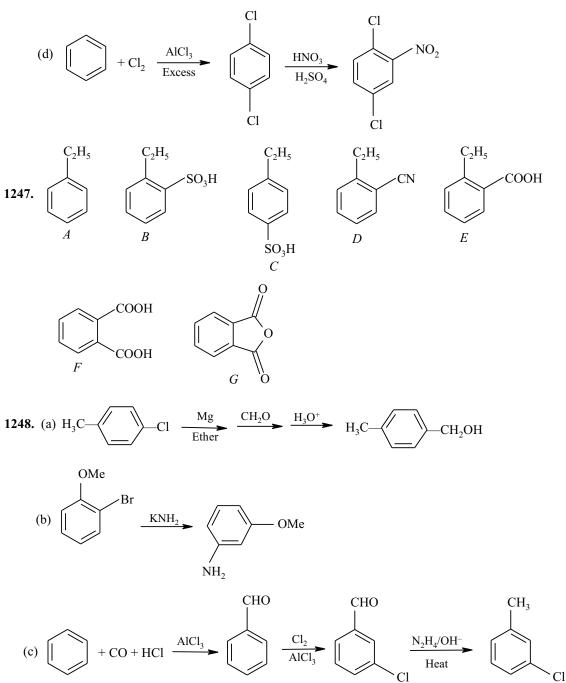




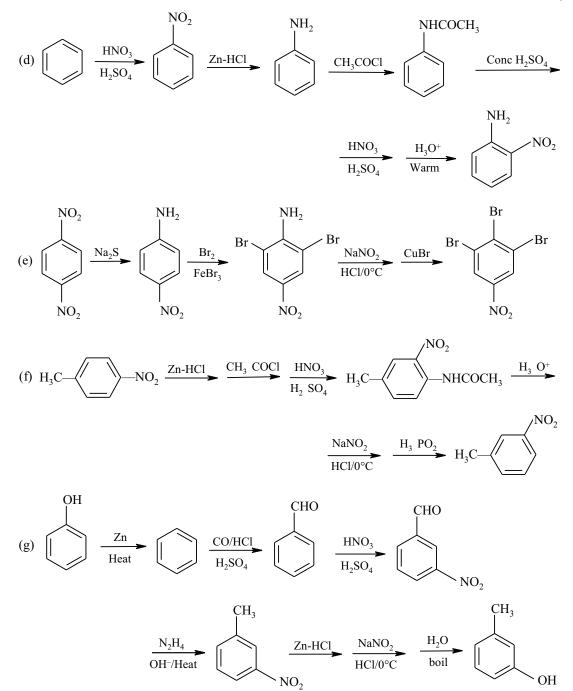


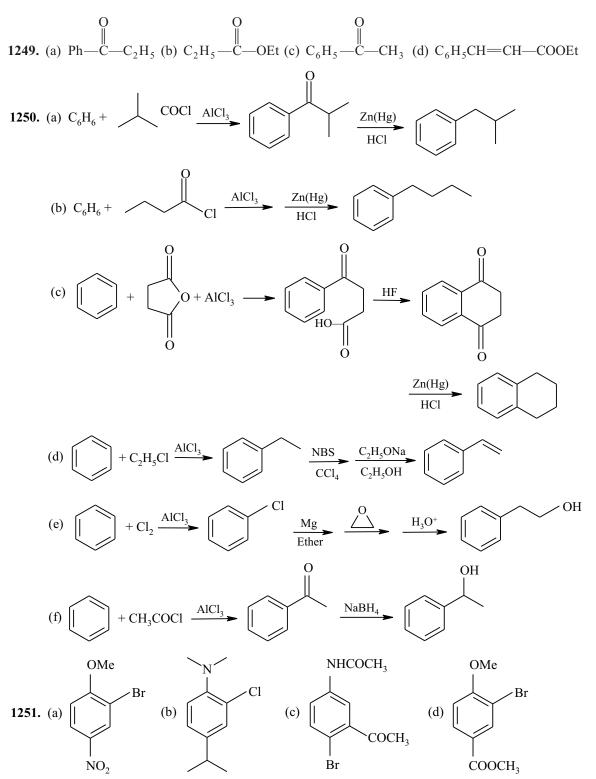
Problems in Chemistry

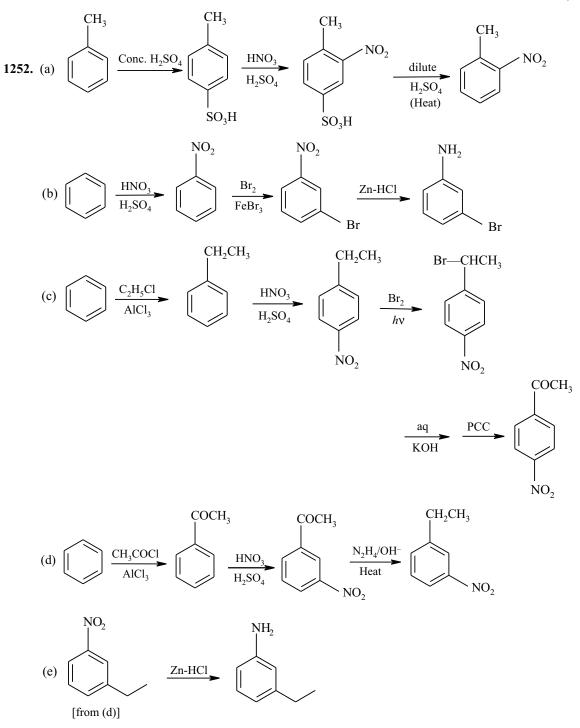


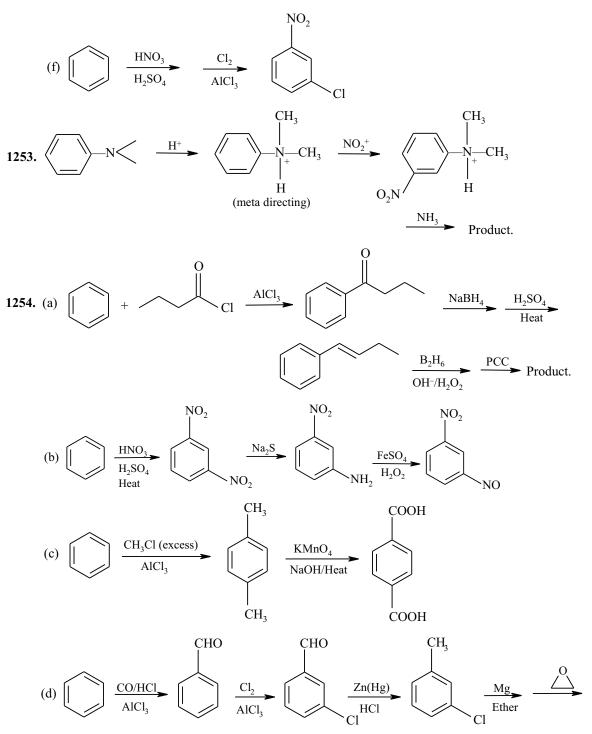


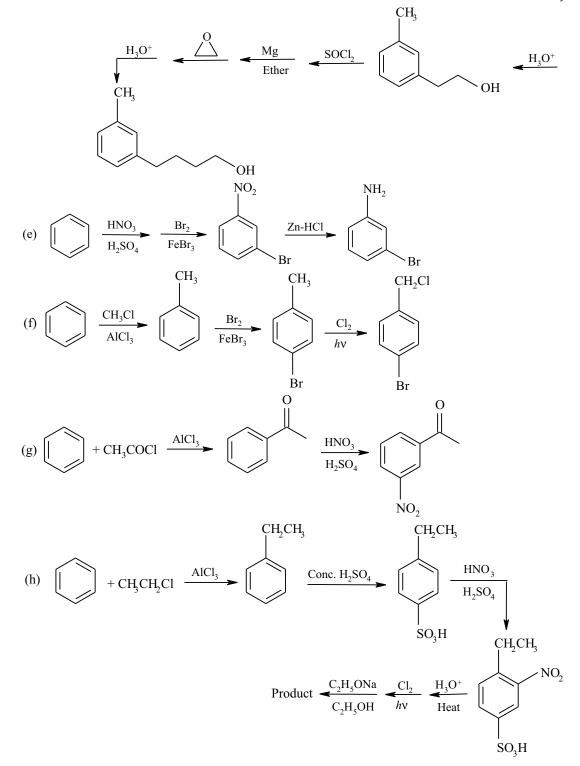
Problems in Chemistry

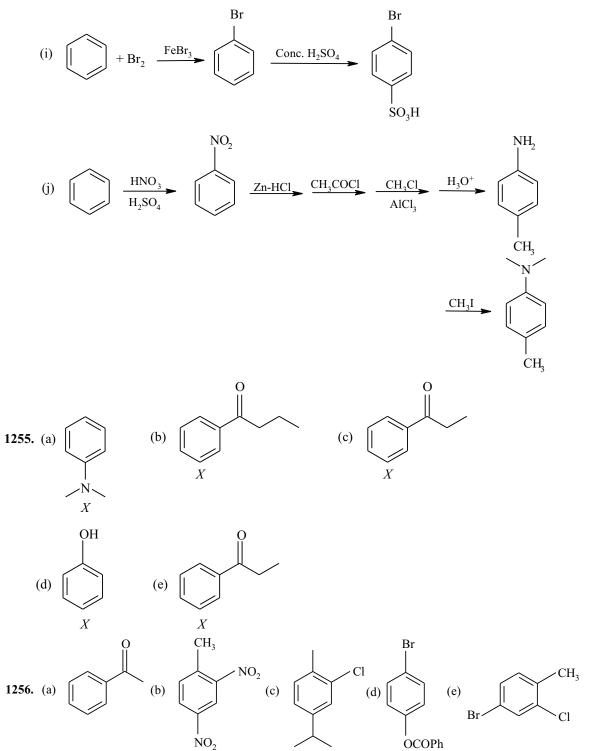


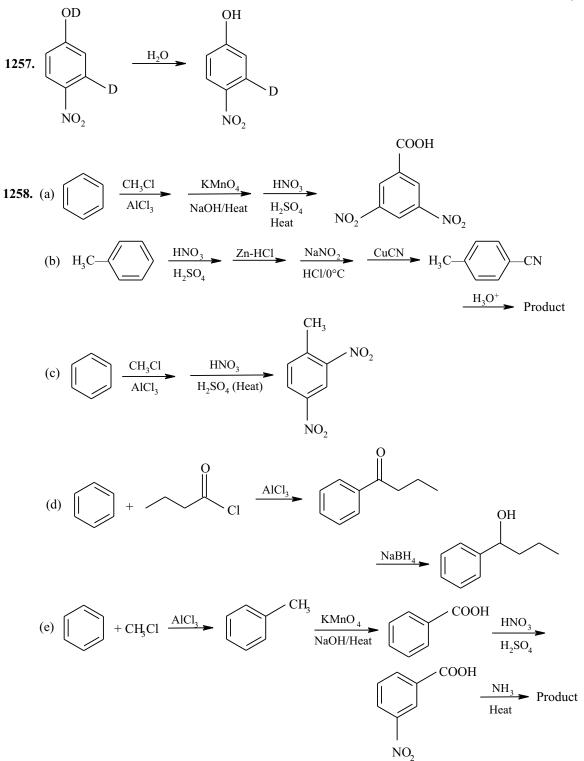


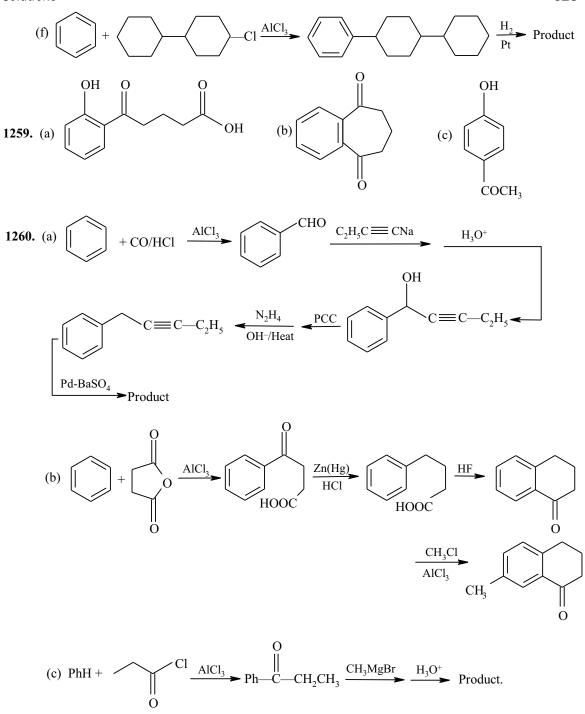


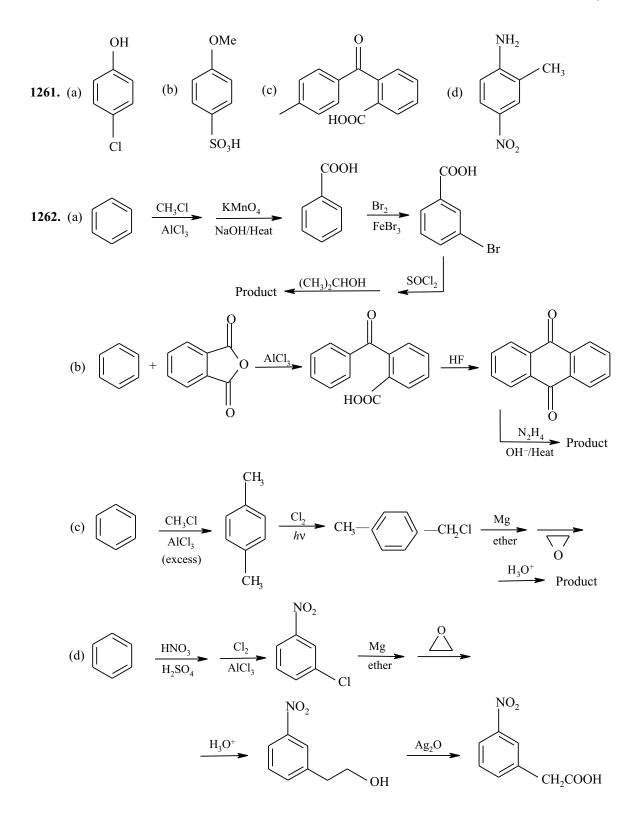


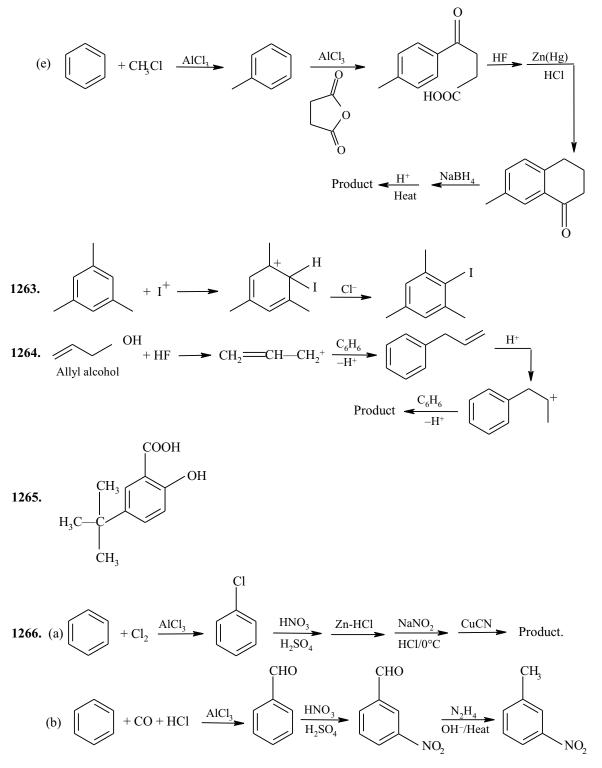


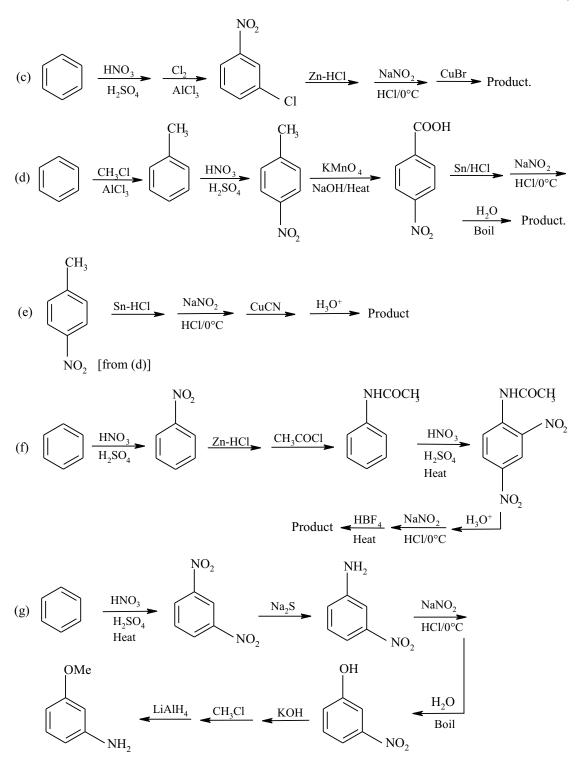


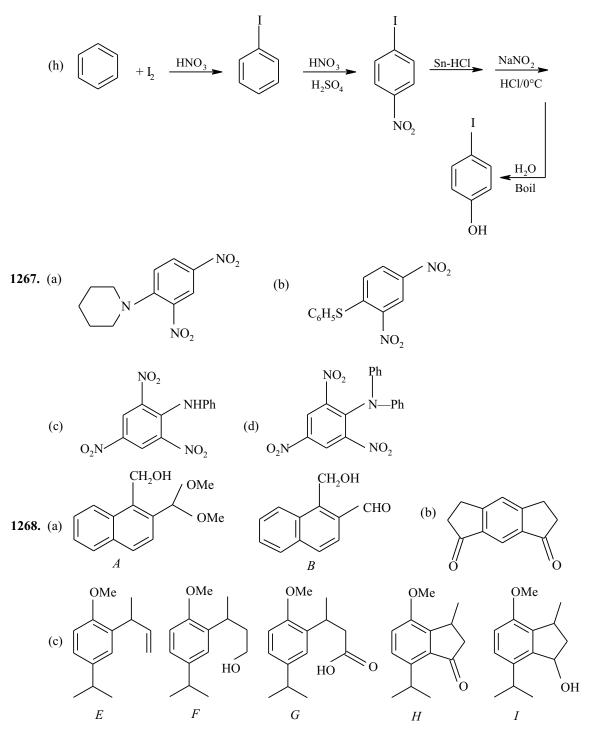


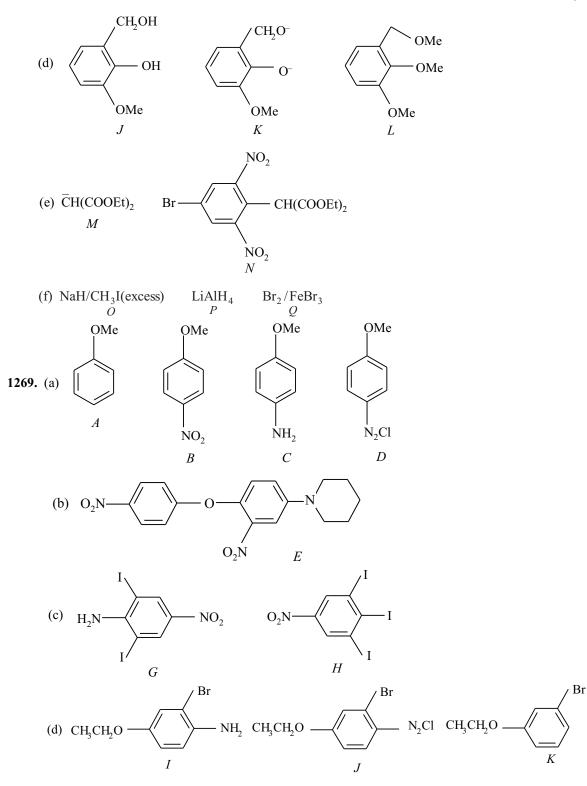


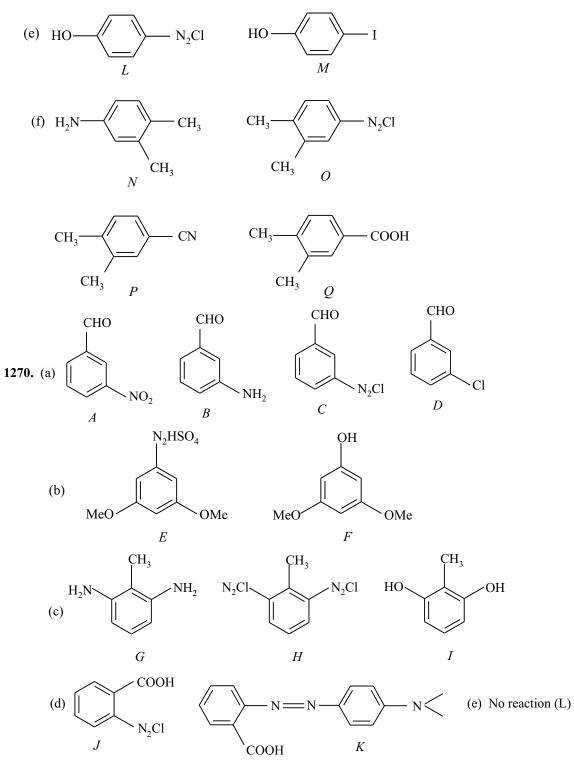


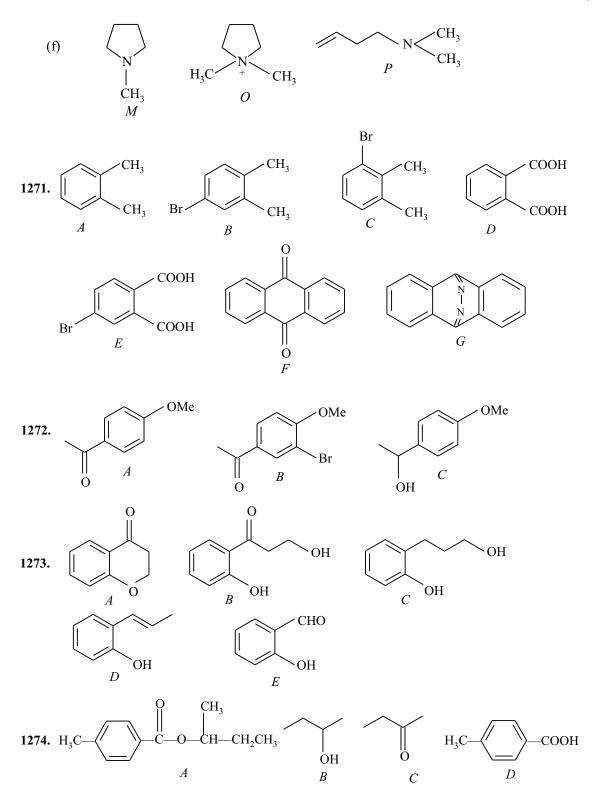


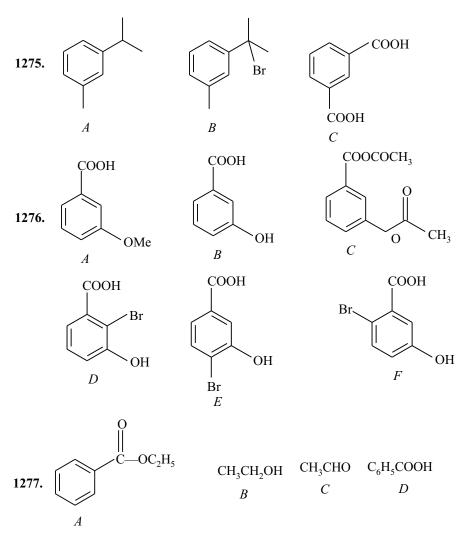




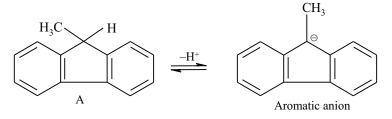


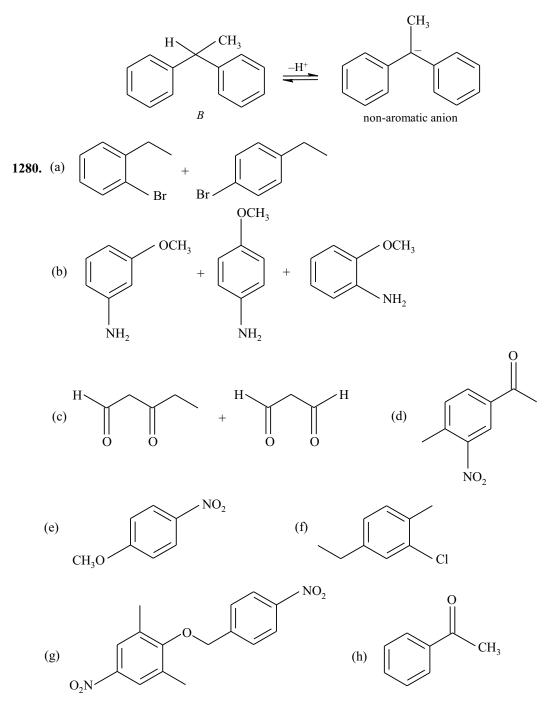


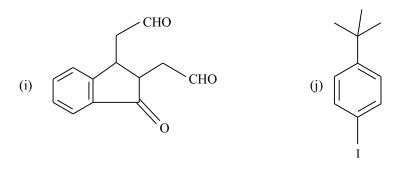




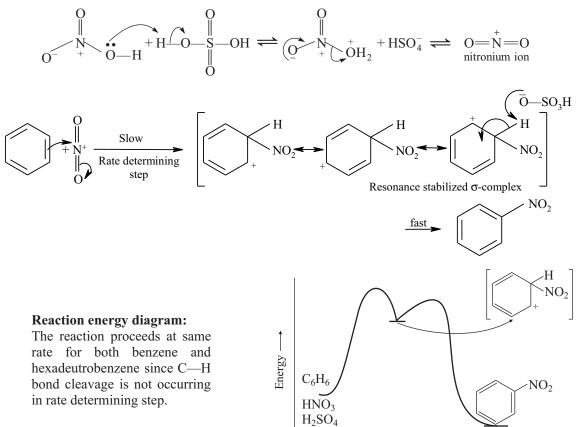
- **1278.**(a) Aromatic, cyclic and fully conjugated with six  $\pi$ -electrons.
  - (b) Antiaromatic, cyclic and fully conjugated with  $4\pi$ -electrons.
  - (c) Non-aromatic, cyclic but not fully conjugated.
  - (d) Antiaromatic, cyclic and fully conjugated with  $4\pi$ -electrons.
- **1279.** Conjugate base of A invoke aromatic character in the middle ring therefore, deprotonation of benzylic H in A is favoured. On the other hand conjugate base of B does not bring any stability by aromaticity deprotonation of benzylic H is not as favoured as in case of A.





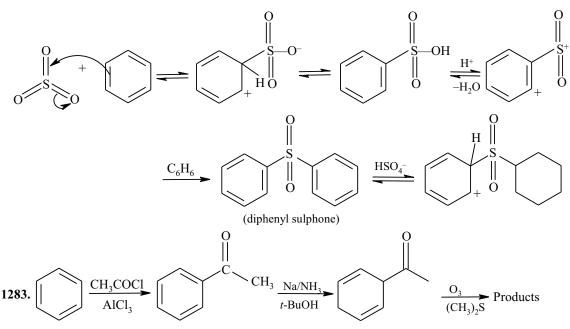


1281. Nitration of benzene proceeds by the following mechanism:



Reaction coordinate

1282. Sulphonation of benzene proceeds by the following mechanism:



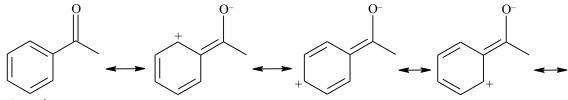
1284.(a) CH<sub>3</sub>COCl/AlCl<sub>3</sub>, Br<sub>2</sub>/FeBr<sub>3</sub>, (b) PCC/CH<sub>2</sub>Cl<sub>2</sub>, NBS/hv,

(c) H<sub>2</sub>/Rh/Pressure, NaIO<sub>4</sub>, (d) CH<sub>3</sub>COCl/AlCl<sub>3</sub>, HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>,

(e) (CH<sub>3</sub>)<sub>2</sub>CHCOCl/AlCl<sub>3</sub>, Na/NH<sub>3</sub>/EtOH, Zn(Hg)/HCl,

(f) NBS/hv, Mg/ether, CH<sub>2</sub>O, PCC(g) Br<sub>2</sub>/FeBr<sub>3</sub>, HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>.

**1285.** The reaction will be slower with acetophenone than with benzene as the acyl group is a deactivating group in electrophilic aromatic substitution.

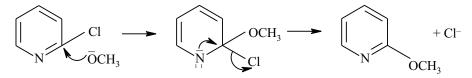


Acetophenone

As shown above, electron withdrawing (-R) effect of acyl group decreases the electron density from the aromatic ring making it less susceptible for attack to an electrophile (Br<sup>+</sup> in bromination reaction).

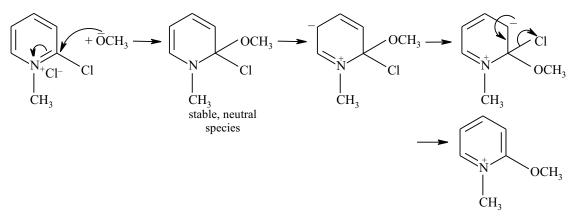
Also, acyl group, by resonance, brings positive charge on ortho and para positions, hence, meta-positions are relatively richer in electrons compared to the ortho/para positions. Hence, electrophile, if attacks at all, it attacks at meta positions only.

1286. The mechanism of substitution reaction is:

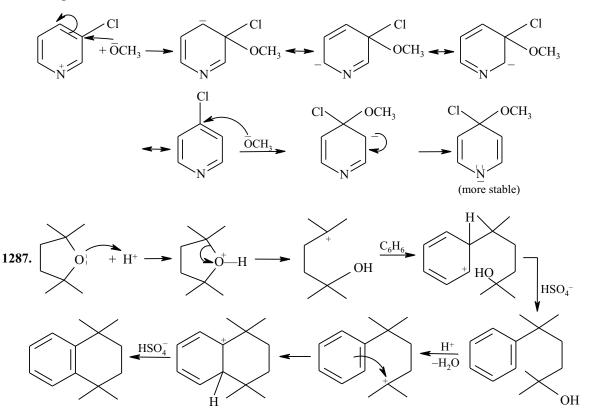


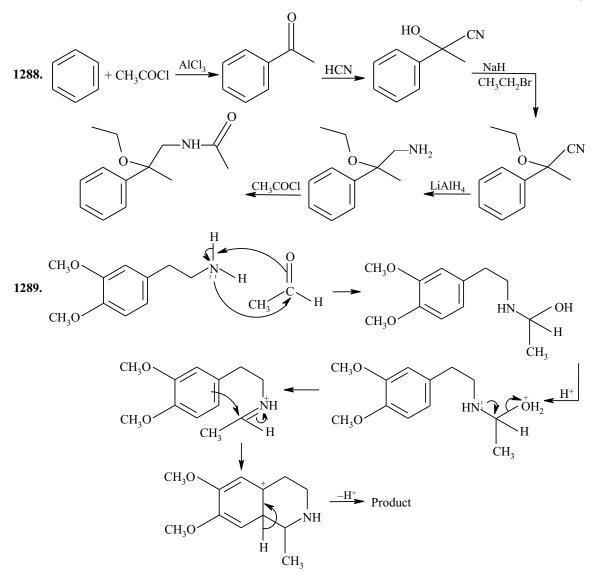
On the basis of above mechanism, it can be concluded that the order of reactivity will be: A < C < B.

The reason for the above order are : For the pyridinium salt, one of the resonance forms bear no charge. This will be a stable, neutral species and the activation energy is, accordingly, low relative to others A and C.



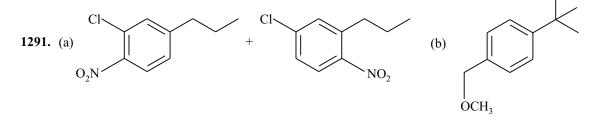
In the case of 3-chloropyridine, the negative charge on intermediate can't be delocalized, therefore, this reaction would be expected to be slower than 4-chloropyridine where the negative charge is delocalized.

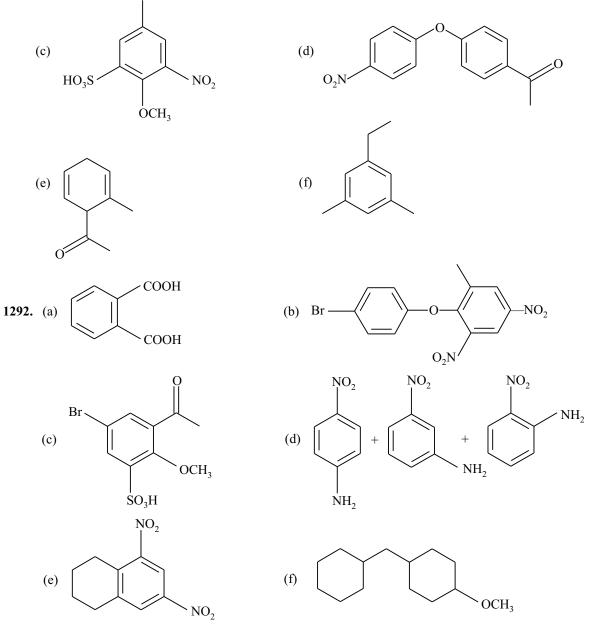


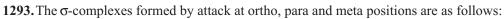


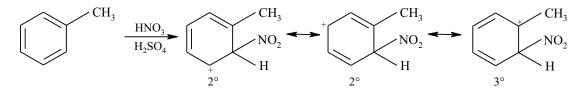
**1290.**(a) Antiaromatic, fully conjugated, planar with  $4\pi$ -electrons.

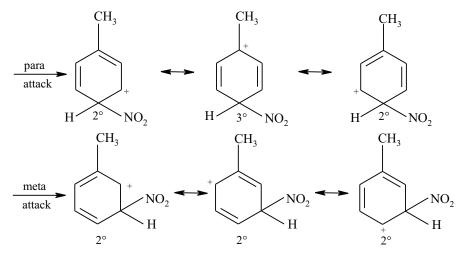
- (b) Aromatic, planar, fully conjugated,  $6\pi$ -electrons (two from ring oxygen).
- (c) Non-aromatic, planar fully conjugated,  $7\pi$ -electrons (one from radical).
- (d) Non-aromatic, not fully conjugated.





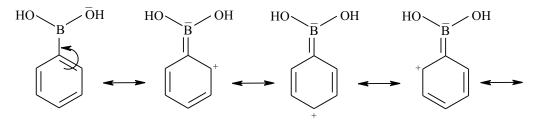




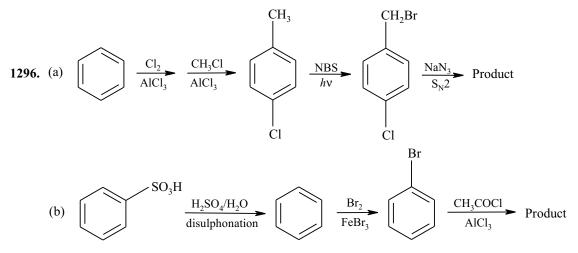


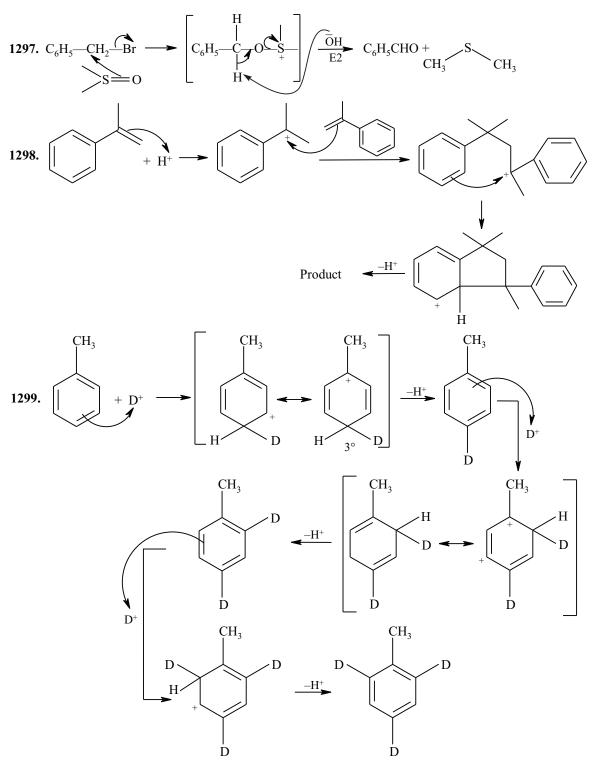
- 1294.(a) CH<sub>3</sub>Cl/AlCl<sub>3</sub>, NBS/hv, CH<sub>3</sub>ONa,
  - (b) CH<sub>3</sub>COCl/AlCl<sub>3</sub>, Fe(Hg)/HCl, Na/NH<sub>3</sub>/EtOH,
  - (c) H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sup>-</sup>/heat, KMnO<sub>4</sub>/NaOH/heat,
  - (d)  $CH_3(CH_2)_2COCI/AICl_3$ , NBS/hv,  $CH_3ONa$ ,  $Rh/H_2/\Delta$ .

**1295.**— $B(OH)_2$  is a meta directing group due to following resonance phenomena:



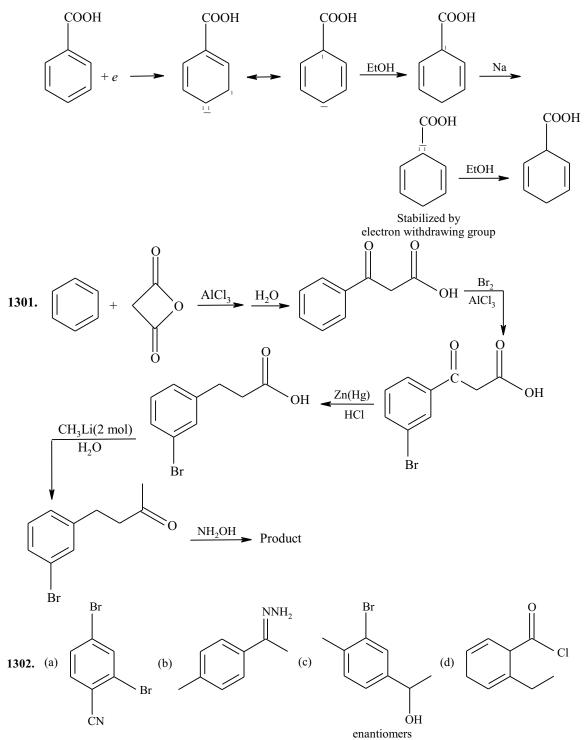
The above resonance structures reveals that  $-B(OH)_2$  withdraw electrons from ortho/para positions deactivating the ring for attack of electrophile. Even, if the compound is subjected to electrophilic attack, it occurs at meta position.

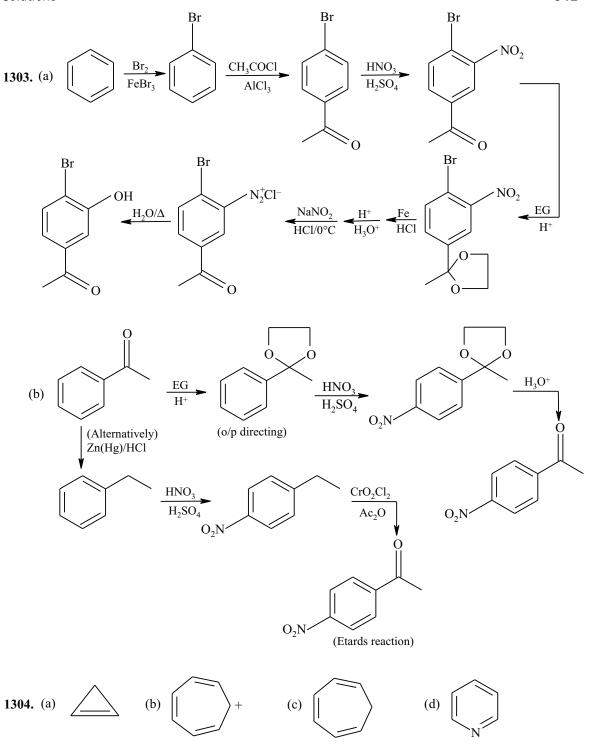


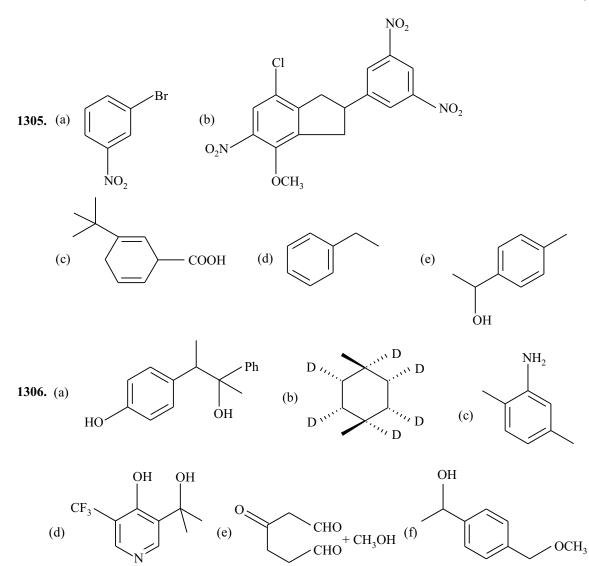


## 1300. Benzoic acid.

The mechanism involves addition of electrons to form a radical anion in the first step as:



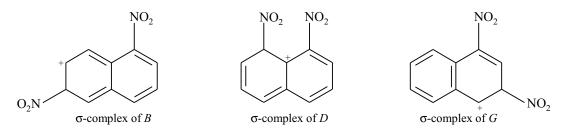




**1307.**(a)  $(CH_3)_2$ CHCOCl/AlCl<sub>3</sub>, Ph<sub>3</sub>P=CH<sub>2</sub>,

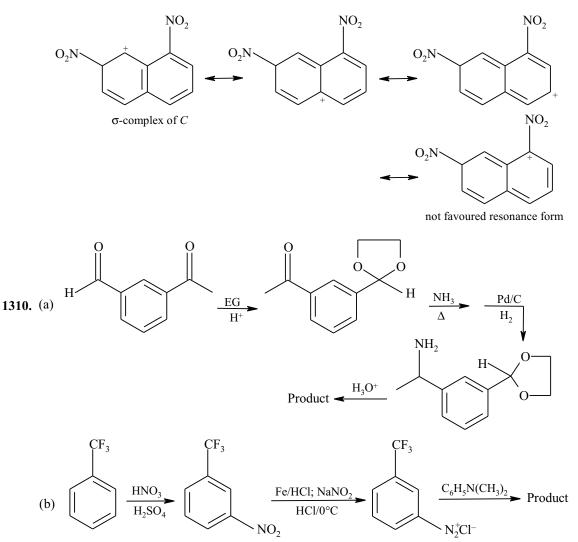
(b)  $O_3/Zn-H_2O$ , Zn(Hg)/HCl,

- (c) Br<sub>2</sub>/FeBr<sub>3</sub>, HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>, Mg/ether/oxirane/H<sub>3</sub>O<sup>+</sup>, PCC/CH<sub>2</sub>Cl<sub>2</sub>,
- (d) Alternative : CH<sub>3</sub>Cl/AlCl<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub>, NBS/hv, Mg/ether/CH<sub>2</sub>O, PCC/CH<sub>2</sub>Cl<sub>2</sub>.
- **1308.**CH<sub>3</sub>OCH=PPh<sub>3</sub> C<sub>6</sub>H<sub>5</sub>CH=CHOCH<sub>3</sub> C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CHO A C<sub>6</sub>H<sub>5</sub>CH=CHOCH<sub>3</sub> C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CHO
- **1309.** Only *B*, *D* and *G* are formed. In order to rationalize, we need to see the sigma complex in each case. In sigma complex leaging to C, E, F, H, one of the resonance form places the positive charge on  $C_1$ , which is the carbon bearing nitro group. These products are then all disfavoured.

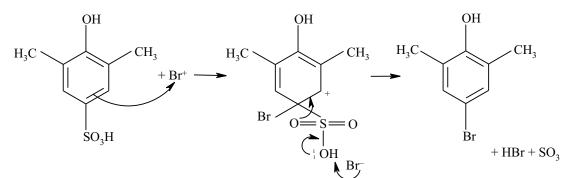


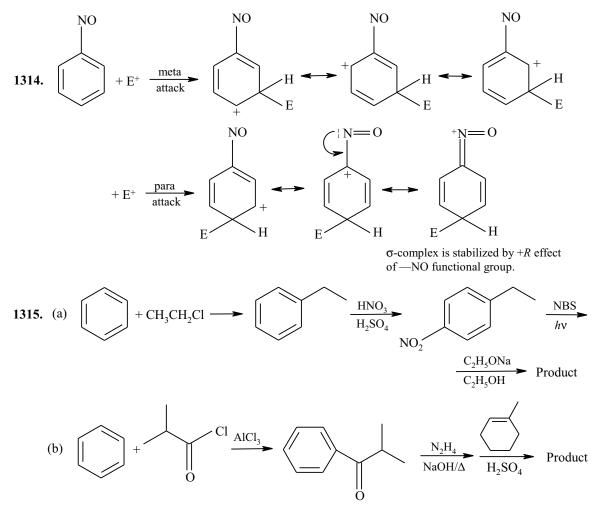
In none of the resonance forms of the above  $\sigma$ -complex it is possible to place positive charge (+) on carbon bearing — NO<sub>2</sub> group.

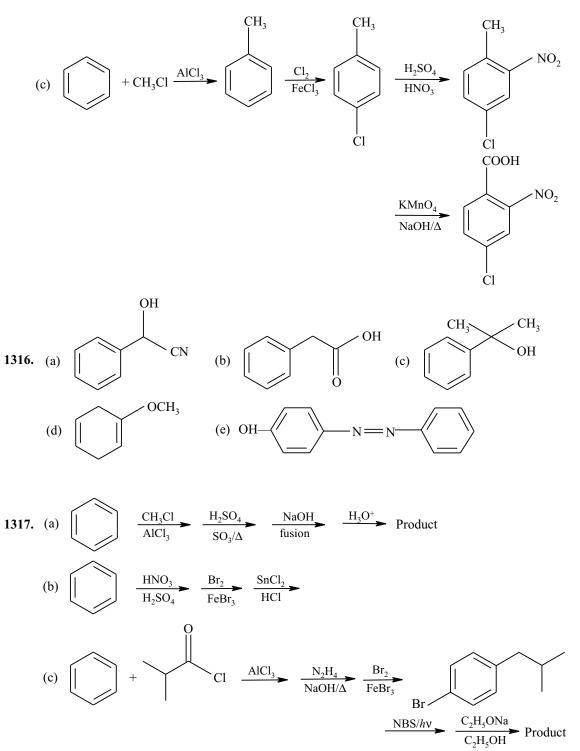
Sigma complex of remaining four places positive charge on C-bearing  $-NO_2$  in one of their resonance form:

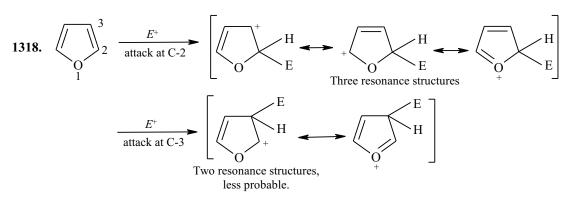


**1311.**  $\operatorname{Br}_2 + \operatorname{FeBr}_3 \longrightarrow \operatorname{Br}^+ + \operatorname{FeBr}_4^-$ 

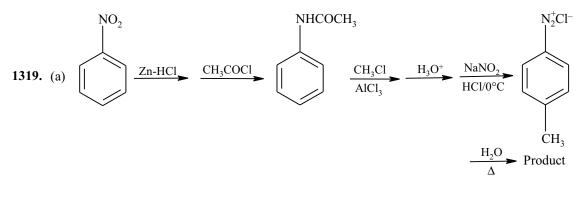


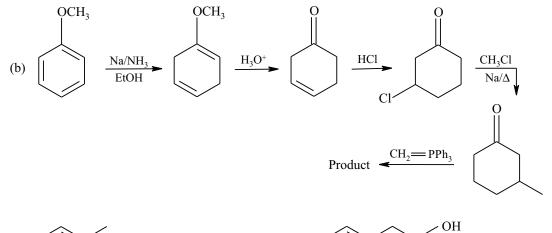


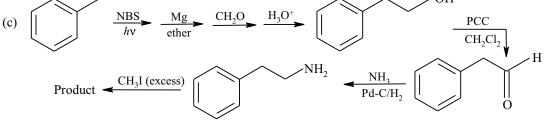


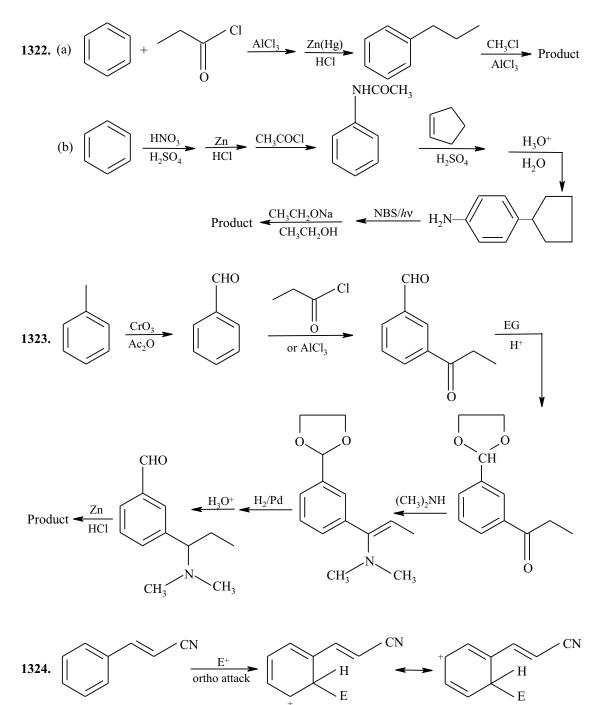


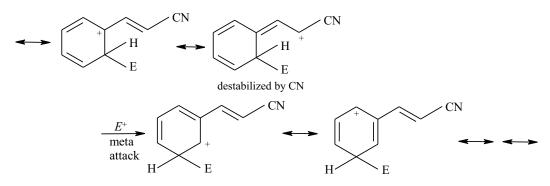
Therefore, electrophile is most likely to attack at C-2 position.



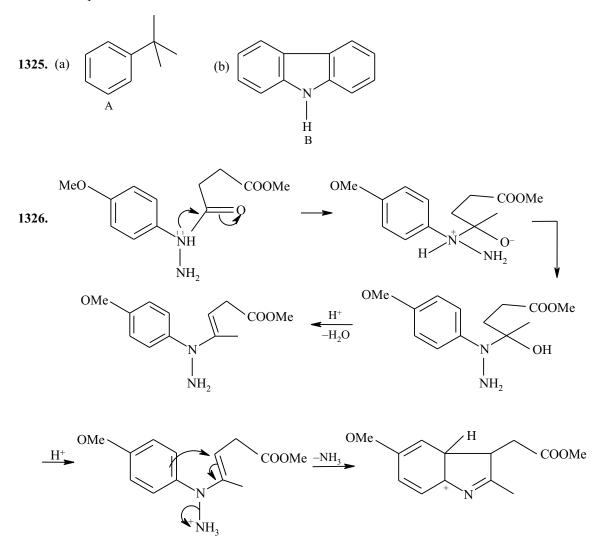


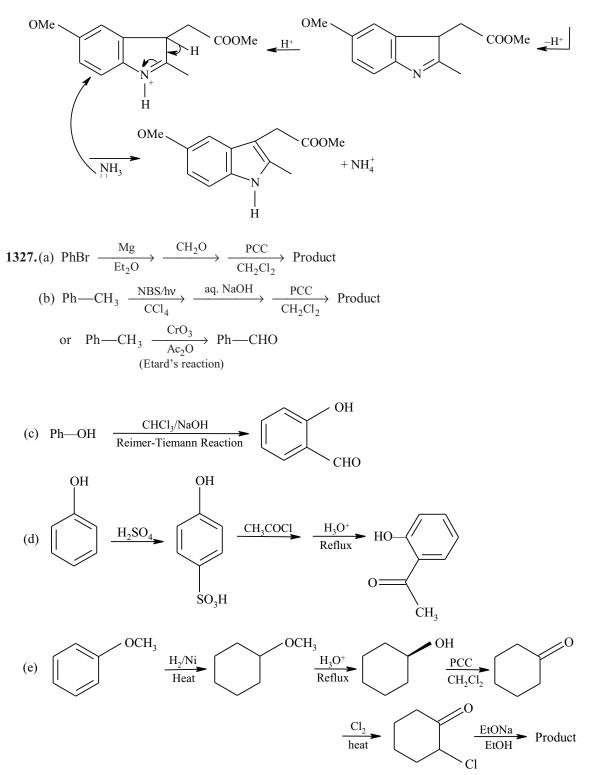


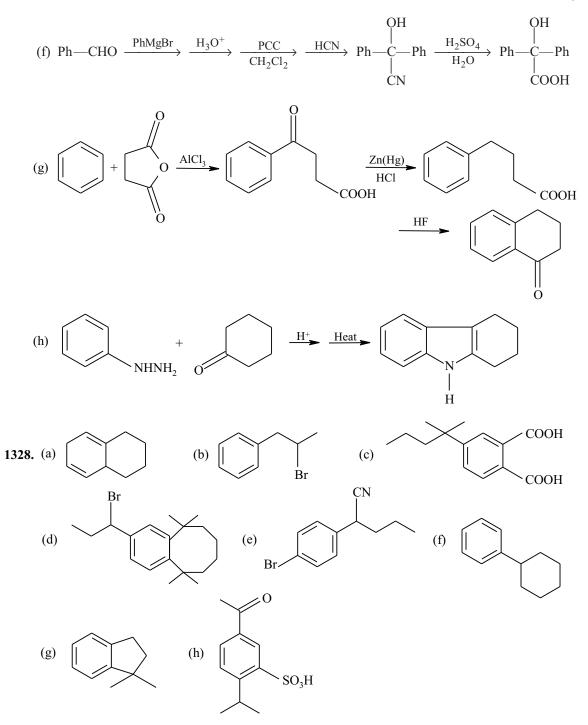


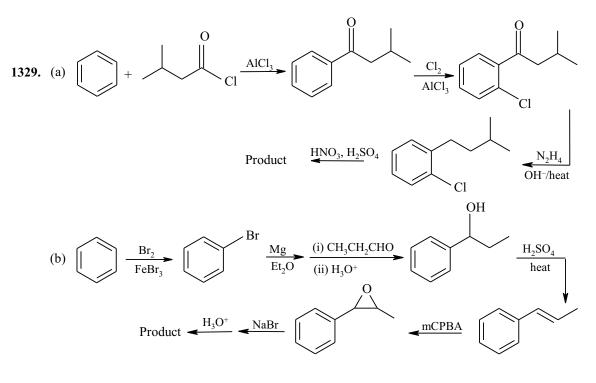


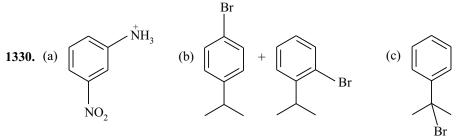
Meta attack of  $E^+$  avoides the electron withdrawing effect of —CN group as positive charge can't interact directly with CN group. Therefore, meta attack is favoured over ortho/para attack of electrophile.

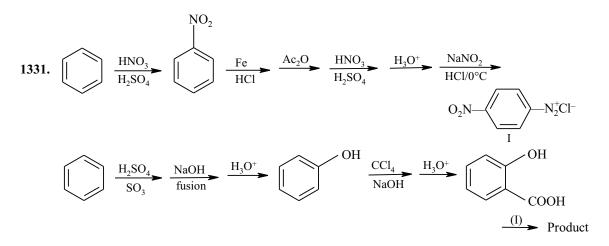


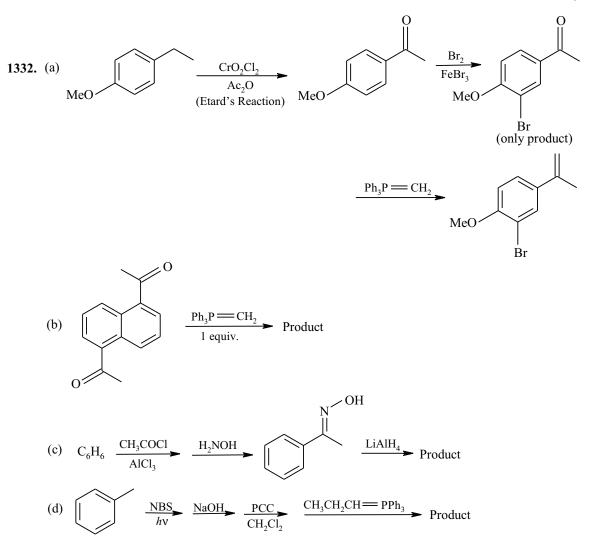




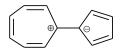








**1333.** (a) Non-aromatic, (b) Aromatic, (c) Aromatic, (d) Nonaromatic, (e) Aromatic, (f) Aromatic. **1334.** Since, both rings are aromatic with the following resonance structure:

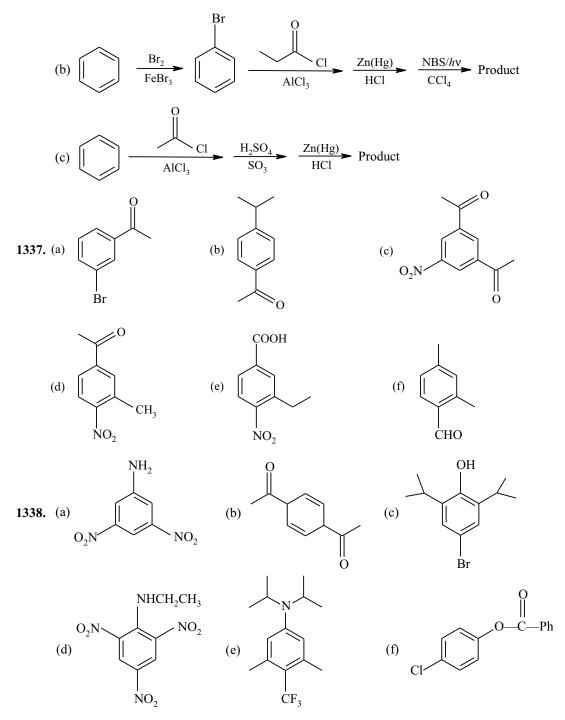


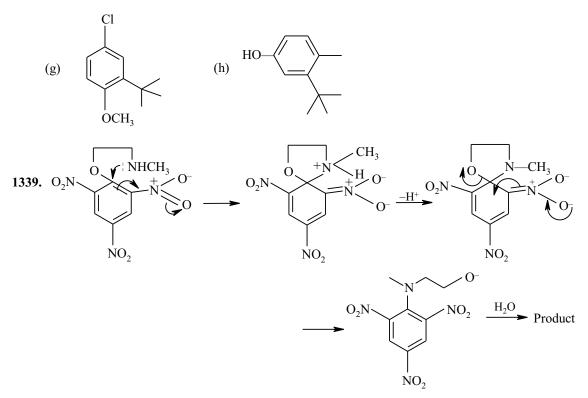
both the rings are now aromatic hence double bond character between the rings are very less, therefore less barrier to rotation,

1335. (a) Deactivated, (b) Deactivated, (c) Activated, (d) Activated, (e) Deactivated, (f) Activated.

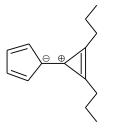
**1336.** (a) 
$$(I_2 \to I_2 \to I_2$$

~



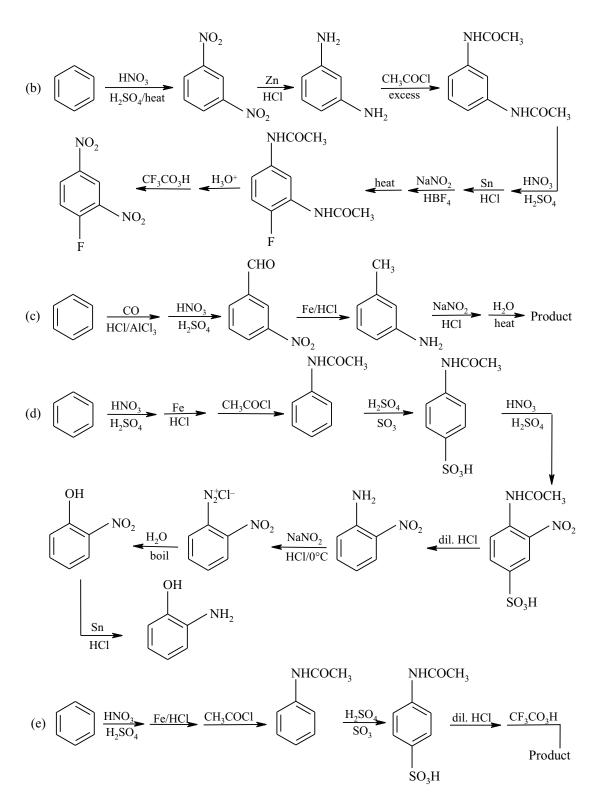


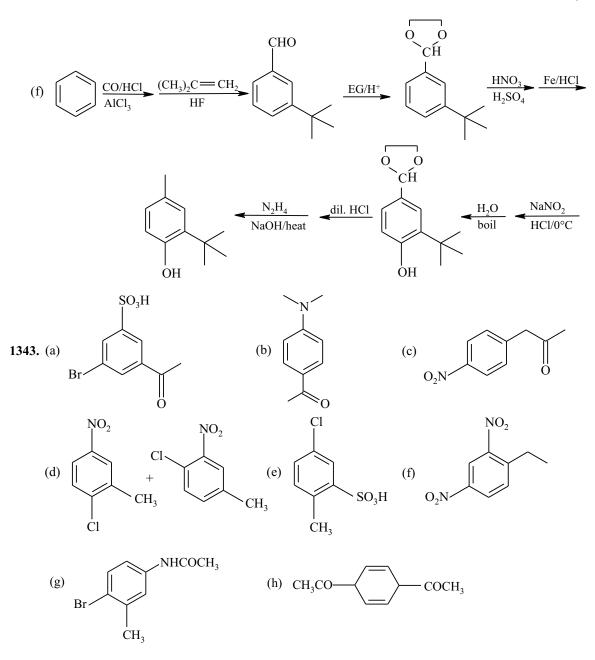
- 1340.(a) Non-aromatic, (b) Non-aromatic, (c) Antiaromatic,
  - (d) Antiaromatic, (e) Antiaromatic, (f) Aromatic,
  - (g) Aromatic, (h) Aromatic.
- 1341. Since, double bond is in resonance and involved in aromaticity as:

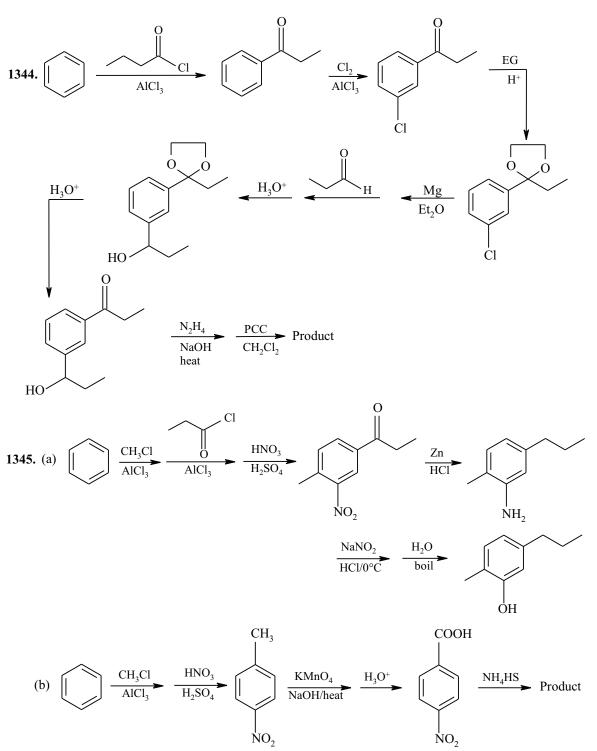


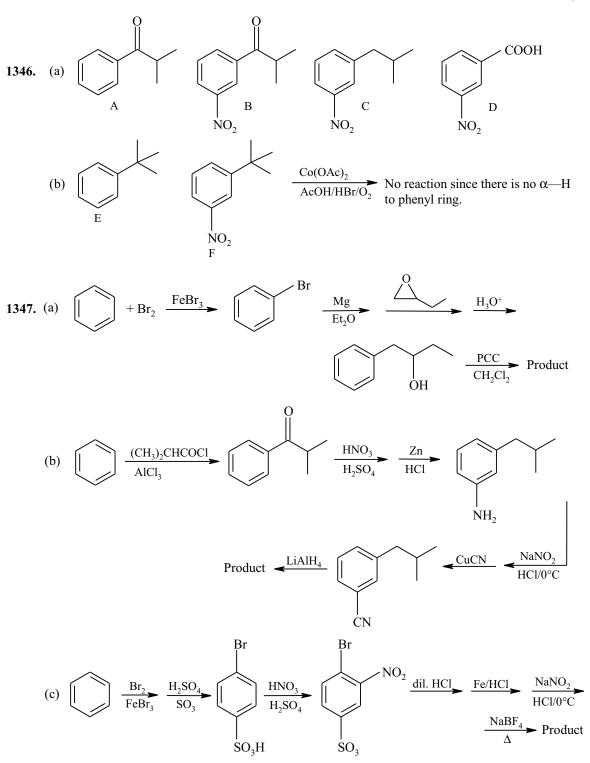
Here, both the rings are aromatic, therefore, this resonance form is a major contributor. Due to this resonance structure the double bond between the two rings has acquired significant single bond character giving low energy barrier to rotation.

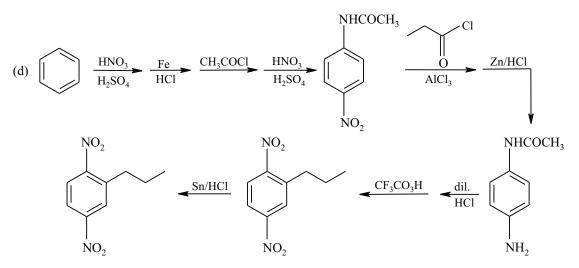
**1342.** (a) 
$$C_6H_6 \xrightarrow{CH_3Cl (excess)} CH_3 \xrightarrow{CH_3-CH_3} CH_3 \xrightarrow{KMnO_4} H_3O^+ \rightarrow Product$$



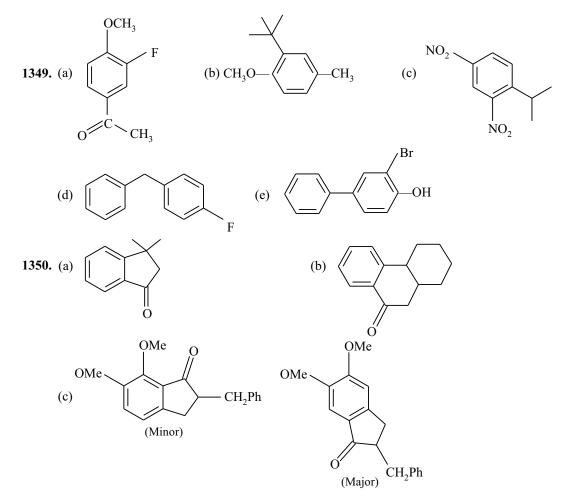


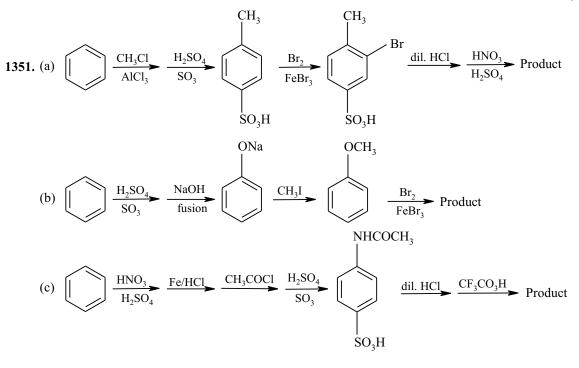


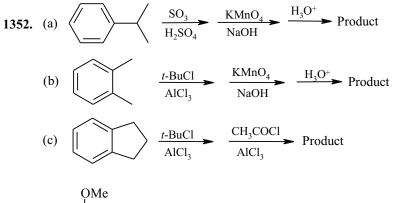


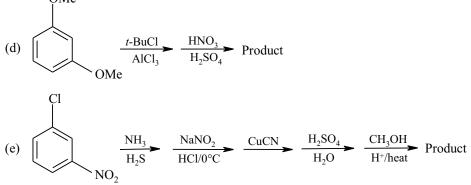


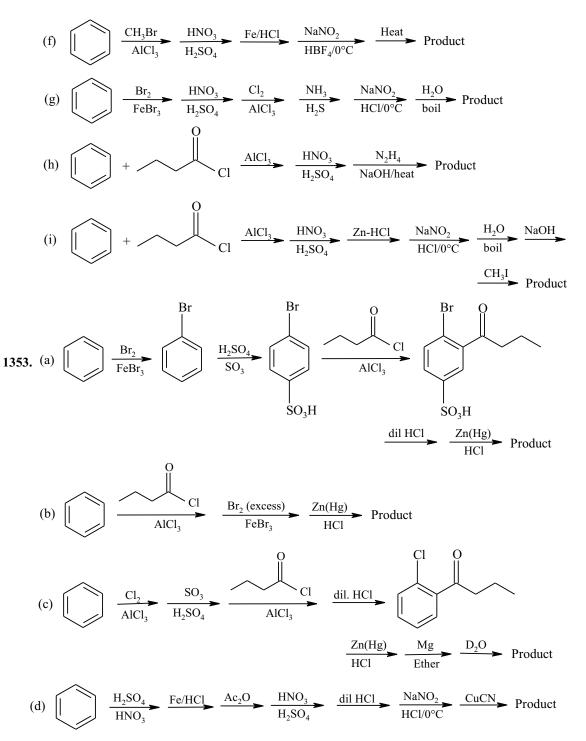
**1348.**(a) Non-aromatic since, it has a  $sp^3$  carbon. (b) Aromatic.

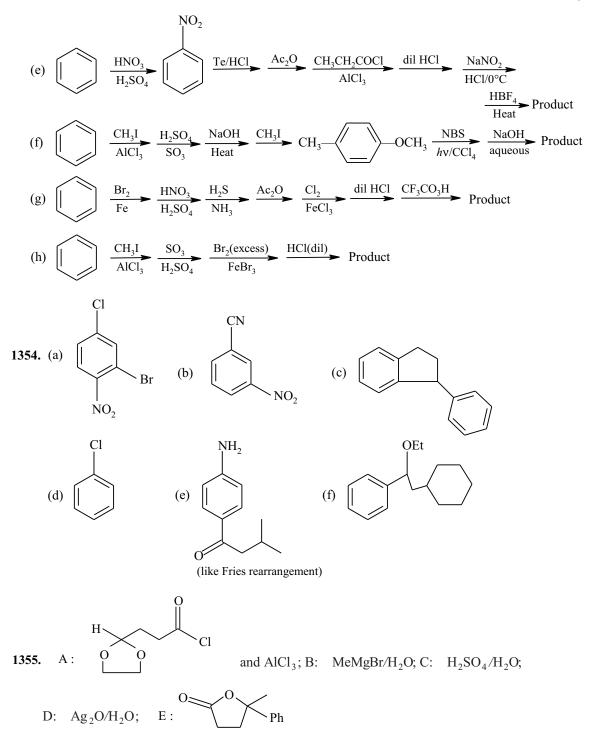


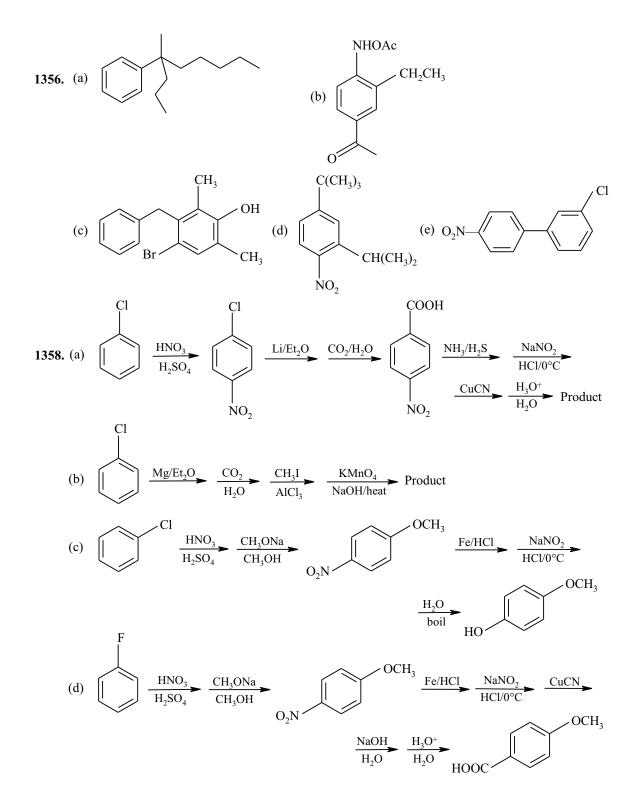


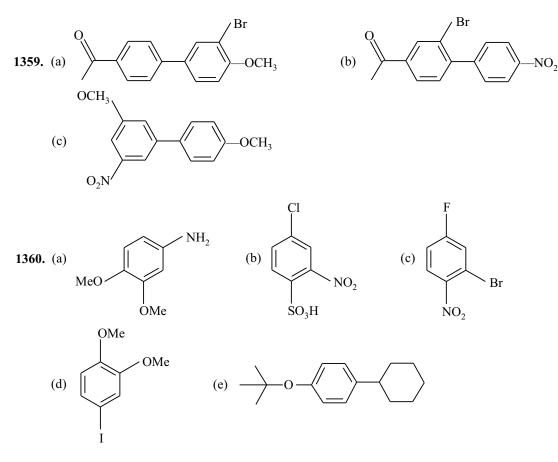












- 1362.(a) Aromatic,
  - (b) Not aromatic, it has a  $sp^3$  carbon which prevent delocalization,
  - (c) Aromatic,
  - (d) Not aromatic.

**1363.** A:  $KMnO_4$ /NaOH/heat; B:  $SOCl_2$ ; C:  $Et_2NCH_2CH_2OH$ ; D:  $Na_2S$ .

