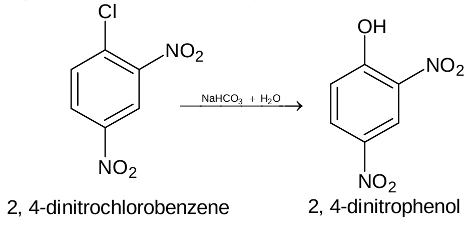
ELECTROPHILIC AROMATIC SUBSTITUTION

SOLUTION TO ASSIGNMENT PROBLEMS (SUBJECTIVE)

LEVEL – I

SHORT ANSWER TYPE QUESTIONS

1. No doubt benzene is highly unsaturated but due to resonance benzene molecule gains stability and does not show addition reactions.
2. During alkylation of bromobenzene, if benzene is used as solvent, alkylation of benzene will take place because benzene is more reactive for S_E reactions than bromobenzene. On the other hand, nitrobenzene does not undergo Friedel-Crafts reaction and can be used as solvent for alkylation of bromobenzene.
3. The steric effect of – $C(CH_3)_3$ is more pronounced in $C_6H_5C(CH_3)_3$ than in $C_6H_5CH_3$ which ultimately inhibits the electrophilic substitution at ortho position. That is why o-isomer formed during nitration of $C_6H_5C(CH_3)_3$ shows poor yield; however better yield of p-isomer is formed.
4. Halogens deactivate benzene ring for further substitution due to – I.E. of halide groups. The – I. E. of F in halogens being maximum and thus deactivating nature in halogens is maximum for F. Thus, nitration of C_6H_5F shows poor yield.
5. Oxidant being electrophilic in nature and thus it can attack and even destroy benzene ring in case of toluene. However, in case p-nitrotoluene, the presence of $–NO_2$ deactivates ring for electrophilic attack on ring and thus only $–CH_3$ group is oxidized to give better yield of p-nitrobenzoic acid.
6. The $–OCH_3$ group is electron repelling and thus activate the ring for o– and p– substitution due to electromeric and mesomeric effect. The group also exerts – I.E. due to the presence of lone pair of electrons and oxygen atom of $–OCH_3$ which deactivates an m-position for substitution. On the other hand, $-CH_3$ group being electron repelling as well as + I.E. of $–CH_3$ group activates the ring for o– and p– substitution only whereas m-position remains unaffected.
7. The order of effectiveness of delocalization of electron density by p-p extended π bonding is F>Cl>Br>I. This is due to increasing size of halogens. Smaller is the size of halogens, more effective is overlapping by p-p orbitals and thus more effective is extended delocalization.
8. 2,4-Dinitrochlorobenzene shows nucleophilic substitution in presence of $NaHCO_3$ showing replacement of – Cl by – OH atom.



9. The phenolic group is readily oxidized and thus yield is poor.

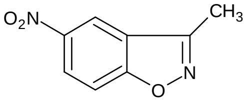
10. Aniline is very susceptible for oxidation and is oxidized easily by HNO_3 present in nitration mixture or by halogens

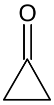
11. **FILL IN THE BLANKS**

(i) NO_2
(ii) p-nitro benzyl alcohol and sodium (p-nitrobenzoate)
(iii) 6
(iv) 6 π-electrons
(v) 2
(vi) 1,2, 3
(vii) base
(viii) Friedel-Crafts reaction
(ix) acetyl chloride

EXPLANATORY QUESTIONS

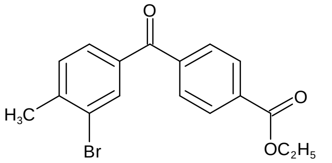
12.



In case of  it is not possible.

13. (i) Aromatic
(ii) Anti-aromatic
(iii) Aromatic
(iv) Aromatic
(v) Anti-aromatic
(vi) Non-aromatic

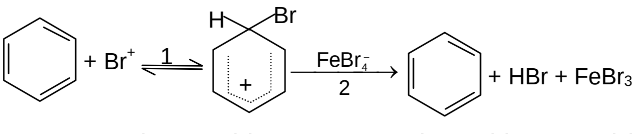
14.



15. (i) The lower reactivity of chlorobenzene is due to partial double bond character of C – Cl bond, it is shorter and stronger bond in comparision to C – Cl bond in ethyl chloride.
(ii) The nitro group in nitrobenzene strongly deactivates the benzene ring. This decreases the reactivity of benzene towards Friedel-Crafts alkylation.
(iii) Because the lone pair of $-NH_2$ group undergoes coordination with Lewis acid catalyst $(AlCl_3)$ i.e. the group becomes electron withdrawing.

16. All the evidence favours a bimolecular mechanism for bromination; this may be written:

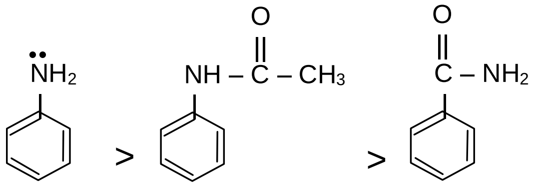
$$Br_2 + FeBr_3 \xrightleftharpoons{fast} Br^+ + FeBr_4^-$$



Steps 1 and 2 are bimolecular and so either could be the rate determining step. Since no kinetic isotope effect is observed when H is replaced by D and C–H or C–D bond fission cannot be involved in r/d step. Hence, 1 is the r/d step and so the rate of bromination is same for C_6H_6 and C_6D_6.

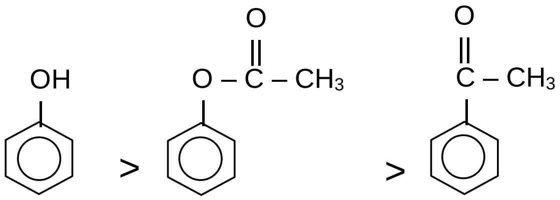
17. In biphenyl, one of the phenyl groups acts as electron donor and the other as electron acceptor. This makes the phenyl ring more reactive than benzene towards electrophilic substitution.

18. (a)

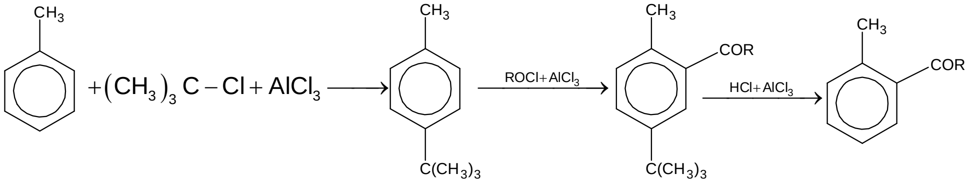


In aniline, NH_2 group is directly attached to benzene ring which releases electrons by resonance effect, whereas the activation of $-NH_2$ group can be decreased by converting it to anilide. But in amide, ring is attached to electron-withdrawing group which deactivates the ring.

(b)



19. The para position in toluene is first protected by t- butylation. The acylation is then done on the t- butyl derivative and the t-butyl group is subsequently removed.

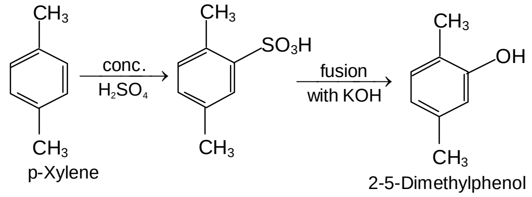


Level – II

1. Benzene is more reactive than bromobenzene and hence would preferentially undergo alkylation. On the other hand, nitrobenzene is very much less reactive than bromobenzene (due to deactivating effect on the –NO_2 group) and hence will not undergo Friedel-Crafts reaction.

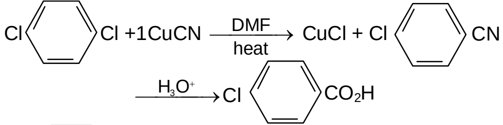
2. $$\underset{\text{Benzene}}{C_6H_6} + CH_3Cl \xrightarrow[AlCl_3]{\text{anhy.}} C_6H_5CH_3 \xrightarrow[\text{UV light}]{Cl_2} C_6H_5CH_2Cl \xrightarrow{Cl_2} C_6H_5CHCl_2 \xrightarrow{Cl_2} \underset{\text{Benzotrichloride}}{C_6H_5CCl_3}$$

3.

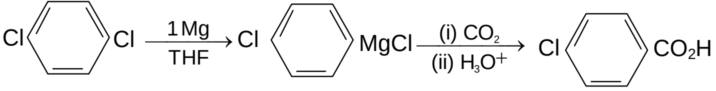


4. (i) One chlorine atom has been replaced by a carboxyl group. Hence, controlled conditions have to be used, and if we work backwards, two immediate possibilities are: (a) $CuCN/H_2O$; (b) Grignard and carbon dioxide.

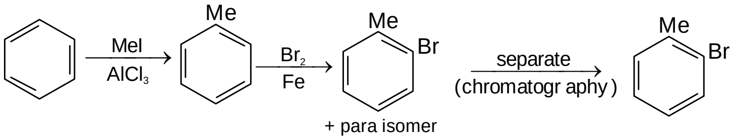
(a)



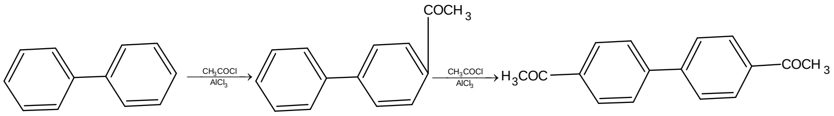
(b)



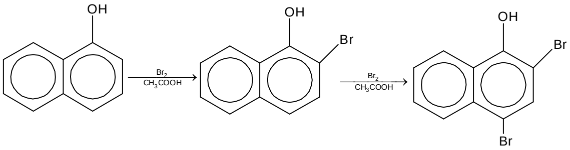
(ii)



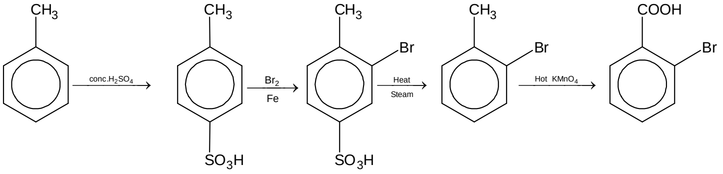
5. (i)



(ii)

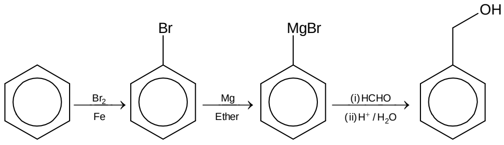


6. (a)



(b) $$C_6H_6 \xrightarrow{H_2/Pd} \underset{\text{Cyclohexane}}{C_6H_{12}} \xrightarrow[h\nu]{Cl_2} \underset{\text{Chlorocyclohexane}}{C_6H_{11}Cl} \xrightarrow{\text{Alc.KOH}} \underset{\text{Cyclohexene}}{C_6H_{10}CH_2} \xrightarrow[H^+]{KMnO_4} \underset{\text{Adipic acid}}{HOOC(CH_2)_4COOH}$$

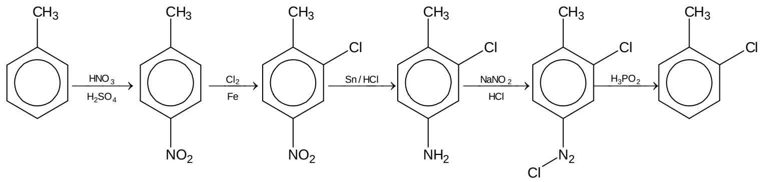
(c)



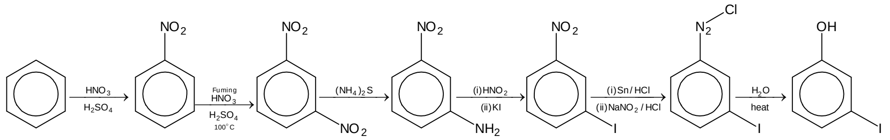
(d) $$C_6H_6 \xrightarrow{Br_2/Fe} C_6H_5Br \xrightarrow[\text{Ether}]{Mg} C_6H_5MgBr \xrightarrow[\text{(ii) } H^+/H_2O]{\text{(i) HCHO}} C_6H_5CH_2OH \xrightarrow[Fe]{Cl_2}$$

$$p-ClC_6H_4CH_2OH \xrightarrow{CrO_3/\text{pyridine}} p-ClC_6H_4CHO$$

(e)

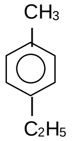


(f)

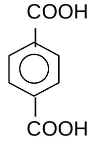


7\.

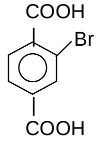
A =



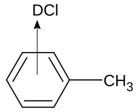
B =



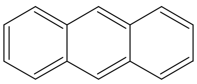
C =



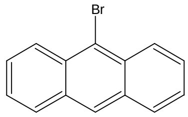
8\. Under the given condition, either a π complex or a α complex usually forms. Since no D is exchanged and since the solution does not conduct electricity, the formation of α complex is ruled out. Hence, the product is a π-complex.



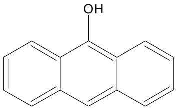
9\. (A)



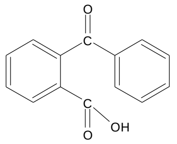
(B)



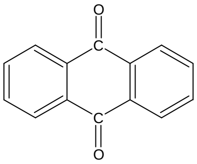
(C)



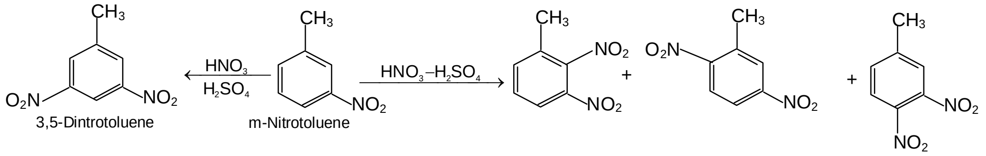
(D)



(E)

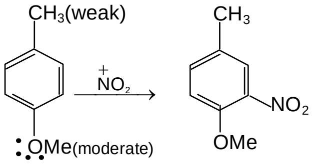


10\.



3,5 - Dinitrotoluene is not likely to be formed.

(b)



(c)