Objective Questions I (Only one correct option)

1. The major product obtained in the given reaction is



 The increasing order of the reactivity of the following compounds towards electrophilic aromatic substitution reaction is (2019 Main, 10 April I)





- 4. The major product of the following reaction is (2019 Main, 9 April I) $(i) Alkaline KMnO_4$ $(i) Alkaline KMnO_4$ $(i) H_3O^+$ (a) (b) (b) (c)
 - COCH₃ CH₂COOH (c) (d) (d)
- 5. The major product of the following reaction is (2019 Main, 9 April I)



 The increasing order of reactivity of the following compounds towards aromatic electrophilic substitution reaction is (2019 Main, 9 April I)



- (a) A < B < C < D(b) B < C < A < D(c) D < A < C < B(d) D < B < A < C
- 7. Polysubstitutiion is a major drawback in (2019 Main, 8 April II)
 - (a) Friedel-Craft's alkylation
 - (b) Reimer-Tiemann reaction
 - (c) Friedel-Craft's acylation
 - (d) Acetylation of aniline
- 8. The major product of the following reaction is (2019 Main, 8 April II)



Among the following four aromatic compounds, which one will have the lowest melting point? (2019 Main, 12 Jan I)



10. Which of the following compounds is not aromatic? (2019 Main, 9 Jan II)



(2015 Main)

Toluene $\xrightarrow{\text{KMnO}_4} A \xrightarrow{\text{SOO}}$	$\xrightarrow{Cl_2} B \xrightarrow{H_2/Pd}_{BaSO_4} C$, the product C is
(a) C ₆ H ₅ COOH	(b) $C_6H_5CH_3$
(c) $C_6H_5CH_3OH$	(d) C_6H_5CHO

12. Match the four starting materials given in Column I with the corresponding reaction schemes provided in Column II and select the correct answer using the code given below the lists.

	Column I		Column II	
А.	НН	p.	Scheme I (i) KMnO ₄ , HO ⁻ , heat (ii) H ⁺ , H ₂ O ? (iii) SOCl ₂ (iv) NH ₃ $C_7H_6N_2O_3$	
В.	ОН	q.	Scheme II (i) Sn/HCl (ii) CH ₃ COCl (iii) Conc. H ₂ SO ₄ ? (iv) HNO ₃ (v) Dil. H ₂ SO ₄ , heat (vi) HO ⁻ C ₆ H ₆ N ₂ O ₂	
C.	NO ₂	r.	Scheme III (i) Red hot iron, 873 K (ii) fuming HNO ₃ , H ₂ SO ₄ , heat (iii) H ₂ S.NH ₃ (iv) NaNO ₂ , H ₂ SO ₄ (v) hydrolysis ? \longrightarrow C ₆ H ₅ NO ₃	
D.	NO ₂ CH ₃	S.	Scheme IV (i) Conc. $H_2SO_4.60^{\circ}C$ (ii) Conc. HNO_3 , conc. H_2SO_4 (iii) Dil. H_2SO_4 , heat ? $\longrightarrow C_6H_5NO_4$	
Codes A (a) p (c) r	BCD sqr sqp		A B C D (b) r p s q (d) s p r q	(2014 Adv.)

13. For which of the following molecule significant $\mu \neq 0$?



14. The compounds P, Q and S



were separately subjected to nitration using HNO_3 / H_2SO_4 mixture. The major product formed in each case respectively, is (2010)







17.
$$P \xrightarrow{(i) O_2/\Delta} P \xrightarrow{(i) O_2/\Delta} Q + Phenol$$

P and Q are respectively

(2006, 5M)





18.



product on monobromination of this compound is



- 19. Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds Benzene (1), Toluene (2), Chlorobenzene (3) and Nitrobenzene (4) (2002)
 (a) 1 > 2 > 3 > 4 (b) 4 > 3 > 2 > 1
 - (c) 2 > 1 > 3 > 4 (d) 2 > 3 > 1 > 4
- 20. A solution of (+) -2-chloro-2-phenylethane in toluene racemises slowly in the presence of small amount of SbCl₅, due to the formation of (1999, 2M)
 (a) carbanion (b) carbene
 (c) free-radical (d) carbocation

21.	Benzyl chlo	repared from toluene		
	by chlorina	tion with		(1998, 2M)
	(a) SO_2Cl_2	(b) SOCl ₂	(c) Cl_2	(d) NaOCl

- 22. Chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives (1990, 1M)
 (a) *o*-cresol
 (b) *p*-cresol
 (c) 2, 4-dihydroxy toluene
 (d) benzoic acid
- 23. The reaction of toluene with chlorine in the presence of ferric chloride (FeCl₃) gives predominantly (1986, 1M)
 (a) benzoyl chloride (b) *m*-chlorotoluene
 (c) benzyl chloride (d) *o* and *p*-chlorotoluene

24. The compound that is most reactive towards electrophilic substitution is (1985, 1M)(a) toluene (b) benzene

(a) tolucite	(b) belizene
(c) benzoic acid	(d) nitrobenzene

25. Among the following, the compound that can be most readily sulphonated is (1982)
(a) benzene (b) nitrobenzene
(c) toluene (d) chlorobenzene

Objective Questions II

(One or more than one correct option)

26. The reaction(s) leading to the formation of 1,3,5-trimethylbenzene is (are) (2018 Adv.)



27. Among the following reactions(s), which gives(give) *tert*-butyl benzene as the major product? (2016 Adv.)



28. The major product U in the following reaction is (2015 Adv.)



29. Which of the following molecules, in pure form, is/are unstable at room temperature? (2012)



- **30.** An aromatic molecule will (1999, 3M) (a) have $4n\pi$ -electrons (b) have $(4n + 2)\pi$ -electrons (c) be planar
 - (d) be plana
 - (d) be cyclic
- **31.** Which compound(s) out of the following is/are not aromatic? (2019 Main, 11 Jan I)



- **32.** Toluene, when treated with Br_2/Fe , gives *p*-bromotoluene as the major product because the CH_3 group (1999, 3M)
 - (a) is para-directing
 - (b) is *meta*-directing
 - (c) activates the ring by hyperconjugation
 - (d) deactivates the ring
- 33. A new carbon–carbon bond formation is possible in (1998)
 (a) Cannizzaro's reaction (b) Friedel-Craft's alkylation
 (c) Clemmensen reduction (d) Reimer-Tiemann reaction

True or False

- 34. An electron donating substituent in benzene orients the incoming electrophilic group to the *meta*-position. (1987, 1M)
- **35.** In benzene, carbon uses all the three *p*-orbitals for

(1987, 1M)

Subjective Questions

hybridisation.

36. Explain the followings :





- (2005)
- **37.** 7-bromo-1, 3, 5-cycloheptatriene exists as ionic species in aqueous solution while 5-bromo-1,3-cyclopentadiene doesn't ionise even in presence of $Ag^+(aq)$. Explain. (2004)
- **38.** What would be the major product in the following reaction? (2000, Main, 1M)



- **39.** Give reasons for the following :
 - (i) *tert*-butylbenzene does not give benzoic acid on treatment with acidic KMnO₄.
 - (ii) Normally, benzene gives electrophilic substitution reaction rather than electrophilic addition reaction although it has double bond. (2000)
- 40. Show the steps to carry out the following transformations.
 (i) Ethylbenzene → benzene
 - (ii) Ethylbenzene \rightarrow 2-phenylpropionic acid
- **41.** Write the structures of the products.

$$CH_3CONHC_6H_5 \xrightarrow{Br_2/Fe}$$
 (1998, 2M)

- **42.** Give reasons for the following in one or two sentences "Nitrobenzene does not undergo Friedel-Craft's alkylation." (1998, 2M)
- **43.** Complete the following, giving the structures of the principal organic products. (1997)



- **44.** Toluene reacts with bromine in the presence of the light to give benzyl bromide, while in presence of FeBr_3 it gives *p*-bromotoluene. Give explanation for the above observation. (1996)
- **45.** Predict the structures of the intermediates/products in the following reaction sequences (1996)



46. Predict the major product in the following reactions (1994)



47. Give reason for the following 'In acylium ion the structure $R - C \equiv O^+$ is more stable than $R - C^+ = O'$ (1994, 1M)

48. Identify the major product in the following reactions :

(i)
$$\langle \bigcirc -\text{COO} \rightarrow & \xrightarrow{\text{HNO}_3/\text{H}_2\text{SO}_4} \\ \hline \text{mononitration} \\ (ii) C_6\text{H}_5\text{COOH} + \text{CH}_3\text{MgI} \rightarrow ? + ?$$
 (1993, 2M)

49. Write the structure of the major organic product expected from the following reaction

$$(1992, 1M)$$

50. Give reasons in two or three sentences only for the following: Phenyl group is known to exert negative inductive effect, but each phenyl ring in biphenyl $(C_6H_5--C_6H_5)$ is more reactive than benzene towards electrophilic substitution.

(1992, 1M)

51. Arrange the following in increasing order of reactivity towards sulphonation with fuming sulphuric acid. Benzene, toluene, methoxy benzene, chlorobenzene.

(1988, 1M)

52. Answer the following with suitable equation wherever necessary

(i) How can you prepare benzene from lime?

- (ii) How will you convert toluene to *m*-nitrobenzoic acid ? (1987, 2M)
- **53.** Write down the main product of the following reaction

Benzene
$$\xrightarrow{\text{CH}_3\text{CH}_2\text{COCl/AlCl}_3}$$
 (1985, 1M)

- 54. How many sigma and pi-bonds are present in a benzene molecule ? (1985, 1M)
- **55.** Write down the reaction involved in the preparation of following using the reagents indicated against in parenthesis. "Ethyl benzene from benzene."

$$[C_2H_5OH, PCl_5, anhyd. AlCl_3]$$
 (1984, 2M)

- **56.** Show with balanced equation what happens when the '*p*-xylene is reacted with concentrated sulphuric acid and the resultant product is fused with KOH'. (1984, 1M)
- **57.** Give reasons for the following in one or two sentences : 'Although benzene is highly unsaturated, normally it does not undergo addition reaction.' (1983, 1M)

Integer Type Questions

58. Among the following, the number of aromatic compound(s) is



Answers

1.	(c)	2. (a)	3. (c)	4. (a)	21. (a)	22. (d)	23. (d)	24. (a)
5.	(a)	6. (c)	7. (a)	8. (d)	25. (c)	26. (a,b,d)	27. (b,c,d)	28. (b)
9.	(b)	10. (b)	11. (d)	12. (c)	29. (b,c)	30. (b,c,d)	31. (b,c,d)	32. (a,c)
13.	(d)	14. (c)	15. (d)	16. (b)	33. (b,d)	34. False	35. False	54. (12σ, 3π)
17.	(c)	18. (b)	19. (c)	20. (d)	58. (5)			

Hints & Solutions

1. The given reaction takes place as follows :



2. Key Idea In electrophilic aromatic substitution (Ar $S_E 2$) reaction, the aromatic (benzene nucleus here) compound (substrate) acts as a nucleophile which gets attacked by an electrophile in the rate determining step (rds).

Higher electron density on the nucleophile, i.e. benzene nucleus will fasten the rate of the reaction. Electron-donating groups (EDG) will increase electron density in benzene nucleus by any or both of their +R/+M and hyperconjugative (HPC) effects. Now, let us consider the given substrate.



As -R effect is more powerful than -I effect, the order of their reactivity, towards an electrophile will be

$$\begin{array}{cccc} ||| & | & || \\ (-R) & < & (-l > +R) & < & (+ \ HPC) \end{array}$$

3. Reactivity of substitution nucleophilic unimolecular $(S_N l)$ reaction depends on the formation of carbocation. Greater the stability of carbocation, greater will be its ease of formation of alkyl halide and faster will be the rate of reaction. So, the correct order of $(S_N l)$ reactivity is



In compound *C*, the carbocation formed is stabilised by activating group ($-OCH_3$). Compound *D* forms benzyl carbocation ($C_6H_5 - CH_2^+$) that is stabilised by resonance. Compound *A* produces a primary carbocation that further rearranges itself to secondary carbocation.



Compound B produces primary carbocation which is least stable among all the given options.

4. The major product of the given reaction is benzoic acid (C_6H_5COOH). On vigorous oxidation of alkyl benzene with acidic or alkaline KMnO₄, aromatic acids are obtained. During oxidation of alkyl benzene, the aromatic nucleus remains intact and the entire chain is oxidised to —COOH group irrespective of the length of carbon chain.



5. In presence of alc. KOH, the given halide undergoes elimination reaction



The alkene produced undergoes polymerisation *via* free radical mechanism. This process involve three steps, i.e. initiation, propagation and termination.



6. Aromatic electrophilic substitution reactions are fast in those compounds in which the attacking site possess high electron density. Electron withdrawing groups (EWGs) reduces the electron density in the benzene ring due to its strong -I effect and makes further substitution difficult. Hence, called as deactivating groups. While electron releasing groups (ERGs) increases the electron density in the benzene ring for the attack by an electrophile. Hence, called as activating groups.

In given options, Activating groups are $-CH_3 < -OCH_3$ (+*I*, +*R*) Strong +*R* effect



7. Through aromatic electrophilic substitution mechanism (ArS_E2) when mono-alkylation (Friedel-Craft's reaction) is performed, we get mono-alkylated benzene. As, the alkyl group is ring activating (towards ArS_E2) in nature, again *o*- and *p*-substituted alkyl benzene will be obtained and so on. e.g.



So, considering the second reaction condition, Cl^- , H_2O , Δ in the statement of the question, the correct answer is option (d).

9. Melting point of a compound depends on size and force of attraction between the molecules. Compound (c) has largest size and also possess weak intermolecular association due to dipole - dipole interactions.

Compound (a) is a dicarboxylic acid and possess high melting point due to intermolecular hydrogen bonding.

As a result, it exist as associated molecule. Compound (d) is an alcohol and possess intermolecular H-bonding. No interactions are present in hydrocarbon (naphthalene) compound (b).

Hence, melting point is lowest for naphthalene ($\simeq 80^{\circ}$ C), i.e. compound (b).

10. Aromaticity of a compound can be decided by Huckel's rule. In cyclopentadienyl cation (b), resonance takes place as follows:



Hence, kis anti-aromatic does not follow

Huckel's rule as it has conjugated 4π -electron $(4n\pi, n = 1)$ system. Rest of the species are aromatic as each of them belongs to 6π -electron $[(4n + 2)\pi, n = 1]$ system.



- 12. PLAN This problem can be solved by using the various concepts synthesis of benzene, electrophilic substitution reaction and directive influence of various substituents, including oxidation and reduction.
 - \Rightarrow —OH and —NH₂ are *o/p*-directing groups.
 - \Rightarrow N-acetylation is more favourable than C-acylation.
 - \Rightarrow N-sulphonation is more favourable than C-sulphonation.
 - \Rightarrow NO₂ is a meta-directing group.
 - \Rightarrow H₂S·NH₃ reduces only one NO₂ group selectively in the presence of two NO₂ groups.

Using above concepts the correct sequence of reaction can be written as





Above reaction proceeds through oxidation, chlorination and amide formation sequentially.

 $\therefore A \rightarrow r, B \rightarrow s, C \rightarrow q, D \rightarrow p$ Hence, the correct choice is (c).

13. Draw the structure of organic compounds indicating net dipole moment which includes lone pair and bond angle also.



- OH is activating while - COOH is deactivating group in S_EAr reaction. Therefore, electrophile attack to *ortho* of the activating - OH group.



Both $-OCH_3$ and $-CH_3$ are activating *ortho/para* directing groups but $-OCH_3$ is stronger activator, electrophile attack to *ortho* of $-OCH_3$.



Ring II is activated while ring I is deactivated in S_EAr reaction. Therefore, electrophile attack at para to ring-II, the less hindered position.

15.
$$\bigcirc$$
 OCH₃ + HBr \longrightarrow CH₃Br + \bigcirc OH

—OH of phenol is not further substituted by bromide due to resonance with the ring.

16. Ring attached to nitrogen is activated while ring attached to C=O is deactivated. Also, electrophilic substitution occur predominantly at *para* position of the activated ring due to immense steric hindrance at *ortho* position.





18. Ring attached to nitrogen is activated by electron donating resonance effect while ring attached to carbonyl group is deactivated by electron withdrawing resonance effect :



19. Both chloro and nitro groups are deactivating in electrophilic aromatic substitution reaction. Also nitro group is stronger deactivating group. Methyl group is activator in electrophilic aromatic substitution.

Hence, overall order of reactivity is :

nitrobenzene < chlorobenzene < benzene < toluene



- **21.** SO₂Cl₂ brings about free-radical chlorination at —CH₃ group.
- **22.** Free radical chlorination occur at —CH₃.



23. The methyl group in toluene is *ortho/para* directing activating group :



- **24.** Toluene is most reactive among these. Nitro and carboxylic groups are deactivating in aromatic electrophilic substitution reaction.
- **25.** Toluene is most readily sulphonated among these because methyl group is electron donating (+ I effect), activate benzene ring for electrophilic aromatic substitution.
- **26.** Reaction shown in option (a) is aldol condensation in the presence of conc. H_2SO_4 at high temperature. In summerised way the formation of mesitylene through this can be visualised as



Reaction given in option (b) is simple polymerisation (trimerisation) reaction of alkyne i.e.,

Me \longrightarrow H or CH₃ \longrightarrow C \cong CH when passed through heated iron tube at 873K then mesitylene is formed as



This reaction is also called aromatisation.

(1) and (2) reactions of option (c) combined to give haloform reaction while (3) reaction given in this option is decarboxylation reaction i.e.,



The above product of haloform reaction on decarboxylation gives benzene as



The reaction given in option (d) is Clemmensen reduction i.e.,

$$C = 0 \xrightarrow{Zn-Hg} CH_2 + H_2C$$

Hence, the final product of this reaction is also mesitylene which can be seen as



27. (a)

- Br $\xrightarrow{\text{NaOC}_2\text{H}_5}$

 $C_2H_5O^-$ (a strong nucleophile) causes E1 reaction to form isobutene as the major product.



28.



Cumene hydroperoxide formed above is an intermediate in the synthesis of phenol.

29. According to Huckel rule, the compounds which have 4n (n = 0, 1, 2, 3...) delocalised π -electrons in a close-loop are anti-aromatic and characteristically unstable. Compound *B* satisfy the criteria of anti-aromaticity as :



Compound C is anti-aromatic in its resonance form :



- alastrong which are also delocalized

Compound A has 4π -electrons which are also delocalised but do not constitute close loop, hence non-aromatic.

Compound D is aromatic, characteristically stable.



Tropyllium ion, aromatic

Order of stability Aromatic > Non-aromatic > Anti-aromatic

30. Aromatic molecule must.

(d) be cyclic.

(b) have $(4n + 2)\pi$ electrons. (c) be planar.

31. A compound is considered to be aromatic, if it follows three rules:

(a) Must be cyclic and planar.

(b) Must have conjugated system in it.

(c) It must follow Huckel rule which states that number of π -electrons = (4n + 2)

(A)
$$\Rightarrow 2\pi \cdot e^{-}$$
 system [$(4n+2)\pi, n=0$] \Rightarrow Aromatic

B)
$$4\pi - e^{-}$$
 system $[4n\pi, n = 1] \Rightarrow$ Anti-aromatic

(C)
$$(1) = 8\pi \cdot e^{-1}$$
 system $[4n\pi, n=2] \Rightarrow$ Anti-aromatic

(D) \implies The sp^3 -carbon does not support conjugation and also devoids planarity. \Rightarrow Non-aromatic



-CH₃ in toluene is *para* directing group. It activates the ring by both inductive and hyperconjugation effect.

33. In both Friedel-Craft's reaction and Reimer-Tiemann reaction, new carbon-carbon bond is formed :



reaction

- 34. An electron donating substituent in benzene orient ortho/para substitution.
- **35.** In benzene, carbons are sp^2 -hybridised only, hence only two *p*-orbitals are involved in hybridisation.





Nitro group from para position activate aromatic nucleophilic substitution.



-NO2 is not in resonance with benzene ring, does not activate the aromatic nucleophilic substitution reaction, hence fluoride is not formed.



Hence, -NO is ortho/para directing although deactivating group. Therefore, ortho/para nitro derivatives are formed on treatment with mixed acid.



Nitro group is meta directing as well as strongly deactivating.



In the above hydrogenation reaction, the anti-aromatic character of three cyclobutadiene rings are relieved that provide stability to the hydrogenation product.

7-bromo-1,3,5-cycloheptatriene

Tropylium ion (aromatic, stable)



5-bromo-1,3-cyclopentadiene





39. (i) Oxidation of side-chain alkyl group of benzene occur through free radical mechanism and it initiates at α –C as.

$$Ph - C - H \longrightarrow Ph - C^{\bullet} + H^{\bullet}$$

In tertiary butyl benzene, there is no α -H, required to initiate free radical oxidation reaction, hence not oxidised with KMnO₄.

$$\begin{array}{c} CH_{3} \\ C-CH_{3} \\ CH_{3} + KMnO_{4} \longrightarrow No \text{ oxidation} \\ takes place \\ tert \text{ butyl benzene} \\ (no \alpha-H) \end{array}$$

(ii) Pi-electrons of double bonds are involved in aromatic delocalisation (aromaticity), hence electrophilic addition do not occur as it would destroy aromatic stability. However, electrophilic substitution do not destroy aromaticity.



NHCOCH₃ is *ortho/para* directing although deactivating group. Therefore, *Ortho/pare* bromoderivatives are fomed or treatment.

42. Nitro group is a very strong deactivating group, the very slow Friedel-Craft's reaction does not takes place in presence of nitro group.



44. In presence of light, free radical reaction takes place at $-CH_3$ group while in presence of FeBr₃, electrophilic substitution occur in the ring.



47. R - C = O K - C = O

I is more stable resonance structure of acylium ion than II on the following grounds.

It has more covalent bonds.

It has complete octet of both carbon and oxygen.



The above resonance activate an aromatic ring for electrophilic substitution reaction.

51. Both — CH₃ and — OCH₃ are activating groups but chloro is deactivating group in electrophilic aromatic substitution reaction.

Also $-OCH_3$ activate more than $-CH_3$ due to resonance effect by the former group. Therefore, the overall order of reactivity is:

Chlorobenzene < benzene < toluene < methoxy benzene

52. (i) Lime is heated with coke at high temperature and then, hydrolysed to form acetylene. This acetylene on passing red hot tube polymerises to form benzene :

$$\begin{array}{ccc} \text{CaO} &+ & 3\text{C} & \xrightarrow{2000^{\circ}\text{C}} & \text{CaC}_2 + & \text{CO} \uparrow \\ \text{Lime} & & \text{Coke} & \end{array}$$

$$CaC_{2} + 2H_{2}O \longrightarrow Ca(OH)_{2} + C_{2}H_{2}$$
Acetylene
$$3C_{2}H_{2} \xrightarrow{Cu} C_{6}H_{6}$$
Benzene

(ii) —CH₃ in toluene is *ortho/para* directing group, first oxidised to —COOH in order to make it *meta* directing and then nitrated.



- **57.** Pi-bonds of benzene are involved in aromaticity, not open for electrophilic addition reaction. Rather, it undergo electrophilic substitution reaction.
- **58.** The aromatic systems are

