Practice Problems

In the Kolbe-Schmidt reaction, sodium phenoxide when treated with CO_2 under pressure at 125°C, followed by acidification gives: a) p-hydroxybenzoic acid b) salicylic acid c) benzoic acid d) o-hydroxybenzoic acid

The major product formed when benzene diazonium chloride reacts with hypophosphorous acid (H_3PO_2) is: a) chlorobenzene b) benzene c) phenol d) diphenyl

In Sandmeyer's reaction, when CuCl is replaced by Cu powder, the reaction is known as: a) Gattermann reaction b) Balz-Schiemann reaction c) Gomberg reaction d) None of these

The major product in the following reaction: $CH_3CH=CH_2$ + HBr (peroxide) → a) $CH_3CHBrCH_3$ b) $CH_3CH_2CH_2Br$ c) $CH_3CHBrCH_2Br$ d) $CH_2BrCH=CH_2$

The Reformatsky reaction is used to prepare: a) β-hydroxy esters b) α-hydroxy acids c) β-hydroxy acids d) α-hydroxy esters

Which intermediate is NOT involved in Wolf-Kishner reduction? a) hydrazone b) carbinolamine c) imine d) diimide

The reagent used in Clemmensen reduction is: a) Zn/HCl b) Zn-Hg/HCl c) Na-Hg/H_2O d) $LiAlH_4$

The correct order of reactivity in Friedel-Crafts alkylation is: a) primary > secondary > tertiary b) tertiary > secondary > primary c) secondary > primary > tertiary d) primary > tertiary > secondary

In the Reimer-Tiemann reaction, the electrophile is: a) $:CCl_2$ b) :CHCl c) $CHCl_3$ d) CCl_4

Which catalyst is used in Stephen's reduction? a) $SnCl_2$/HCl b) $LiAlH_4$ c) Na/Hg d) $NaBH_4$

The Hofmann bromamide reaction proceeds through: a) nitrene intermediate b) carbene intermediate c) carbocation intermediate d) free radical intermediate

In Gabriel phthalimide synthesis, the protecting group is removed by: a) hydrazine hydrate b) NH_3 c) NaOH d) HCl

Wurtz reaction fails to give pure product when: a) starting alkyl halides are same b) starting alkyl halides are different c) alkyl halides are primary d) alkyl halides are secondary

The Hunsdiecker reaction converts: a) carboxylic acids to alkyl halides b) silver salts of carboxylic acids to alkyl halides c) alcohols to alkyl halides d) aldehydes to alkyl halides

In the HVZ reaction (Hell-Volhard-Zelinsky), the halogenating agent is: a) Cl_2/red P b) Br_2/red P c) PCl_5 d) $SOCl_2$

SOLUTIONS TO THE ABOVE QUESTIONS:

1. Answer: (b) salicylic acid Explanation: Kolbe-Schmidt reaction involves carboxylation of sodium phenoxide under pressure. CO_2 attacks the ortho position specifically due to the directing effect of ONa group, followed by acidification to give salicylic acid (o-hydroxybenzoic acid).
2. Answer: (b) benzene Explanation: Hypophosphorous acid (H_3PO_2) acts as a reducing agent in diazonium salt reactions. It reduces the diazonium group ($-N_2^+$) to H, forming benzene. This is a key example of removal of the diazo group.
3. Answer: (a) Gattermann reaction Explanation: When copper powder is used instead of CuCl in the Sandmeyer reaction, it's called the Gattermann reaction. Both reactions convert $ArN_2^+Cl^-$ to ArCl, but Gattermann reaction uses cheaper Cu instead of CuCl.
4. Answer: (b) $CH_3CH_2CH_2Br$ Explanation: This is an anti-Markovnikov addition due to the peroxide effect (Kharasch effect). The reaction proceeds via free radical mechanism, giving the primary bromide as the major product.
5. Answer: (a) β-hydroxy esters Explanation: Reformatsky reaction involves zinc-mediated addition of α-halo esters to carbonyls, forming β-hydroxy esters. It's similar to Grignard reaction but specific for esters.
6. Answer: (d) diimide Explanation: Wolf-Kishner reduction proceeds through hydrazone and carbinolamine intermediates. The imine is formed temporarily, but diimide is not involved in this mechanism.
7. Answer: (b) Zn-Hg/HCl Explanation: Clemmensen reduction uses zinc amalgam (Zn-Hg) and concentrated HCl to reduce carbonyls to methylenes (CH_2). It works best for aromatic ketones.
8. Answer: (b) tertiary > secondary > primary Explanation: In Friedel-Crafts alkylation, carbocation stability determines reactivity. Tertiary carbocations are most stable, hence most reactive.
9. Answer: (a) $:CCl_2$ Explanation: Reimer-Tiemann reaction involves dichlorocarbene ($:CCl_2$) as the reactive species, generated from chloroform in basic conditions.
10. Answer: (a) $SnCl_2$/HCl Explanation: Stephen's reduction uses $SnCl_2$/HCl to convert nitriles to aldehydes. It's a selective reduction that stops at the aldehyde stage.
11. Answer: (a) nitrene intermediate Explanation: Hofmann bromamide degradation proceeds through a nitrene intermediate after base-induced rearrangement, leading to a primary amine with one carbon less.
12. Answer: (a) hydrazine hydrate Explanation: In Gabriel synthesis, hydrazine hydrate ($NH_2NH_2 \cdot H_2O$) cleaves the phthalimide group, releasing the primary amine product.
13. Answer: (b) starting alkyl halides are different Explanation: With different alkyl halides, Wurtz reaction gives a mixture of products (R-R, R'-R', and R-R'), making isolation of pure product difficult.
14. Answer: (b) silver salts of carboxylic acids to alkyl halides Explanation: Hunsdiecker reaction decarboxylates silver carboxylates using bromine to form alkyl bromides with one carbon less.

15. Answer: (b) Br_2/red P Explanation: HVZ reaction uses Br_2/red P to α-halogenate carboxylic acids. Red P acts as a catalyst and carrier for bromine.

JEE Advanced 2018:

1. The product formed when cyclopentanone reacts with I_2/NaOH is: a) $HCO_2Na + CHI_3$ b) Only CHI_3 c) No reaction d) Ring opening doesn't occur Answer: (a) Explanation: Cyclopentanone undergoes oxidative cleavage due to lack of α-methyl group.
2. Benzene on monochlorination gives 'A' which on treatment with sodium amide yields 'B'. 'B' on acid hydrolysis produces 'C'. Identify C: a) Phenol b) Aniline c) Chlorobenzene d) Benzamide Answer: (b) Explanation: Sequence is: $C_6H_6 \rightarrow C_6H_5Cl \rightarrow C_6H_5NH_2$ (Hoffmann amination)

JEE Main 2019: 3. In Friedel-Crafts acylation of anisole with acetyl chloride and $AlCl_3$, the major product is: a) o-methoxyacetophenone b) p-methoxyacetophenone c) m-methoxyacetophenone d) mixture of o- and p-products in equal amounts Answer: (b) Explanation: $-OCH_3$ directs para due to less steric hindrance.

JEE Advanced 2017: 4. The major product in: Propene → HBr/peroxide → KOH/ethanol → X is: a) Propene b) Propan-1-ol c) Propan-2-ol d) Propane Answer: (a) Explanation: Anti-Markovnikov addition followed by E2 elimination.

JEE Main 2016: 5. Which compounds give positive iodoform test? a) Only acetone b) Acetone and 2-pentanone c) All ketones d) Only aldehydes Answer: (b) Explanation: Compounds with CH_3CO- group give positive test.

JEE Advanced 2016: 6. Major product in: $PhCH_2CH_2Br + KCN \rightarrow ?$ a) $PhCH_2CH_2CN$ b) $PhCH=CHCN$ c) PhCN d) $Ph-CH(CN)-CH_3$ Answer: (a) Explanation: SN2 substitution at primary carbon.

JEE Main 2015: 7. Identify A: $C_6H_5NH_2 \rightarrow C_6H_5N_2Cl \rightarrow A$ a) C_6H_5Cl b) C_6H_5F c) C_6H_5OH d) C_6H_5CN Answer: (b) Explanation: Balz-Schiemann reaction gives fluorobenzene.

JEE Advanced 2015: 8. Product when benzaldehyde reacts with concentrated KOH: a) Only benzyl alcohol b) Only potassium benzoate c) Benzyl alcohol + Potassium benzoate d) Benzene Answer: (c) Explanation: Cannizzaro reaction gives alcohol and salt.

JEE Main 2014: 9. Reagent to convert acid chlorides to aldehydes: a) $LiAlH_4$ b) $Pd/BaSO_4 + H_2$ c) Na/ethanol d) Zn-Hg/HCl Answer: (b) Explanation: Rosenmund reduction is selective.

JEE Advanced 2014: 10. Product of: $CH_3COCH_2COOC_2H_5 + NaOH + I_2 \rightarrow$ a) Only CHI_3 b) Only CH_3COONa c) $CHI_3 + CH_3COONa + CO_2$ d) No reaction Answer: (c) Explanation: Both iodoform and ester hydrolysis occur.

JEE Main 2013: 11. Decreasing order of reactivity towards nucleophilic addition: a) $HCHO > CH_3CHO > PhCHO > CH_3COCH_3$ b) $CH_3COCH_3 > PhCHO > CH_3CHO > HCHO$ c) $PhCHO > HCHO > CH_3CHO > CH_3COCH_3$ d) $CH_3CHO > HCHO > CH_3COCH_3 > PhCHO$ Answer: (a) Explanation: Based on steric hindrance and electronic effects.

JEE Advanced 2013: 12. In: $PhCH_2Br \rightarrow PhCH_2MgBr \rightarrow PhCH_2CH_2OH$, second step uses: a) H_2O b) CH_2O c) CO_2 d) O_2 Answer: (b) Explanation: Grignard addition to formaldehyde.

JEE Main 2012: 13. Major product in Reimer-Tiemann reaction of phenol: a) p-hydroxybenzaldehyde b) m-hydroxybenzaldehyde c) o-hydroxybenzaldehyde d) mixture of all isomers Answer: (c) Explanation: Ortho-formylation is preferred.

JEE Advanced 2012: 14. Acetophenone with Zn(Hg)/HCl gives: a) Ethylbenzene b) Acetaldehyde c) Ethanol d) Benzyl alcohol Answer: (a) Explanation: Clemmensen reduction of ketone.

JEE Main 2011: 15. Best sequence for benzene → benzoic acid: a) $CH_3Cl/AlCl_3 \rightarrow KMnO_4/OH^-$ b) Direct oxidation c) $CO_2/AlCl_3$ d) $CH_3OH/AlCl_3$ Answer: (a) Explanation: Friedel-Crafts followed by oxidation.