SEMESTER-III (Hons)

CEMACOR07T: ORGANIC CHEMISTRY-III

Chemistry of alkenes and alkynes

1. What is NBS? What is the major bromination product in the following reaction?

CH_3-CH=CH-CH_3 + NBS $\longrightarrow$

2. What happens when ethyl chloride is treated with sodium metal?

3. Give evidence to show that chlorination of methane involves a free radical mechanism.

4. How will you synthesize propane from methane?

5. An alkane with molecular weight 72 formed only one substitution product. Suggest a structure for the alkane.

6. How are alkenes prepared? Describe their important reactions.

7. What happens when propene is treated with hydrogen bromide in the presence of peroxide?

8. What happens when propene is subjected to ozonolysis?

9. How will you distinguish between 1- hexene and n- hexane.

10. Write a note on Markovnikov rule.

11. Give the mechanism of addition of HBr to propene in the presence of peroxide.

12. Give the general mechanism of electrophlic addition reactions.

13. Write the structure of the alkene which on ozonolysis gives 2-butanone and 2-methylpropanal.

14. What happens when calcium carbide is treated with water?

15. Which one of the following alkanes cannot be synthesised by Wurtz reaction in good yield and why? How can this alkane be synthesizing using Corey-House synthesis?

$(CH_3)_2CHCH_2CH_2CH(CH_3)_2$, $CH_3CH_2-C(CH_3)_2-CH_2CH_3$.

16. Acetylene is less reactive towards bromine addition than ethylene. Explain

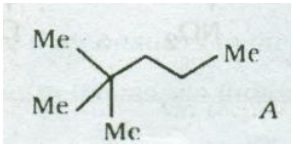
17. Treatment of Me_3C-CH = CH_2 and Me_3C-CHOH-CH_3 with cone. HCl gives two same isomeric chlorides. What are the two products? Explain.

19. Carry out the following conversion:

$CH_3-C\equiv CH \rightarrow CH_3CH_2CHO$

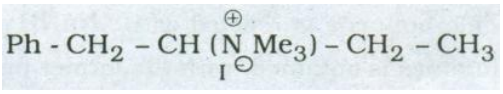
20. Free radical reaction between toluene and chlorine takes place at the side chain not at the nucleus. Explain.

21. Apply Corey-House met.hod to synthesize compound A using two suitable substrates having four carbon and three carbon respectively. Give argument for your choice.

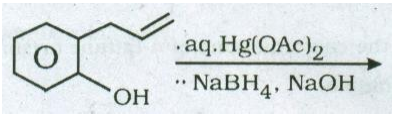


22. Show how many ozonides are expected to form when 2-pentene is reacted with ozone in the presence of formaldehyde.

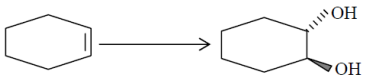
23. Among the halogen hydractds, only HBr is capable of showing peroxide effect when added to an unsymmetrical alkene. Justify.

24. What happens when?  is heated with moist Ag_2O ? Explain with the help of mechanism.

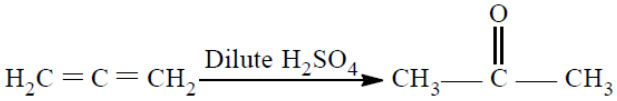
25. Predict the product(s) with mechanism indicating the major one and the stereochemistry wherever applicable:



26. Carry out the following conversion showing plausible mechanism:

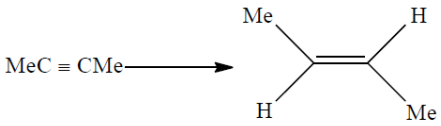


27. Give the mechanism of the following reaction:



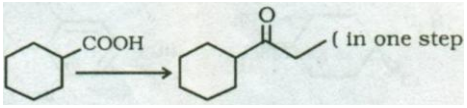
29. Two ozonides are formed when $Me_2C = CMe_2$ is treated with O_3 in CH_2Cl_2 as solvent in the presence of HCHO. Give the mechanism of formation of two ozonides.

30. Give the mechanism of the following reaction:

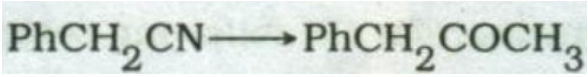


Carbonyl and Related Compounds

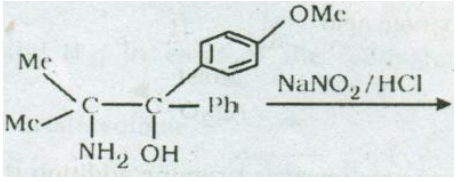
1. What happens when acetaldehyde is treated with dilute NaOH?
2. How will you distinguish between acetaldehyde and acetone?
3. Give the mechanism of nucleophilic addition reactions of carbonyl compounds.
4. How can you carry out the following transformation?



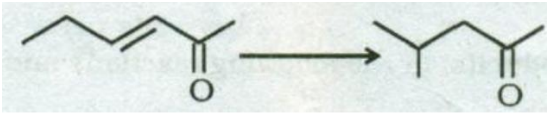
5. Discuss the mechanism of Cannizazaro reaction.
6. An alkene C_6H_{12}, after ozonolysis yielded two products one of these gave a positive iodoform reaction but negative Tollens' test. The other product gave a positive Tollens' test but negative iodoform reaction. What is the structure and IUPAC name of the alkene?
7. How can you carry out the following transformation?



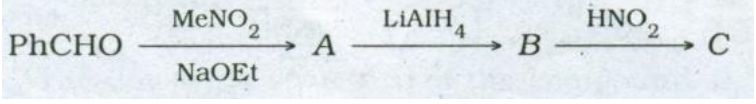
8. What happens when benzaldehyde is heated with acetic anhydride in the presence of sodium acetate ? Write the mechanism of the reaction and explain the formation of styrene as one of the products.
9. Complete the following reaction



10. Chloral reacts rapidly with ethanol to give hemiacetal. but gives acetal very slowly in presence of anhydrous acid. Explain.
11. How can you carry out the following transformation?

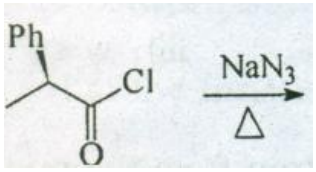


12. Identify the products *A* - C in the following sequence of transformations. Suggest a mechanism for the conversion of B to C.



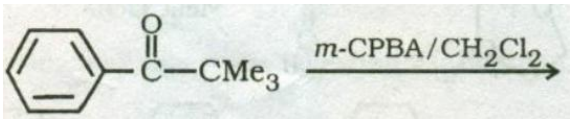
13. Chloral reacts rapidly with ethanol to give hemiacetal. but gives acetal very slowly in presence of anhydrous acid. Explain.

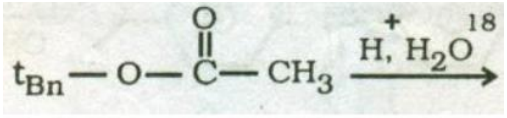
14.



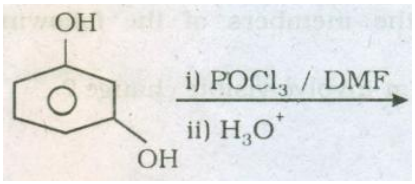
15. $CH_3CHO + HCHO \text{ (excess)} \xrightarrow{Ca(OH)_2} ?$

16. Predict the products of the following reactions and give mechanism:





17. Identify the product with plausible mechanism



18. In the Perkin reaction of PhCHO with Ac_2O and NaOAc, little styrene is obtained. – Explain

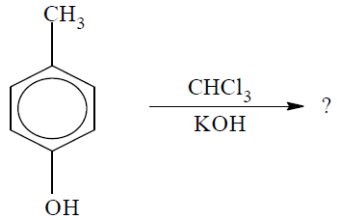
19. For the synthesis of Me-O-CMe_3 two plausible reaction routes are given below. Find out the favourable reaction route with explanation.

Route - I $CH_3 - Br + (CH_3)_3\,COK \longrightarrow$

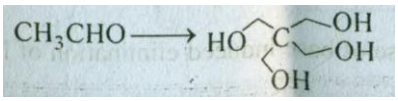
Route - II $(CH_3)_3\,C–Br + CH_3OK \longrightarrow$

20. 3-Hydroxybenzaldehyde undergoes Cannizzaro reaction; however 2-hydroxybenzaldehyde and 4-hydroxybenzaldehyde fail to react. Explain

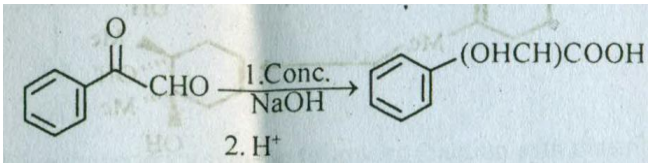
21.



22. Carry out the following conversion:



23. Give the mechanism of the following reaction:



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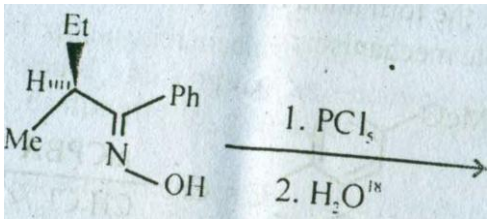

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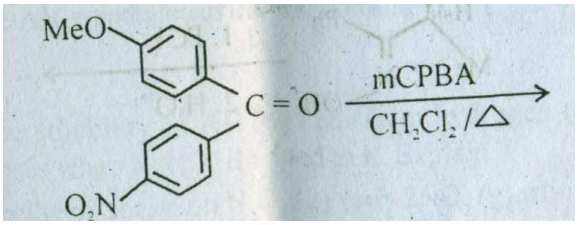
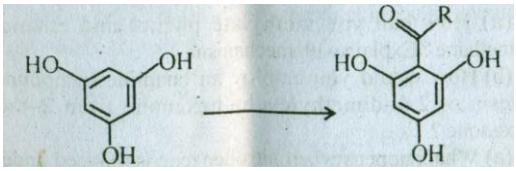
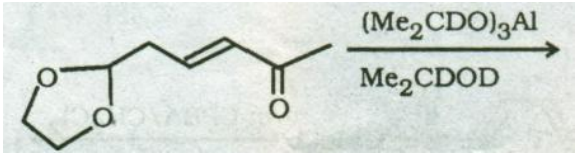


26. Carry out the following transformation with mechanism:



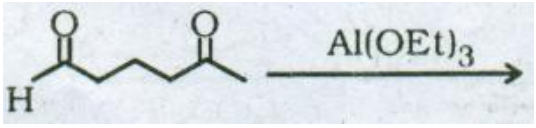
27. "Better yields are obtained if the Claisen condensation is carried out in ether with alcohol free sodium ethoxide catalyst instead of ethyl alcohol." Explain.

28. Indicate the product of the following reaction with plausible mechanisms.



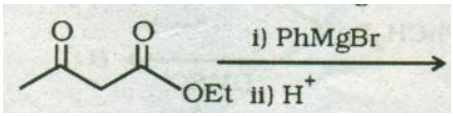
29. When the benzoin $Ar^1CHOHCOAr^2$ is heated with an aldehyde Ar^2CHO in the presence of KCN. a mixed benzoin $Ar^2CHOHCOAr^I$ is obtained. Explain.

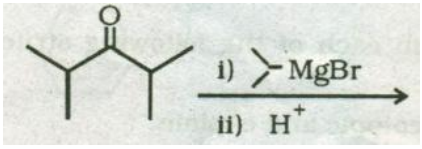
30. Predict the product(s) of the following reaction and give plausible mechanism.



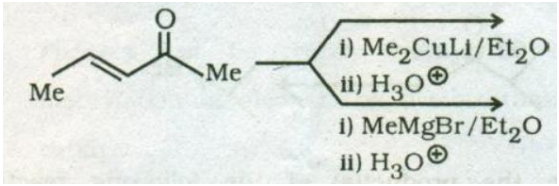
Aromatic Substitution & Organometallics

1. Predict the product(s) in the following reactions and suggest mechanisms for their formation.





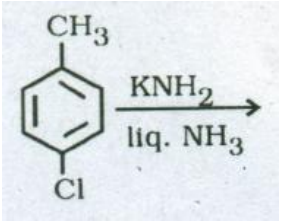
2. Identify the product/ products formed in the following reactions, indicating the major product. Offer explanation.



3. Both chlorobenzene and nitrobenzene undergo aromatic electrophilic substitution with deactivation. whereas chlorobenzene forms mainly ortho and para substituted products. Nitrobenzene produces mainly meta substituted product. Explain.

4. What is activated aromatic nucleophilic substitution reaction? Explain with an example.

5. Predict the product(s) of the following reaction with mechanism.



6. Which would you expect to be more reactive towards electrophilic substitution in the following pairs? Give reason for your answer.

$PhCF_3$ and PhF

$PhOCH_3$ and PhSMe

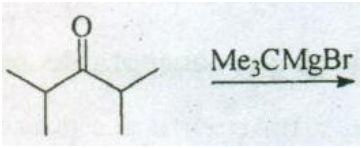
7. What happens when chlorobenzcnc is treated with sodamide in liquid NH_3? Write the product(s) of the reaction with mechanism and evidence.

8. What is ipso-substitution? Explain with an example.

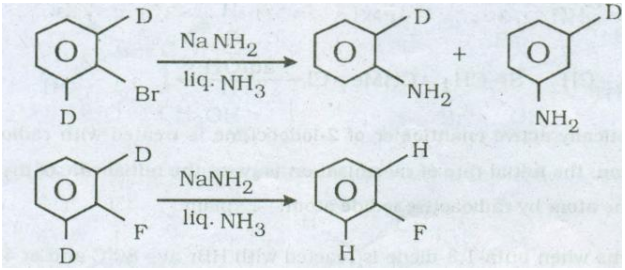
9. What is meant by σ and π complexes in aromatic electrophllic substitution? Draw an energy diagram showing them in a 'specific reaction with mechanism.

10. What happens when benzoic acid is separately treated with excess of methyl magnesium bromide and excess of methyl lithium?

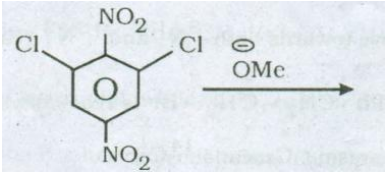
11. Predict the product(s) in the following reaction and suggest plausible mechanism:



12. Explain the observations as shown in the following reactions.

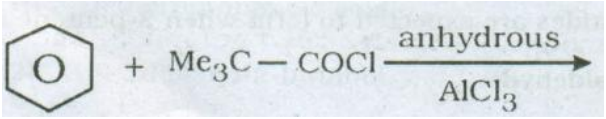


13. Predict the product(s) with plausible mechanism in the following reaction.

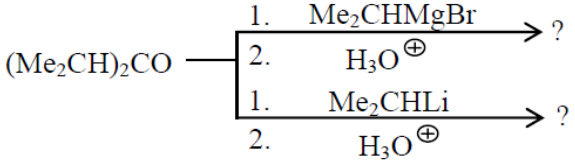


14. When p-chlorotoluene is reacted with $NaNH_2$ in liq. NH_3 at - 33°C, a mixture of rn-and p-toluidines is obtained, with the former predominating. Explain.

15.



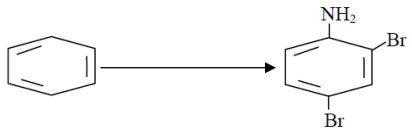
16. Complete the following reactions and justify the formation of product.



17. Explain the following observations.

Nitrobenzene undergoes chlorination with deactivation and shows meta orientation. Chlorobenzene undergoes nitration with deactivation and shows *O*/*P* orientation.

18. Carry out the following conversions



20. Give the mechanism of Friedel-Craft acylation of benzene with acid anhydrides. Explain why more than 2 equivalents of $AlCl_3$ are needed for this reaction.

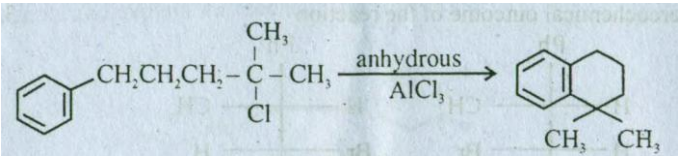
21. What happens when one equivalent of PhCH = CH - COPh in ether is separately treated with one equivalent of the following reagent followed by hydrolysis with acid? Explain the mechanism involved.

(i) EtMgBr in ether

(ii) EtLi in ether

(iii) Et_2CuLi in ether.

22. Write down the mechanism of the following reaction:



23. Compare reactivity of $PhNHCOCH_3$, aniline and benzene toward bromination reaction with proper justification. What is the major monosubstituted product formed during bromination of $PhNHCOCH_3$.

24. Pivaloyl chloride (Me_3CCOCl) reacts with benzene in presence of anhydrous $AlCl_3$ to give mainly tert-butylbenzene whereas anisole under same reaction condition gives mainly *p*-methoxypivalophenone - Explain.

25. Why Zn is a specific reagent for Reformatsky reaction?

26. How can you prepare the acid $R_3C–CO_2H$ from R_3COH?

27. Write down all the possible products from a mixed Claisen condensation with $CH_3CH_2CH_2COOCH_3$ and $PhCH_2COOCH_3$.

28. Account for the following observation:

The amination of both *O*-chloroanisole and *m*-chloroanisole yields only *m*-anisidine.

29. Predict the favoured position of aromatic electrophilic substitution of the following compounds and justify your answer in each case:

(i) Ph-CH=CH-CO_2H (ii) Ph-CO_2H

30. Predict the product giving proper mechanism.