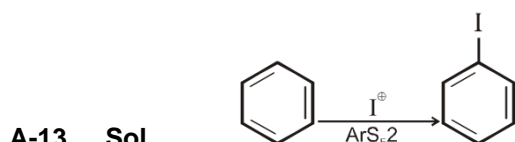
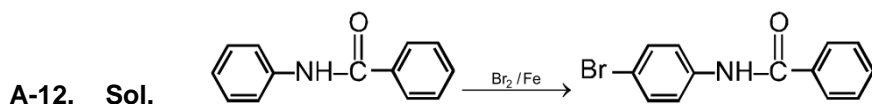


Exercise-1

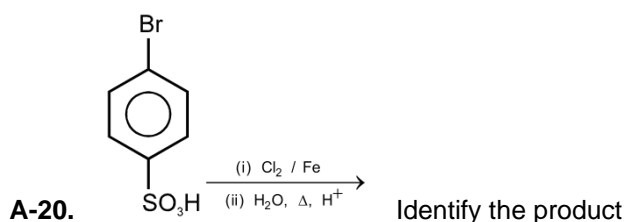
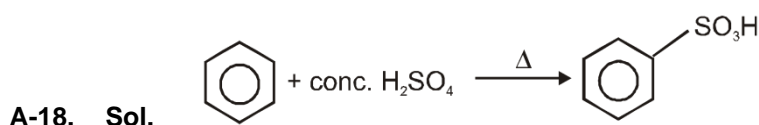
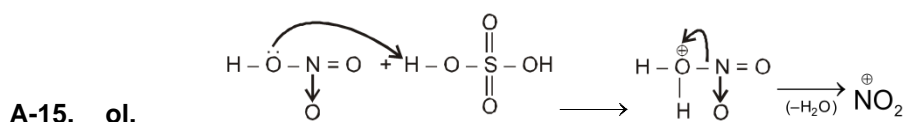
OBJECTIVE QUESTIONS

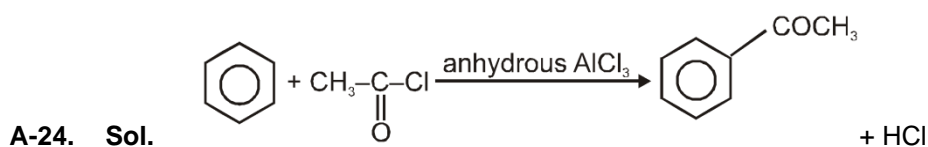
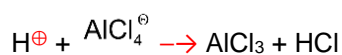
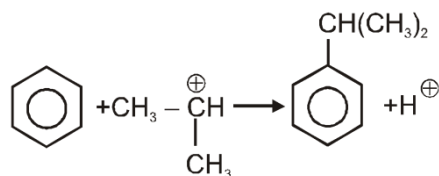
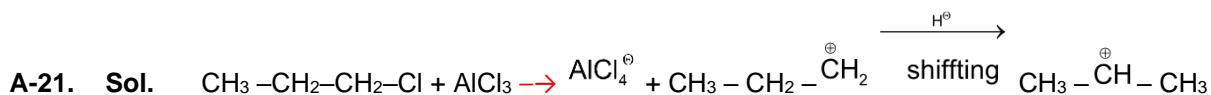
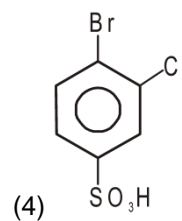
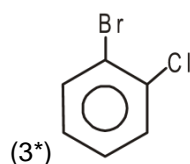
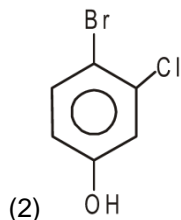
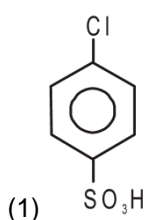
Section (A) : Preparation and chemical properties of benzene

- A-1. **Sol.** The characteristic reaction of benzene is electrophilic substitution.
- A-2. **Sol.** A deactivating group deactivates o-and p-more than m-position because m-position does not have conjugation with the group.
- A-7. **Sol.** Cinnanyl system is ortho-para directing group.
- A-8. **Sol.** As the number of Cl atom increases deactivation increases.
- A-9. **Sol.** $-\text{O}^-$ is strongest activators and o/p- director.
- A-11. **Sol.** Rate of electrophilic substitution reaction \propto Stability of arenium ion.

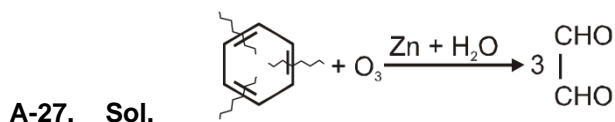


- A-14. **Sol.** The direct iodination of benzene is not possible because resulting $\text{C}_6\text{H}_5\text{I}$ is reduced to C_6H_6 by HI

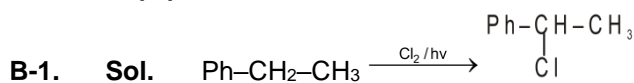




A-26. Sol. Lindane is another name of B.H.C

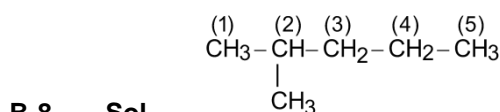
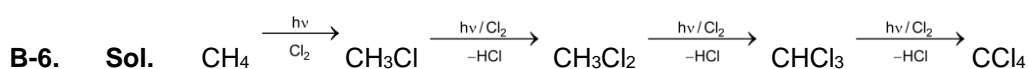


Section (B) : Alkanes

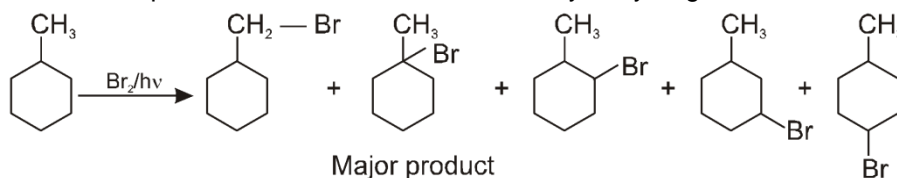


B-2. Sol. $3^\circ\text{H} > 2^\circ\text{H} > 1^\circ\text{H}$.

B-3. Sol. Halogenation of alkanes is an example of free radical substitution reaction



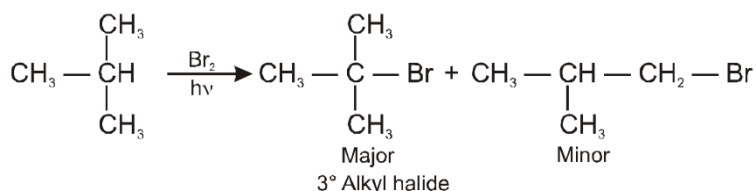
B-9. Sol. For photochemical bromination reactivity of hydrogen atom is $3^\circ\text{H} > 2^\circ\text{H} > 1^\circ\text{H}$.



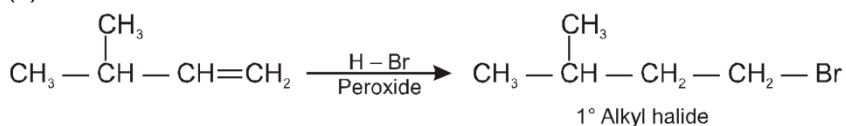
∴ Ans. is (3)

B-10. Sol. Iodination of an alkane is carried out in presence of HNO_3 or HIO_3

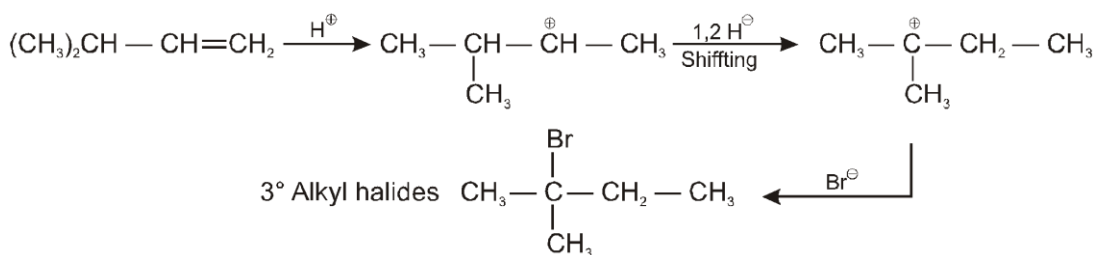
Section (C) : Free radical addition and substitution in alkenes/alkynes



C-1. Sol. (1)



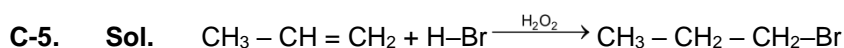
(2)



(3)

So, answer is (4)

C-4. Sol. Peroxide effect is observed only with HBr

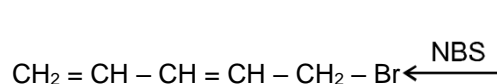
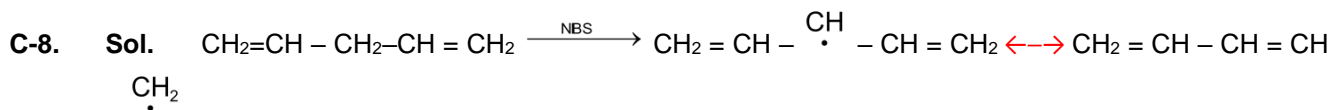


C-7. Sol. $\text{CH}_3 - \text{CH} = \text{CH}_2$

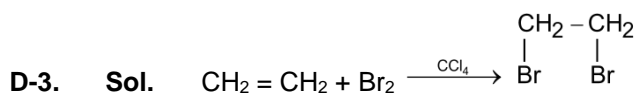


(1) Free radical site for Reaction

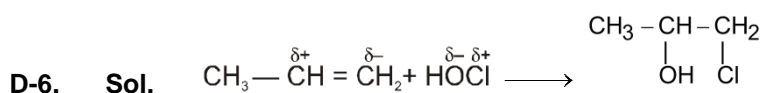
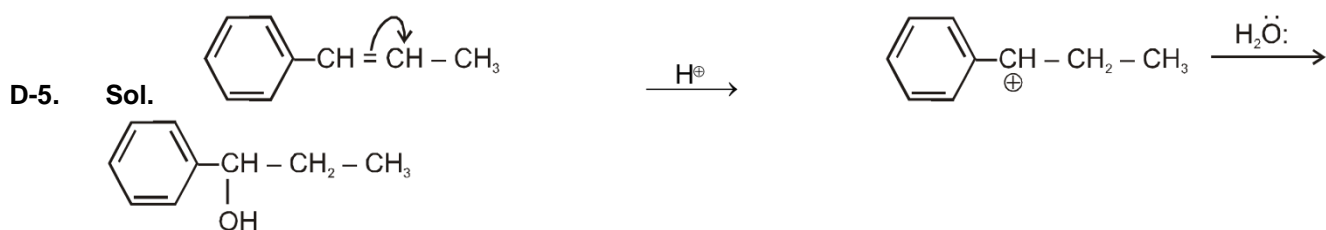
(2) Alkane like character



Section (D) : Alkene

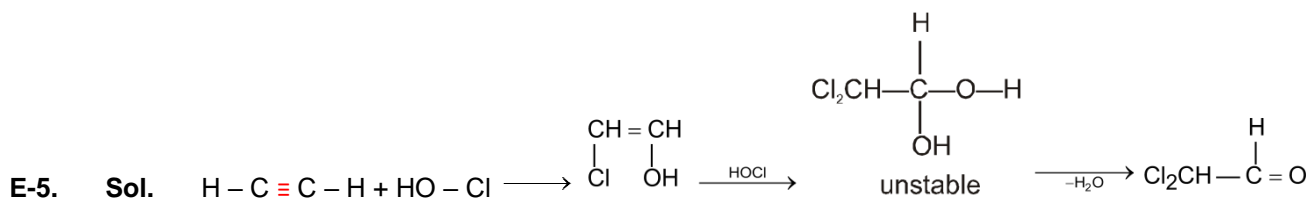
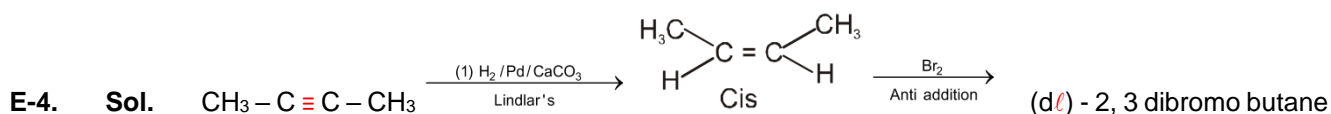


D-4. Sol. Bromination is anti addition.

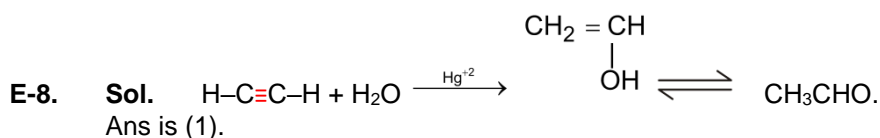
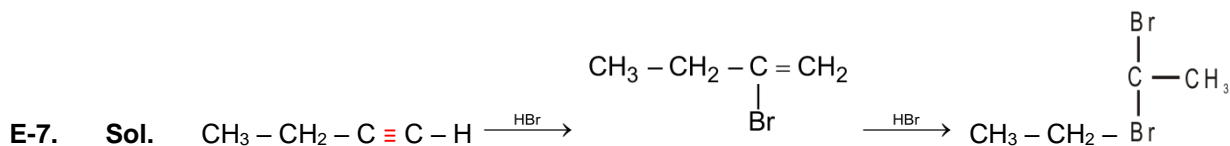


Section (E) : Alkyne

E-2. Sol. Most Acidic hydrogen is present in ethyne.



E-6. Sol. 1-Butyne can be converted into 1-bromo-1-butene by antimarkownikoff. Addition of H-Br in presence of peroxide.



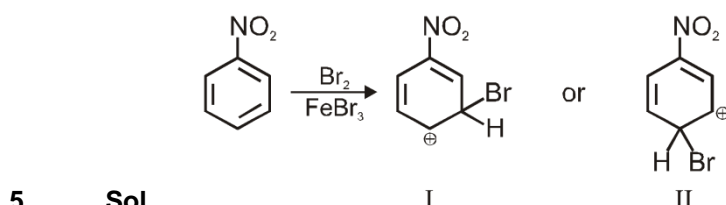
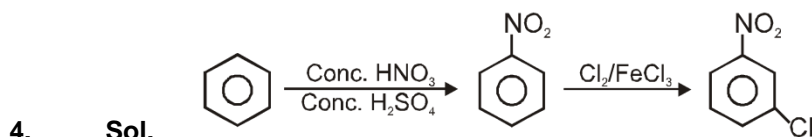
E-10. Sol. 1-butyne and 2-Butyne can be distinguish by ammonical silver nitrate solution.

Exercise-2

PART - I : OBJECTIVE QUESTIONS

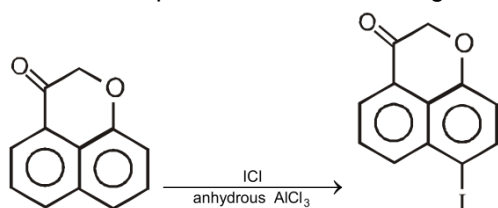
- Sol.** According to energy profile diagram.
- Sol.** Ar S_E2 reaction occurs in 5-membered ring. because 5 member ring has high electron density compare to 7 membered ring.

- Sol.** Rate of electrophilic substitution \propto Stability of arenium ion.

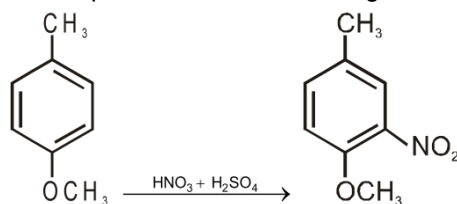


- Sol.** I II stability of intermediate I > II

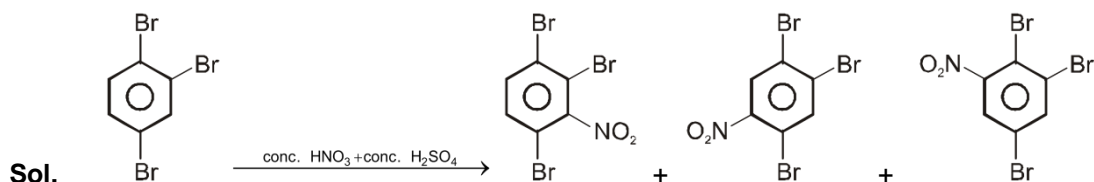
- Sol.** Electrophile attacks on that ring which has more +M effect.



- Sol.** Electrophile attacks on that ring which has more +M effect.



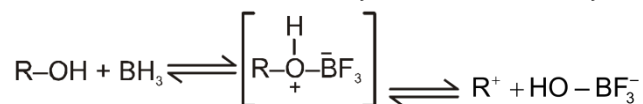
8._



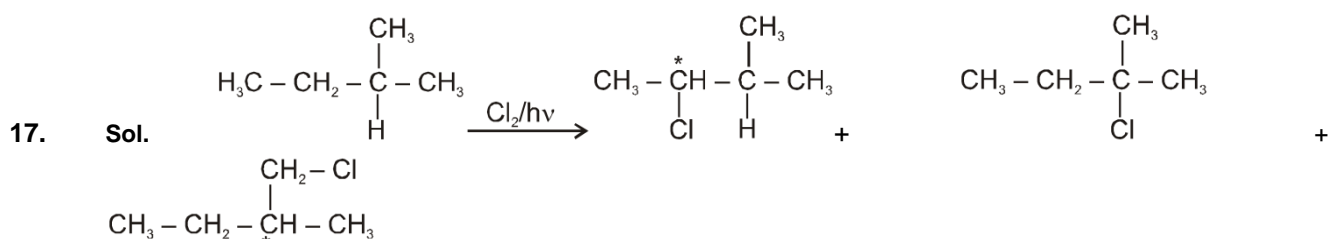
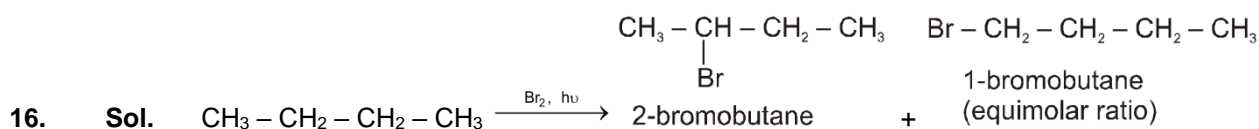
- Sol.** According to hyperconjugation effect.

- Sol.** Electrophile attacks on that ring which has more +M effect.

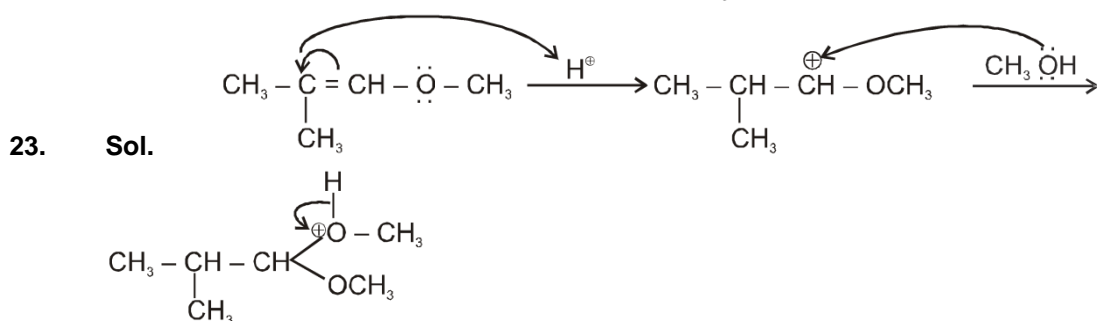
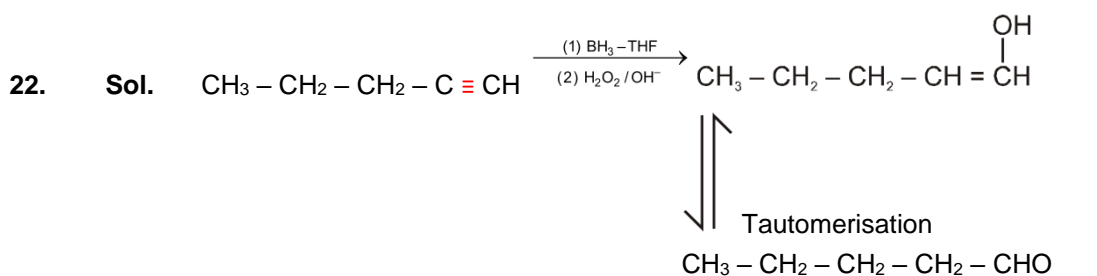
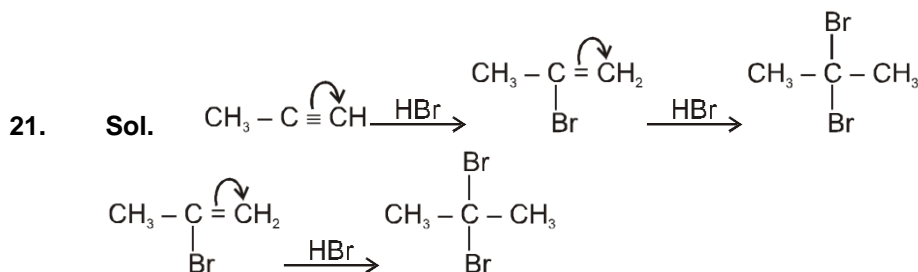
- Sol.** It is Friedel-Crafts alkylation reaction. Alkyl carbocation is formed alcohol as follow .



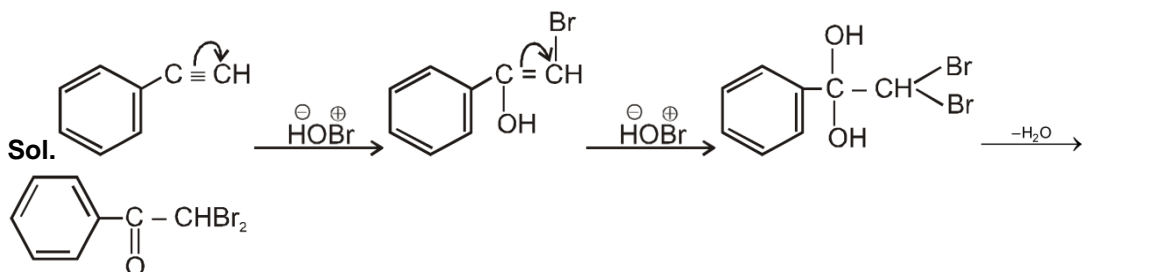
12. **Sol.** In vinyl chloride, lone pair of chlorine atom take part in resonance so partial double bond character introduce in C-Cl bond.
13. **Sol.** Aniline form salt with lewis acid and deactivates the benzene ring so Friedel Craft reaction doesnot take place.
14. **Sol.** Reactions (3) is free radical substitution reaction.



20. **Ans.** Cis + Antiaddition → Racemic mixture



24.



PART - II : MISCELLANEOUS QUESTIONS

Section (A) : ASSERTION/REASONING

A-1. Ans. 2

A-2. Ans. (2)

Sol. Self explanatory.

A-3. Ans. (3)

A-4. Ans. (2)

A-5. Ans. (2)

Sol. Isomerisation reaction of alkane.

A-6. Ans. (1)

A-7. Ans. (1)

A-8. Ans. (4)

Sol. Carbocation of But-2-ene is more stable than But-1-yne.

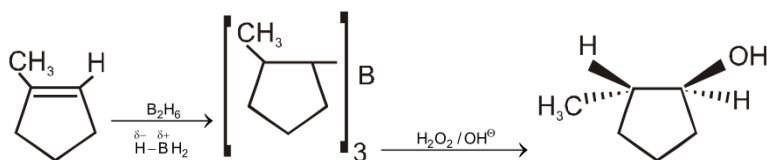
Section (B) : MATCH THE COLUMN

B-1. Ans. (P) \rightarrow c, (Q) \rightarrow b, (R) \rightarrow d, (S) \rightarrow aB-2. Ans. (P) \rightarrow c ; (Q) \rightarrow a ; (R) \rightarrow d ; (S) \rightarrow b

Section (C) : ONE OR MORE THAN ONE OPTIONS CORRECT

C-2.

Sol.



Stereospecific **syn** addition
Boron act as electrophile.

C-5.

Sol.

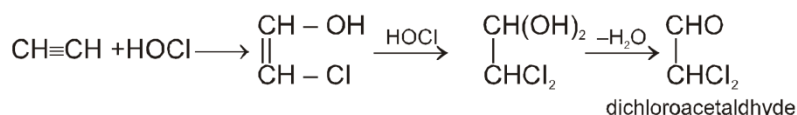
Highly deactivating and highly activating rings do not undergo Friedel craft acylation.

Exercise-3

PART - I : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

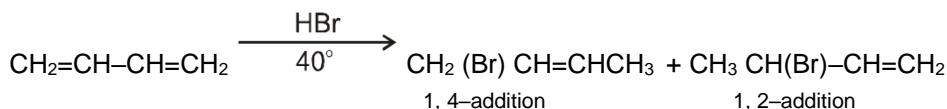
1.

Sol.



2.

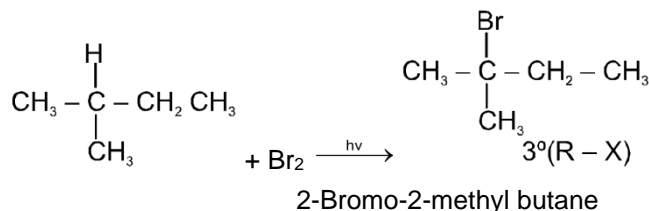
Sol.



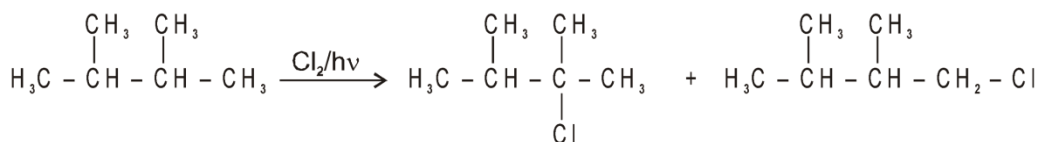
Therefore, 1-bromo-2-butene will be the main product under thermodynamically controlled conditions.

4.

Sol.



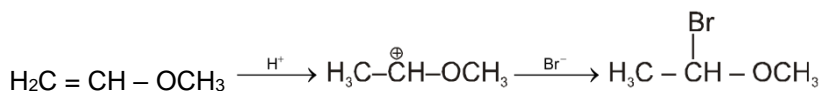
5.



Sol.

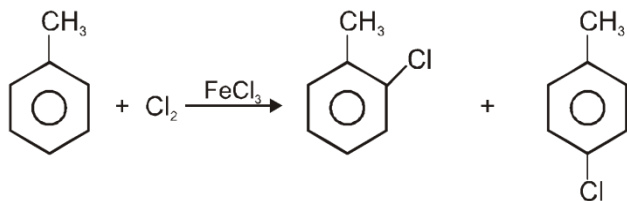
6.

Sol.

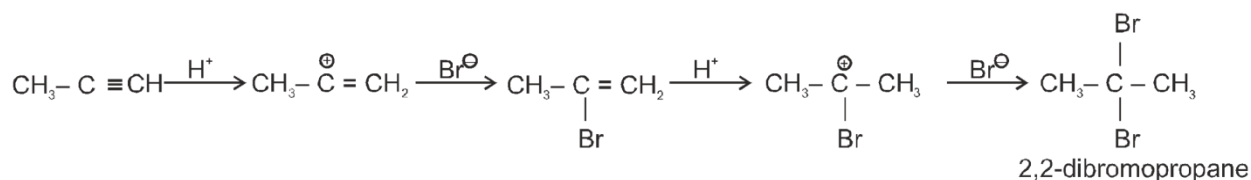


7.

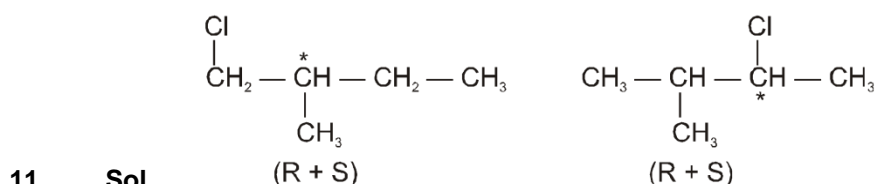
Sol.



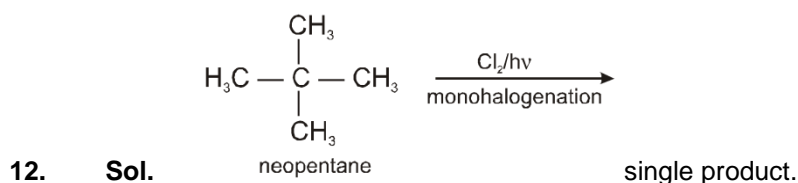
8. Sol.



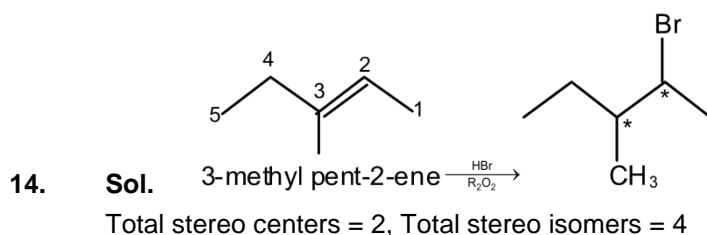
9. Sol. $-\text{NO}_2$ group in benzene ring shows $-I$ and $-M$ effect, which deactivates the ring towards electrophilic substitution but activates towards nucleophilic substitution.



Four monochloro derivatives are chiral.



13. Sol. $\text{CH}_3-\text{CH}^+-\text{CH}_2-\text{Cl}$

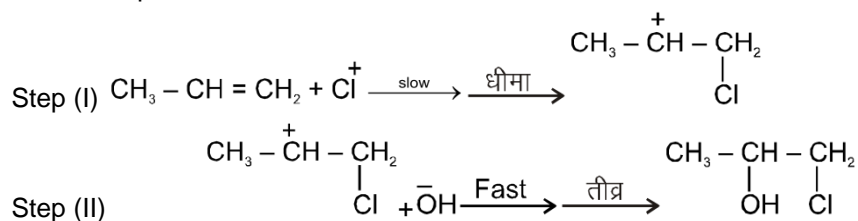


PART - II : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

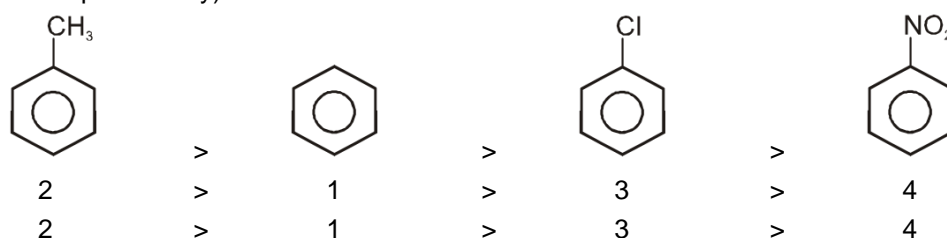
* Marked Questions may have more than one correct option.

1. Sol. Reaction being endothermic, here sufficient energy is not available in these cases.

2. Sol. It is an example of electrophilic addition (Markonikov's Addition).
It can be represented as follows :

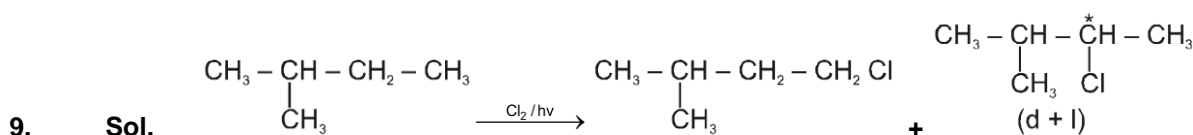
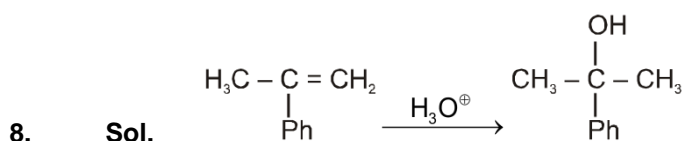
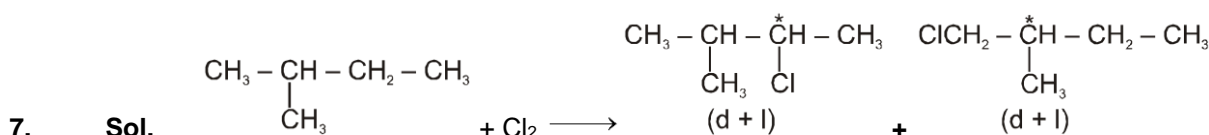
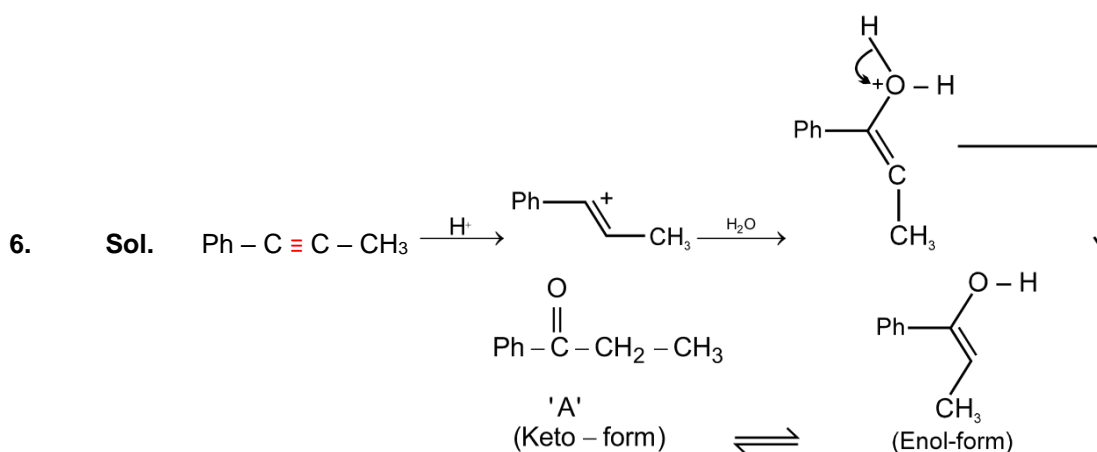


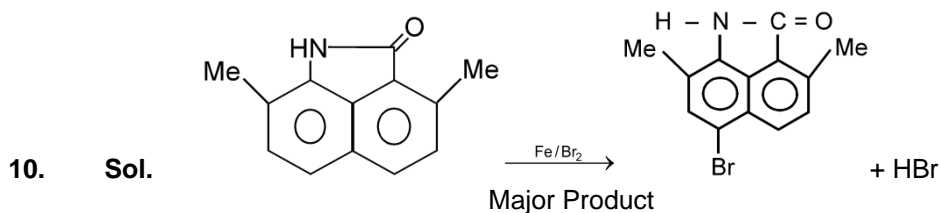
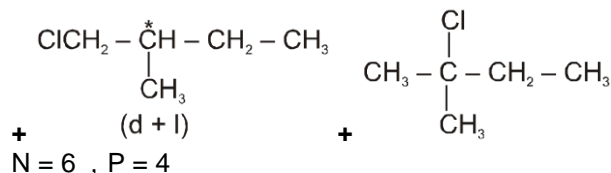
3. **Sol.** $-\text{NO}_2$ group is electron attractive group, so it deactivates the benzene ring largely, $-\text{Cl}$ atom is also deactivate the benzene ring but this deactivation is lower to $-\text{NO}_2$ group; while $-\text{CH}_3$ group activates they have the following order of electrophilic attraction (because more activated group attracts electrophile easily)



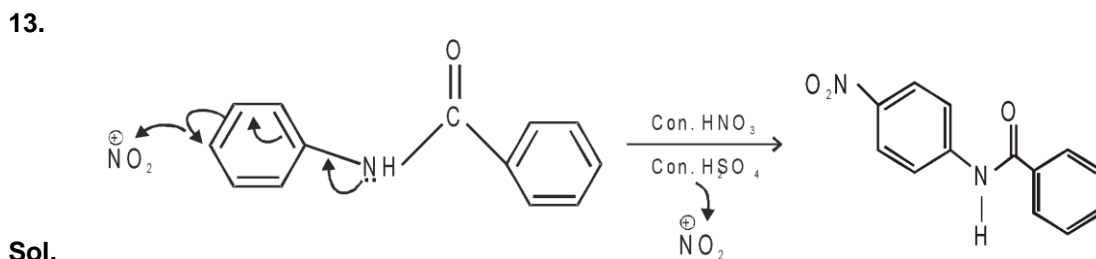
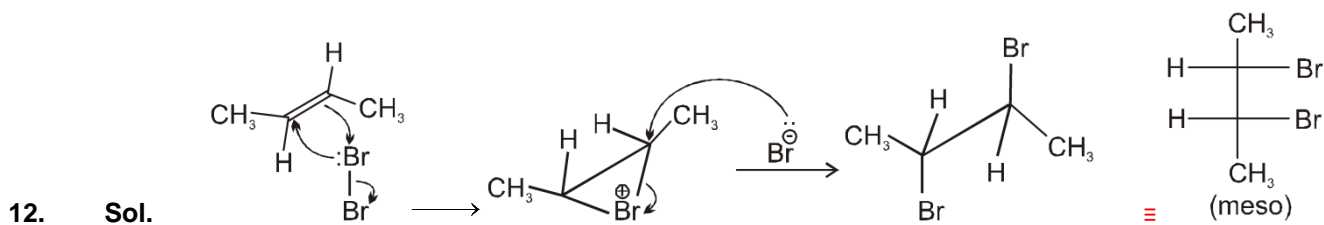
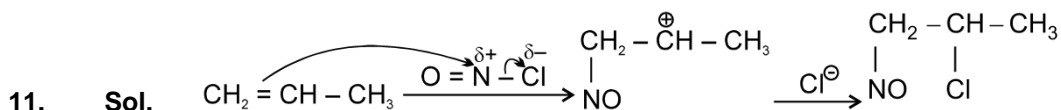
4. **Sol.** $\text{CH}_3 - \underset{\text{D}}{\text{CH}} - \overset{\bullet}{\underset{\text{CH}_3}{\text{C}}} - \text{CH}_3$ is more stable free radical among all other free radicals because t-alkyl free radical is more stable than secondary or primary alkyl free radical (Based upon hyperconjugation)

5. **Sol.** Addition of bromine to an alkene is an anti addition a symmetrical trans alkene on anti addition forms a meso compound. Also in addition of alkene first of all Br^\oplus attacks therefore it is an electrophilic addition.





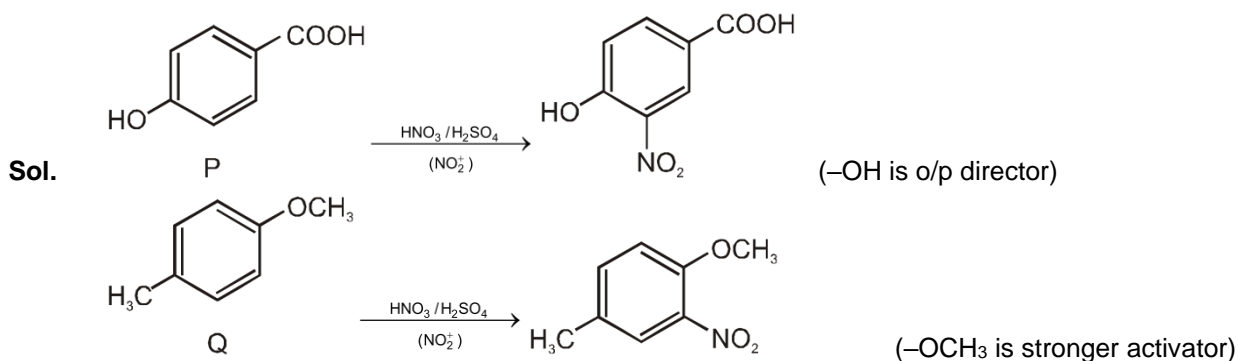
It is electrophilic substitution, so electrophile must be attached on o/p-position due to higher electron density on these position. In this ring the attached $-\text{NH}-$ group will have high electron density due to resonance and ortho position is blocked, so electrophile is attached on para position.

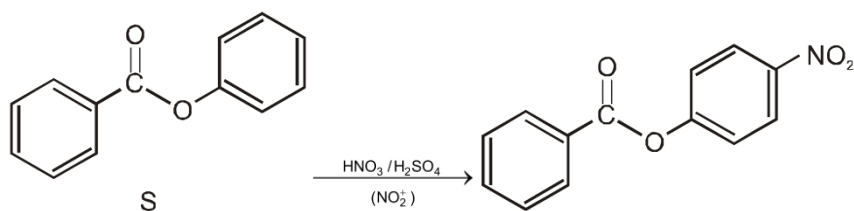


Note : ($-\text{NH}-$ part is p-directing).

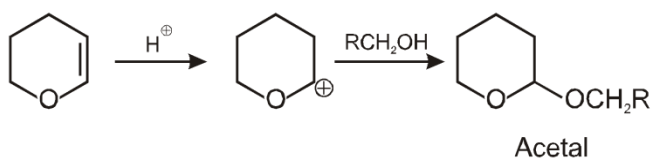


15.



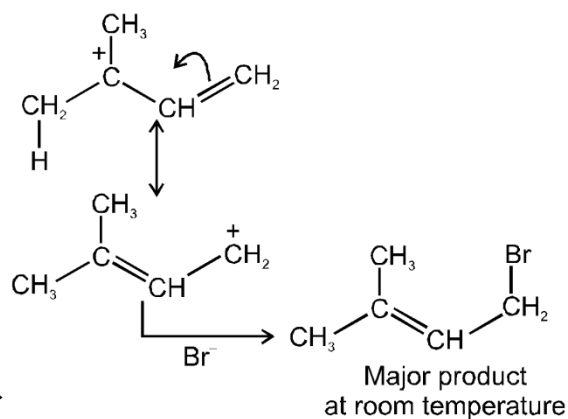


(Substitution takes place in activated ring on least crowded p-position)



16. Sol.

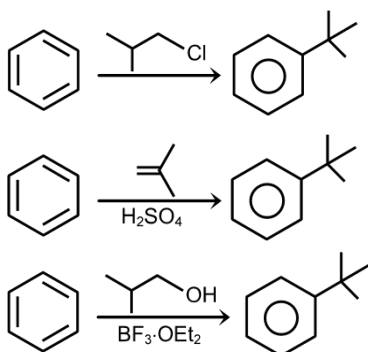
17. Ans. (D)



Sol.

18.* Ans. (B,C,D)

Sol.

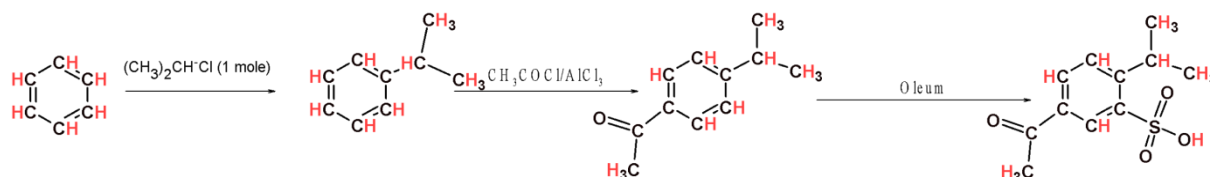


APSP Solutions

PART - I

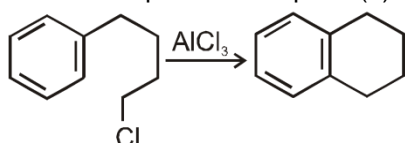
- It is allylic substitution reaction.
- Reaction A is free radical addition reaction and all are electrophilic addition reactions.
- Rate of nitration at benzene does not affect by H or D because H or D leave in the fast step.

7. $EAS \propto \frac{1}{EWG}$ on Benzene ring.
8. In presence of +M effect rate of mononitration increase and in presence of -M effect rate will decrease.
14. As in previous question.

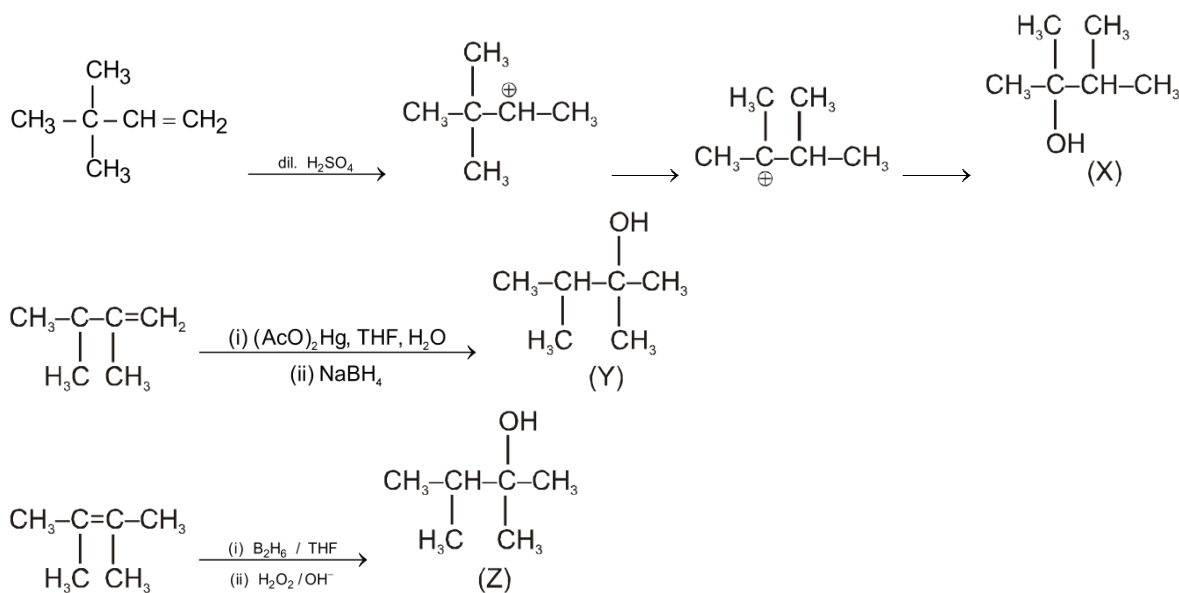


16.

23. Reaction is possible in option (3) only.

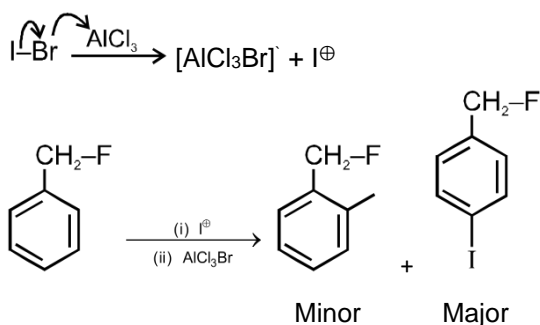


25.



All products are identical.

26.



29. In the presence of peroxide, HBr undergoes free radical addition and HCl undergoes electrophilic addition, because of H-Cl bond have high bond energy.

PART - II

8. It is Friedal-Crafts reaction and is used for the preparation of diphenylmethane.

9. Formation of carbocation is the rate determining step.

10. Oxymercuration-Demercuration take place.

(Addition of $-\text{OH}$ takes place according to Markovnikoff's rule)

11. Most stable alkene less heat of hydrogenation.

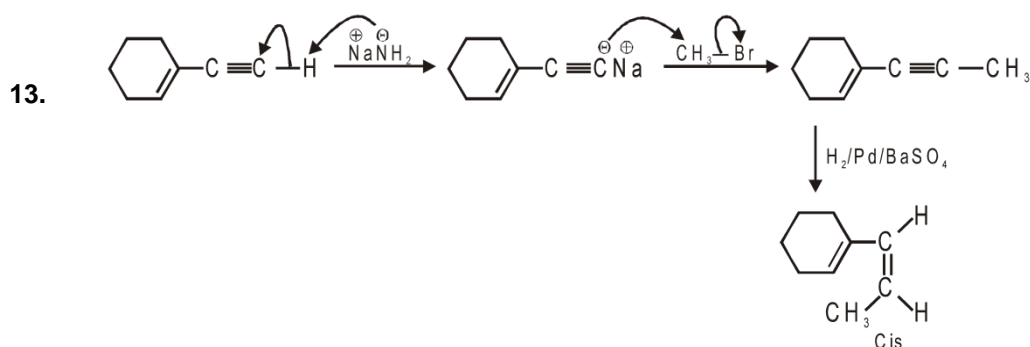
a $\rightarrow 4\alpha\text{H}$

b $\rightarrow 10\alpha\text{H}$

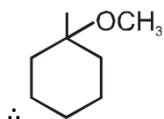
c $\rightarrow 6\alpha\text{H}$

d $\rightarrow 3\alpha\text{H}$

12. All alkyne on catalytic hydrogenation give 3-ethylhexane.



14. Addition of CH_3OH , according to Markovnikoff's rule take place.



16. In anti addition, trans reactant will give meso.

17. Addition of water by oxymercuration reduction without rearrangement.

18. Product will have two chiral carbon, so total product will be $2^n = 2^2 = 4$.

19. Conceptual

