CSIR NET Chemical Science Questions Answers With Solutions
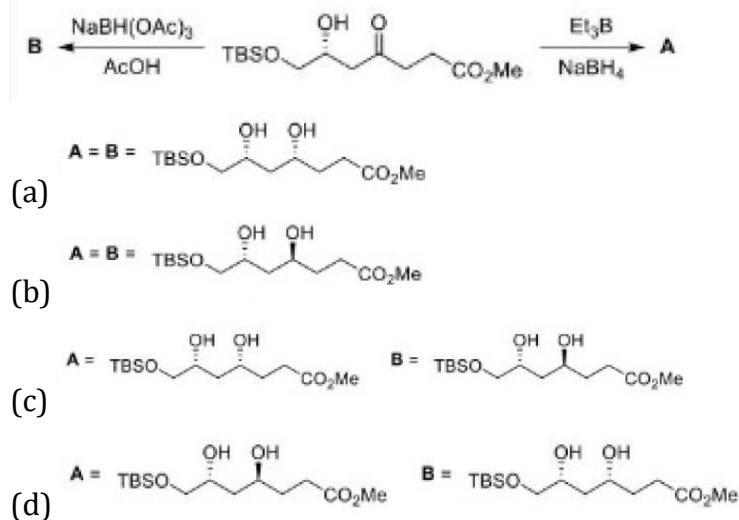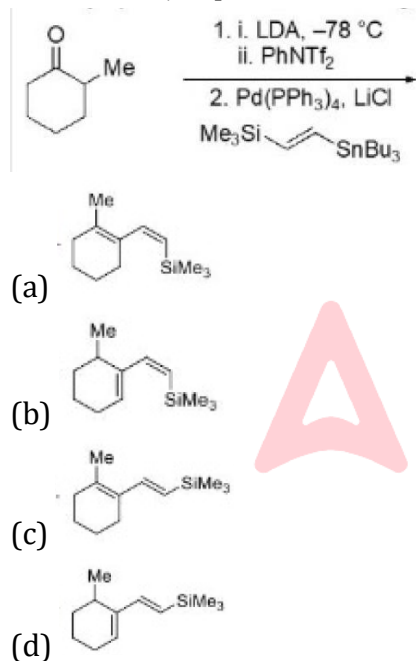
Q1. The major products A and B formed in the following transformations are

(a) A = B = TBSO with OH OH and CO_2Me

(b) A = B = TBSO with OH OH and CO_2Me

(c) A = TBSO with OH OH and CO_2Me B = TBSO with OH OH and CO_2Me

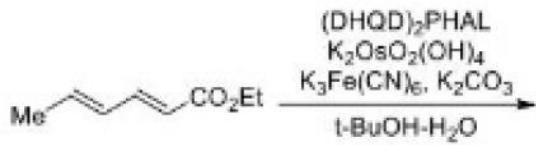(d) A = TBSO with OH OH and CO_2Me B = TBSO with OH OH and CO_2Me

Q2. The major product formed in the following reaction sequence is

1. i. LDA, −78 °C
   ii. PhNTf$_2$
2. Pd(PPh$_3$)$_4$, LiCl
   Me$_3$Si — SnBu$_3$

(a) Me / SiMe$_3$
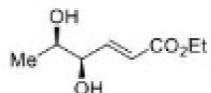
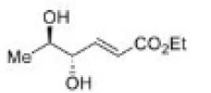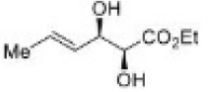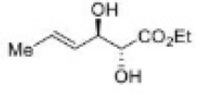(b) Me / SiMe$_3$

(c) Me / SiMe$_3$

(d) Me / SiMe$_3$

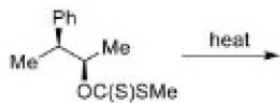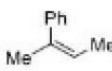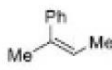**Q3.** The correct set of reagents that can affect the following conversion is

(a) i. *m*-CPBA; ii. NaBH$_3$CN, BF$_3$·OEt$_2$

(b) i. OsO$_4$, NMO; ii. TsCl, pyridine; iii. LiAlH$_4$

(c) i. *m*-CPBA; ii. LiAlH$_4$

(d) i. OsO$_4$, NMO; ii. PhCO$_2$H, PPh$_3$, DEAD

Q4. The major product formed in the following reaction is

Me ⟶⟶⟶CO$_2$Et $\xrightarrow[\text{t-BuOH-H}_2\text{O}]{\substack{\text{(DHQD)}_2\text{PHAL} \\ \text{K}_2\text{OsO}_2\text{(OH)}_4 \\ \text{K}_3\text{Fe(CN)}_6, \text{ K}_2\text{CO}_3}}$

(a)
Me ⟶ (OH)(OH) ⟶ CO$_2$Et

(b)
Me ⟶ (OH)(OH) ⟶ CO$_2$Et

(c)
Me ⟶ (OH)(OH) CO$_2$Et

(d)
Me ⟶ (OH)(OH) CO$_2$Et
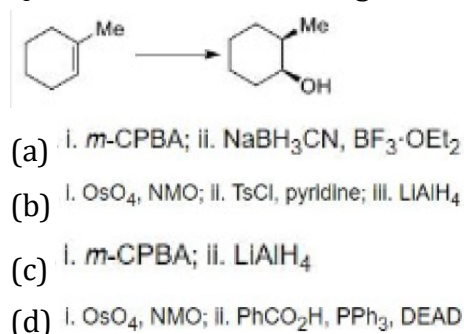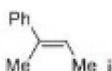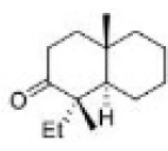
Q5. The correct statement about the following reaction is

Ph
Me ⟶ Me $\xrightarrow{\text{heat}}$
   OC(S)SMe

(a)
Ph
Me ⟶ Me is formed through *anti* elimination

(b)
Ph
Me ⟶ Me is formed through *syn* elimination

(c)
Ph
Me ⟶ Me is formed through *anti* elimination

(d)
Ph
Me ⟶ Me is formed through *syn* elimination

Q6. The major product formed in the following reaction is

$\xrightarrow[\text{then EtI}]{\text{Li, liq. NH}_3}$

(a)
Et H

(b)

(c)

(d)
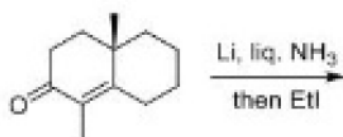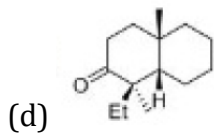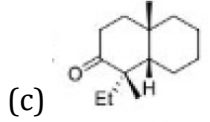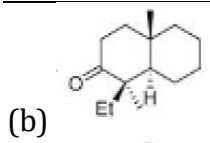
Q7. Upon catalysis by hinesene synthase, eudesmyl cation shown below undergoes a sequential hydride shift, ring contraction and loss of proton to form (–)–hinesene. The correct structure of (–)–hinesene is

Me

⊕

Me H

eudesmyl cation ⟶ (–)-hinesene

(a)

Me

Me

(b)

Me

Me

(c)

Me

Me

(d)

Me

Me
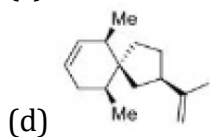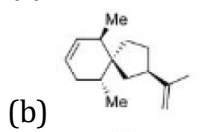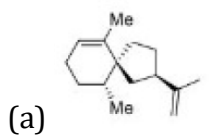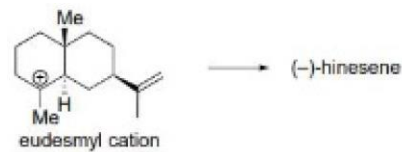
Q8. The mechanism of the following reaction involves

CO₂Me

CHO ⟶ heat ⟶ CO₂Me

O

A. 4e⁻ conrotatory electrocyclic reaction

B. [2+2] cycloreversion

C. 6e⁻ disrotatory electrocyclic reaction

D. [4+2] cycloaddition

(a) A and B
(b) A and C
(c) B and D
(d) C and D

Q9. The major product formed in the following reaction sequence is

1. PhMgBr, CuBr
2. KOH, EtOH
3. Na, i-PrOH
   toluene, reflux
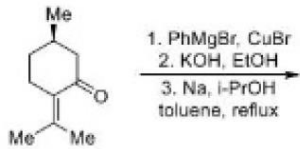
(a)

(b)

(c)

(d)

Q10. The transition state (TS) structure that would lead to the product in the following reaction is

heat → [TS] →
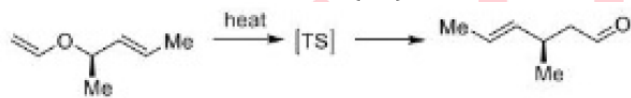
(a)

(b)

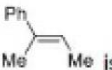(c)

(d)

Q11. The major product formed in the following reaction is

Ac_2O
heat

(a)

(b)

(c)

(d)
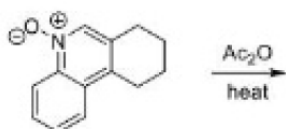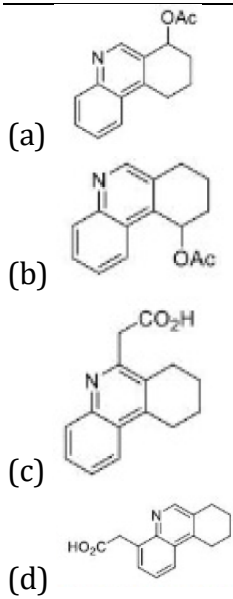
Q12. The tosylates that on solvolysis will give the mixture of products as shown in the reaction are
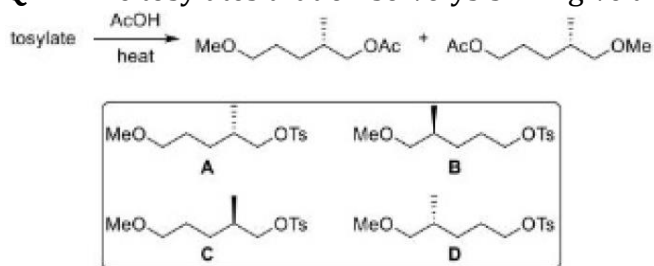
(a) A and C
(b) B and D
(c) A and B
(d) C and D

Q13. The major product formed in the following reaction sequence is

(a)

(b)

(c)

(d)

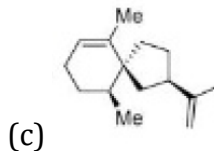**Q14.** The major product formed in the following reaction sequence is

1. Na, liq. NH₃
2. H₂, Rh(PPh₃)₃Cl
3. BH₃·THF
then NaOH, H₂O₂
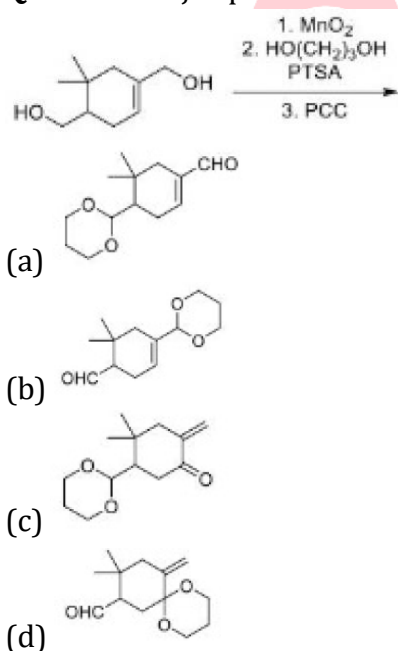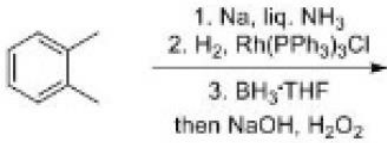
(a)

(b)

(c)

(d)

Q15. The correct order of relative rates of the following reactions is
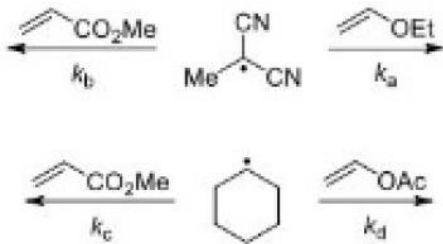
(a) $k_b \gg k_a;\ k_c \gg k_d$
(b) $k_b \gg k_a;\ k_d \gg k_c$
(c) $k_a \gg k_b;\ k_d \gg k_c$
(d) $k_a \gg k_b;\ k_c \gg k_d$

Q16. Consider the following compound where $^3J_{ab}$ and $^3J_{bc}$ represent three bond coupling between H_a & H_b and H_b & H_c protons, respectively.
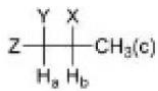
In two different scenarios,

i. $^3J_{ab} < {}^3J_{bc}$ and
ii. $^3J_{ab} = {}^3J_{bc}$

the multiplicity of H_b proton, respectively, will be

(a) i = quintet; ii = quartet of doublets
(b) i = quartet of doublets; ii = quintet
(c) i = triplet of triplets; ii = quartet of doublets
(d) i = triplet of triplets; ii = quintet

Q17. The major product formed in the following reaction is
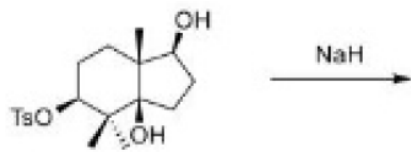
(a)

(b)

(c)

(d)

Q18. The major product formed in the following reaction sequence is
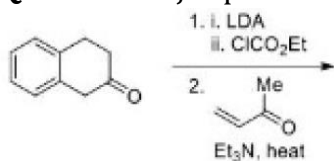
(a)

(b)

(c)

(d)

Q19. ^{31}P NMR spectrum of P_4S_3 consists of $(^{31}P, I = \frac{1}{2}$ 100% abundance$)$
(a) two doublets of triplets
(b) triplet of triplets
(c) two triplets of equal intensity
(d) a doublet and a quartet

Q20. The intermediate formed in the following reaction is
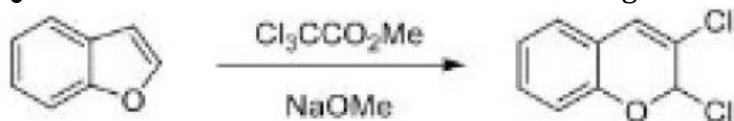
(a)

(b)

(c)

(d)

Solutions

S1. Ans.(c)

Sol. Sodium triacetoxyborohydride, also known as sodium triacetoxyhydroborate, commonly abbreviated STAB, is a chemical compound with the formula $Na[(CH_3COO)_3BH]$. Like other borohydrides, it is used as a reducing agent in organic synthesis. Sodium triacetoxyborohydride is a milder reducing agent than sodium borohydride. It reduces aldehydes but not most ketones.
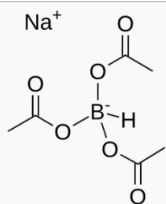
Sodium borohydride, also known as sodium tetrahydridoborate and sodium tetrahydroborate, is an inorganic compound with the formula $NaBH_4$. $NaBH_4$ reduces many organic carbonyls, depending on the conditions. Most typically, it is used in the laboratory for converting ketones and aldehydes to alcohols.
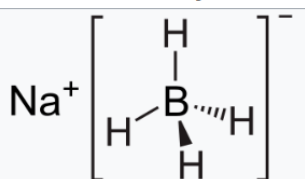
In the formation of A, due to the presence of bulky group below the plane, H^- will attack from above the plane and therefore OH group goes below the plane.

In the formation of B, due to the presence of bulky group (containing H⁻) below the plane, the attack of H⁻ will occur from below the plane and therefore OH group goes above the plane.

Trialkylboranes are also effective chelation agents in stereoselective NaBH₄ reductions of β-hydroxy ketones to 1,3-*syn* diols.[131]

90%; 95:5, *syn* : *anti*

1,3-*anti* diol

internal H⁻
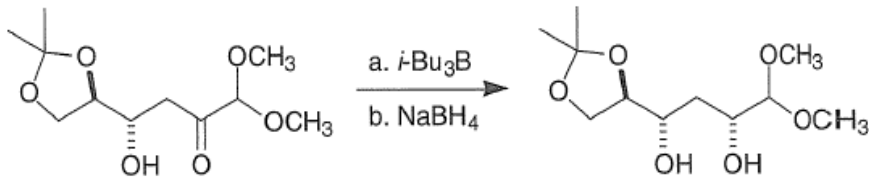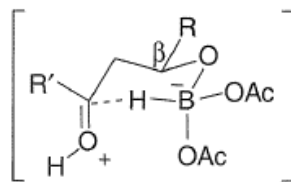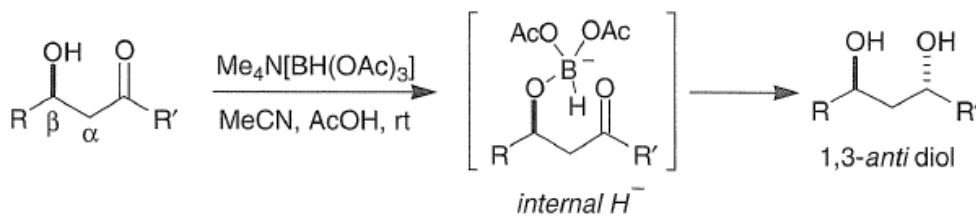
intramolecular hydride delivery
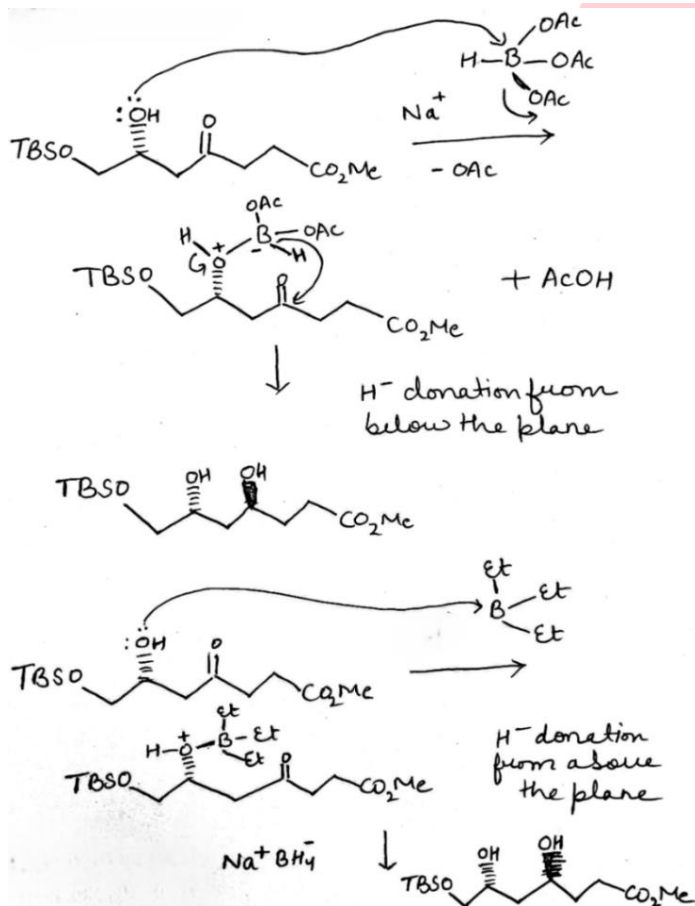
S2. Ans.(d)
Sol. Lithium diisopropylamide (commonly abbreviated LDA) is a chemical compound with the molecular formula $LiN(CH(CH_3)_2)_2$. It is used as a strong base and has been widely utilized due to its good solubility in non-polar organic solvents and non-nucleophilic nature.
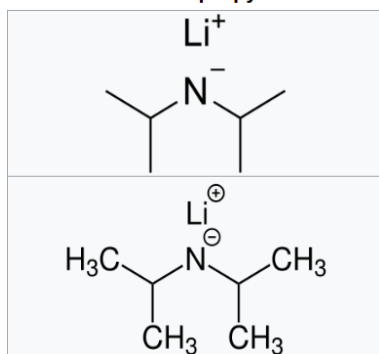
Lithium enolates are usually made at low temperature in THF with a hindered lithium amide base (often LDA) and are stable under those conditions because of the strong O–Li bond. The formation of the enolate begins with Li–O bond formation before the removal of the proton from the position by the basic nitrogen atom.
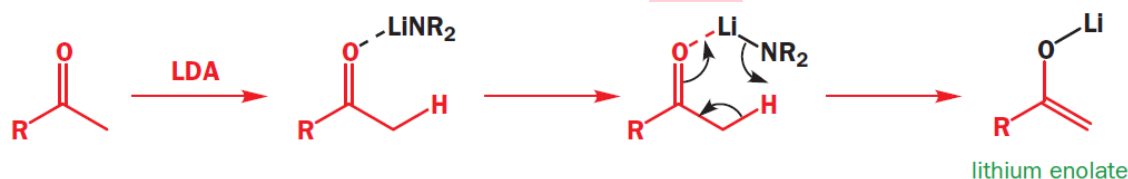
LDA is too hindered to attack C=O, so it attacks C–H instead. And, if there is a choice of C–H bonds, it will attack the least hindered possible. It will also prefer to attack more acidic C–H bonds, and C–H bonds on less substituted carbons are indeed more acidic.

These factors multiply to ensure that the enolate that forms will be the one with the fewer substituents-provided we now prevent equilibration of the enolate to the more stable, more substituted one. This means keeping the temperature low, typically –78 °C, keeping the reaction time short, and using an excess of strong base to deprotonate irreversibly and ensure that there is no remaining ketone to act as a proton source. The enolate that we then get is the one that formed faster—the kinetic enolate—and not necessarily the one that is more stable.
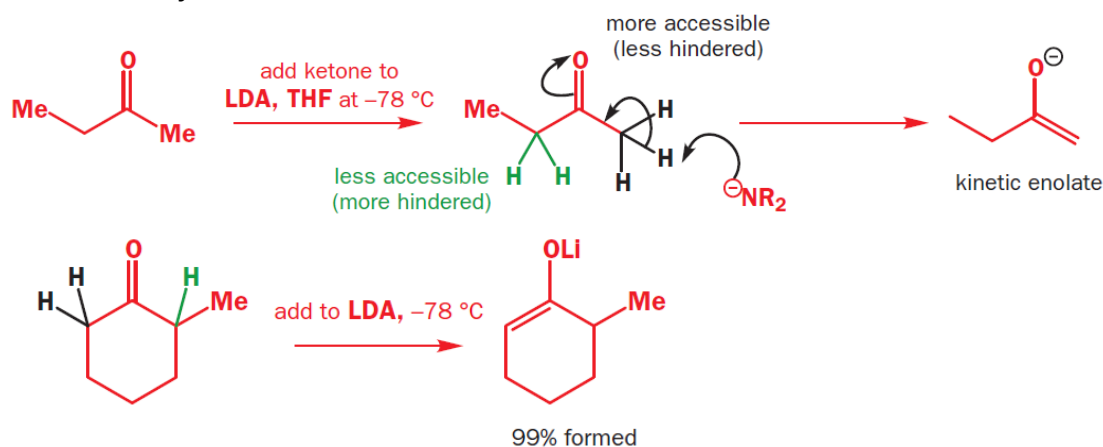
Bis(trifluoromethanesulfonyl)aniline is the organic compound with the formula $C_6H_5N(SO_2CF_3)_2$. It is a white solid. The compound is used to install the triflyl group (SO_2CF_3).

Bis(trifluoromethanesulfonyl)aniline
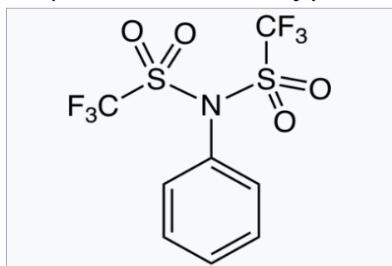
The Stille coupling has been widely used for the coupling of both aromatic and vinylic systems.
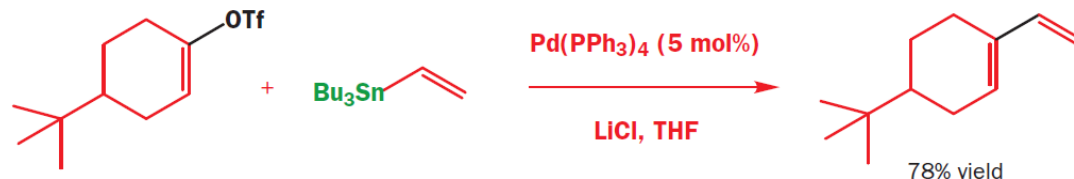
The mechanism involves the oxidative addition of the vinyl or aromatic triflate or halide to give a palladium intermediate. This then undergoes a transmetallation reaction with the organostannane, giving an organopalladium intermediate in which both components are σ-bound. This complex then undergoes a reductive elimination step, releasing the product and thereby regenerating the palladium (0) catalyst.
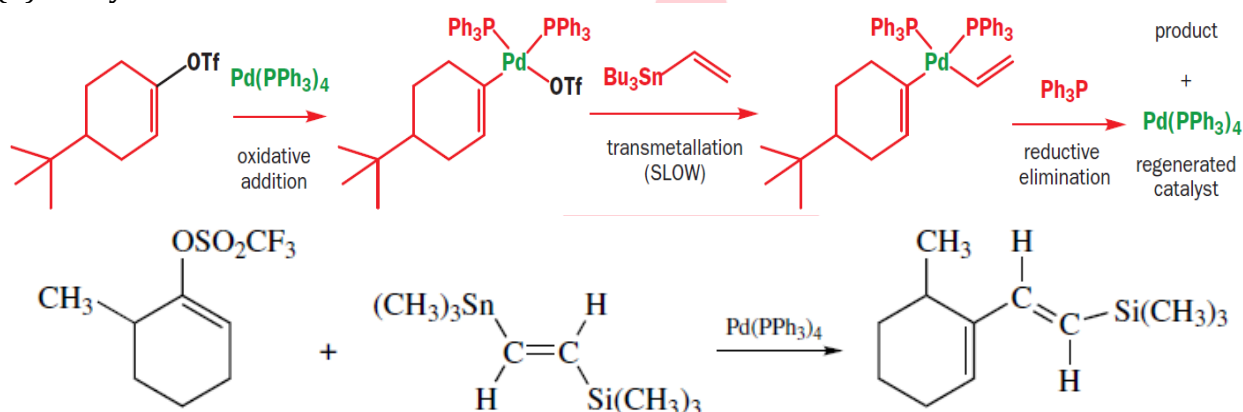
Information Booster

Oxidative addition is a process that increases both the oxidation state and coordination number of a metal centre.

Reductive elimination is an elementary step in organometallic chemistry in which the oxidation state of the metal center decreases while forming a new covalent bond between two ligands.

Transmetalation is a type of organometallic reaction that involves the transfer of ligands from one metal to another. It has the general form:

$$M_1–R + M_2–R' \rightarrow M_1–R' + M_2–R$$
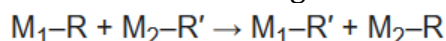
where R and R' can be, but are not limited to, an alkyl, aryl, alkynyl, allyl, halogen, or pseudohalogen group.

S3. Ans.(a)

Sol. The simplest epoxide, ethylene oxide (or oxirane itself), can be produced on the tonne scale by the direct oxidation of ethene by oxygen at high temperature over a silver catalyst. These conditions are hardly suitable for general lab use, and the most commonly used epoxidizing agents are peroxy-carboxylic acids. **Peroxy-acids** (or **peracids**) have an extra oxygen atom between the carbonyl group and their acidic hydrogen—they are half-esters of hydrogen peroxide (H_2O_2). They are rather less acidic than carboxylic acids because their conjugate base is no longer stabilized by delocalization into the

carbonyl group reagent. But they are electrophilic at oxygen, because attack there by a nucleophile displaces carboxylate, a good leaving group. The LUMO of a peroxy-carboxylic acid is the σ* orbital of the weak O–O bond.

The most commonly used peroxy-acid is known as *m*-CPBA, or *meta*-ChloroPeroxyBenzoic Acid. *m*-CPBA is a safely crystalline solid. Here it is, reacting with cyclohexene, to give the epoxide in 95% yield.
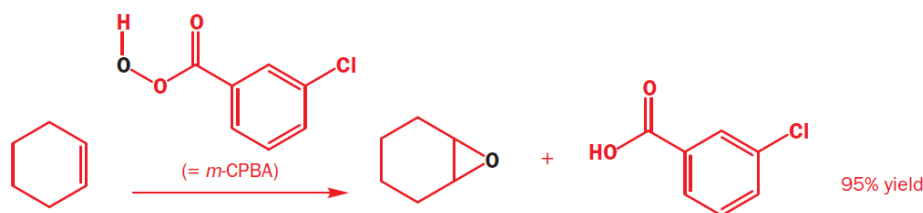
electrophilic attack by a peroxy-acid on an alkene
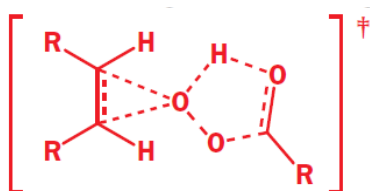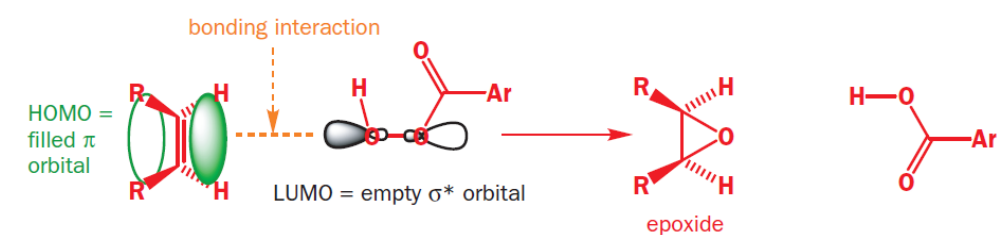
transition state for epoxidation

Start with the nucleophilic π bond: send the electrons on to oxygen, breaking O–O and forming a new carbonyl bond. Use those electrons to pick up the proton, and use the old O–H bond's electrons to make the second new C–O bond.

Because both new C–O bonds are formed on the same face of the alkene's π bond, the geometry of the alkene is reflected in the stereochemistry of the epoxide. The reaction is therefore stereospecific. *Cis*-alkene gives *cis*-epoxide and *trans*-alkene gives *trans* epoxide.

Sodium cyanoborohydride

Sodium cyanoborohydride is a chemical compound with the formula $Na[BH_3(CN)]$. The electron-withdrawing cyanide substituent draws electron density away from the negatively charged boron; thus, reducing the electrophilic capabilities of the anionic component. This electronic phenomenon causes sodium cyanoborohydride to have more mild reducing qualities than other reducing agents.

Reduction of the epoxide with sodium cyanoborohydride in the presence of boron trifluoride etherate gives *cis*-2-methylcyclohexanol by backside attack of hydride on the epoxide–Lewis acid complex. The direction of ring-opening is dictated by the formation of the more-stable carbocation intermediate.
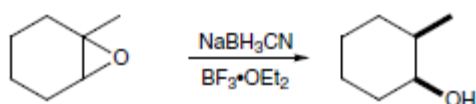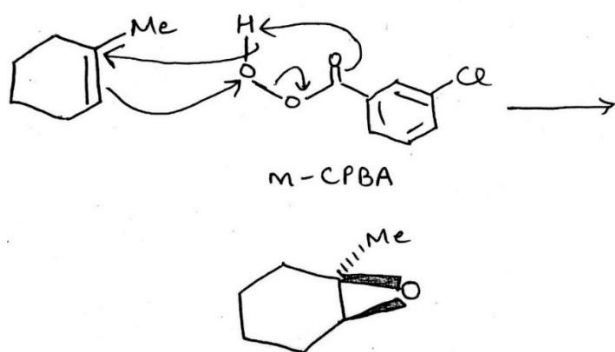
Additional Knowledge

The Mitsunobu reaction is an organic reaction that converts an alcohol into a variety of functional groups, such as an ester, using triphenylphosphine and an azodicarboxylate such as diethyl azodicarboxylate (DEAD).
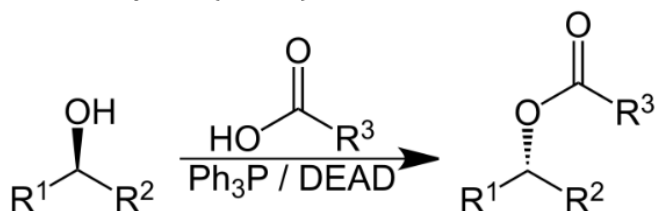
Alkenes add to OsO_4 to give diolate species that hydrolyze to *cis*-diols. The net process is called dihydroxylation. OsO_4 is expensive and highly toxic, making it an unappealing reagent to use in stoichiometric amounts. However, its reactions are made catalytic by adding reoxidants to reoxidise the Os(VI) by-product back to Os(VIII). Typical reagents include N-methylmorpholine N-oxide. These reoxidants do not react with the alkenes on their own.

S4. Ans.(a)

Sol. The dihydroxylation of alkenes provides 1,2-diol products, present in a great many natural products and biologically active molecules. The transformation has, therefore, received considerable interest and methods are now well developed for catalytic, racemic and asymmetric dihydroxylation. The most common of these is *syn* (or *cis*) dihydroxylation, in which the two hydroxy groups are added to the same side of the double bond.

Asymmetric dihydroxylation has been developed into an extremely efficient and selective process for a wide variety of substituted alkenes. Chiral amine ligands provide the required rate enhancement and asymmetric induction, by coordinating to the osmium atom. The most popular ligands are based on the naturally occurring cinchona alkaloids dihydroquinine (DHQ) and dihydroquinidine (DHQD). In particular, the ligands (DHQ)₂PHAL and (DHQD)₂PHAL, in which two of the alkaloids are connected to a phthalazine ring, have found widespread use.

(DHQD)₂PHAL
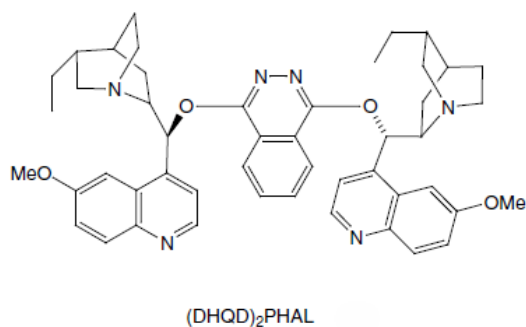
The dihydroxylation reaction can be carried out with osmium tetroxide as a catalyst (typically added in the lower oxidation state as the solid $[K_2OsO_4 \cdot 2H_2O]$), and the favoured co-oxidant is $[K_3Fe(CN)_6]$. Due to the high oxidation state of Os (VI), electron rich alkene will convert into a syn diol.

S5. Ans.(d)

Sol. The Chugaev elimination is a chemical reaction that involves the elimination of water from alcohols to produce alkenes. The intermediate is a xanthate.
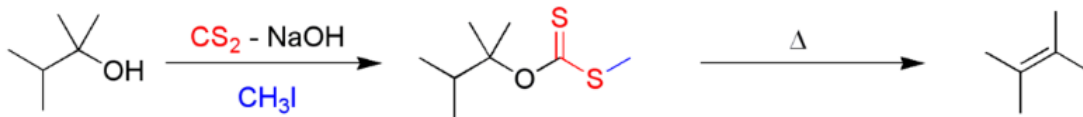
In the first step, a xanthate salt is formed out of the alkoxide and carbon disulfide (CS_2). With the addition of iodomethane, the alkoxide is transformed into a methyl xanthate.
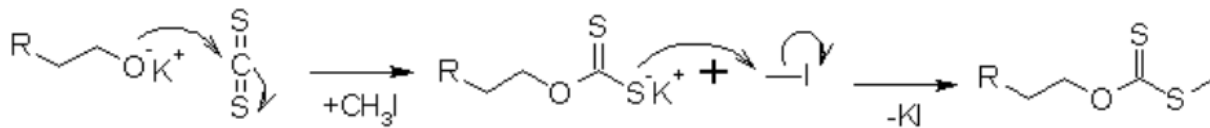
At about 200 °C, the alkene is formed by an intramolecular elimination. In a 6-membered cyclic transition state the hydrogen atom is removed from the carbon atom β to the xanthate oxygen in a *syn-*elimination. The side product decomposes to carbonyl sulfide (OCS) and methanethiol.
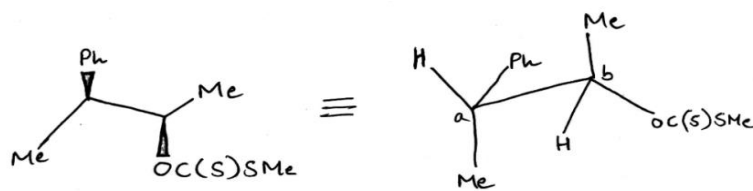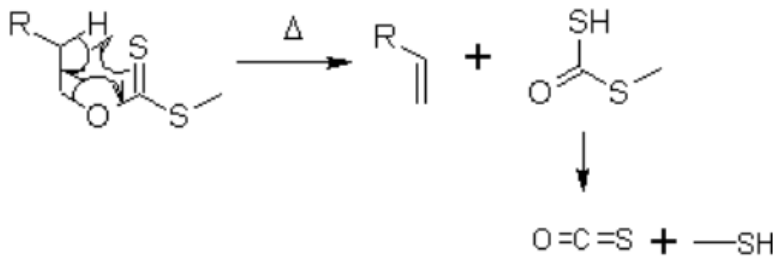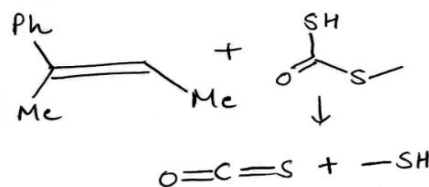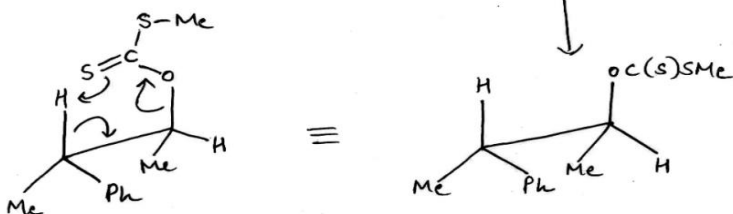
S6. Ans.(a)

Sol. Group 1 metals, such as sodium or lithium, readily give up their single outer-shell electron as they dissolve in solvents such as liquid ammonia or ethanol. Electrons are the simplest reducing agents, and they will reduce carbonyl compounds, alkynes, or aromatic rings—in fact any functional group with a low-energy π^* orbital into which the electron can go.

The dissolving metal reduction of aromatic rings is known as the Birch reduction.

The first thing to note is that when lithium or sodium dissolve in ammonia they give an intense blue solution. Blue is the colour of solvated electrons: these group 1 metals ionize to give Li^+ or Na^+ and e^- $(NH_3)_n$-the gaps between the ammonia molecules are just the right size for an electron. With time, the blue colour fades, as the electrons reduce the ammonia to $(NH_2)^-$ and hydrogen gas.

Birch reductions use those blue solutions, with their solvated electrons, as reducing agents. The reduction of NH_3 to $(NH_2)^-$ and H_2 is quite slow, and a better electron acceptor will get reduced in preference. The electrons go into benzene's lowest lying antibonding orbital (its LUMO).

The radical anion is very basic, and it picks up a proton from the ethanol that is in the reaction mixture. The molecule is now no longer anionic, but it is still a radical. It can pick up another electron, which pairs with the radical to give an anion, which is quenched again by the proton source (ethanol).

Reduction of cyclic α,β-unsaturated ketones in which there are substituents on the β- and γ-carbon atoms could give rise to two stereoisomeric products. In many cases one isomer is formed predominantly, generally the more stable of the two. The guiding principle appears to be that protonation of the intermediate anion takes place orthogonal to the enol double bond (axially in six-membered rings). Thus, reduction of the enone led almost exclusively to the *trans*-decalone through axial protonation.
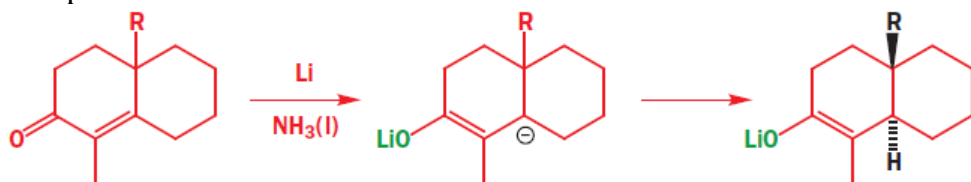
The lithium enolate remains and can be alkylated with an alkyl halide in the usual way. When there are hydrogen atoms at both ring junction positions, axial alkylation occurs just as you should now expect, and a new ketone with three stereogenic centres is formed with >95% stereoselectivity.

>95% this diastereoisomer
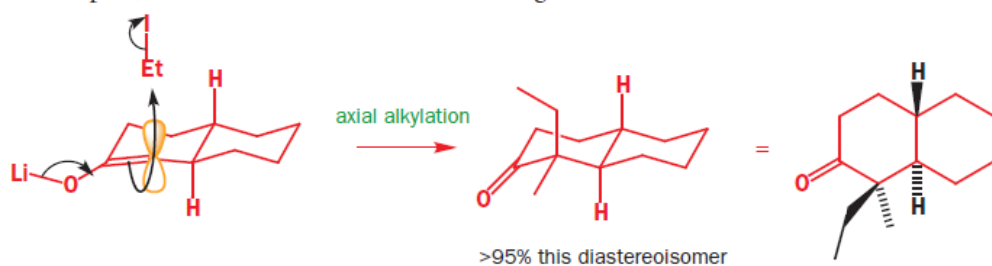
However, if there is anything else—even a methyl group—at the ring junction, so that axial approach would give a bad 1,3-diaxial interaction in the transition state, the stereoselectivity switches to >95% equatorial alkylation. This unexpected reversal of normal stereoselectivity is a result of the extra rigidity of the *trans*-decalin system.

>95% this diastereoisomer

99%   1%

3D conformation
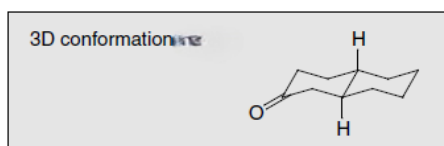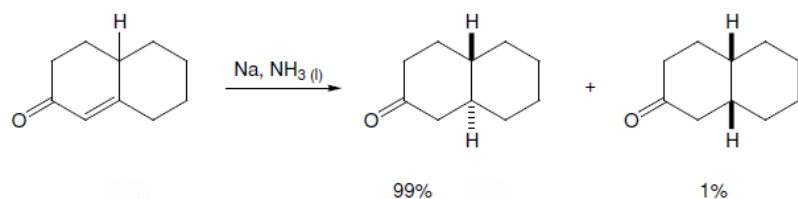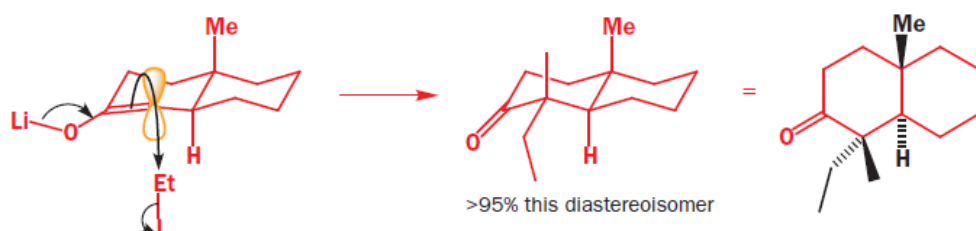
S7. Ans.(c)
Sol. A carbocation is any cation containing an even number of electrons in which a significant portion of the positive charge resides on a carbon atom.
Carbocations can be stabilized by the migration of hydrogen, alkyl, or aryl groups, and occasionally, functional groups. Carbocations tend to change or shift their positive charge to the most stable configuration. This process is known as carbocation rearrangement.

In the first step, hydride migration occurs rather than hydrogen (or proton) because the H atom migrates *with* its pair of electrons. Therafter, ring contraction converts the six membered ring to a five membered ring. Finally, loss of proton gives the desired product.
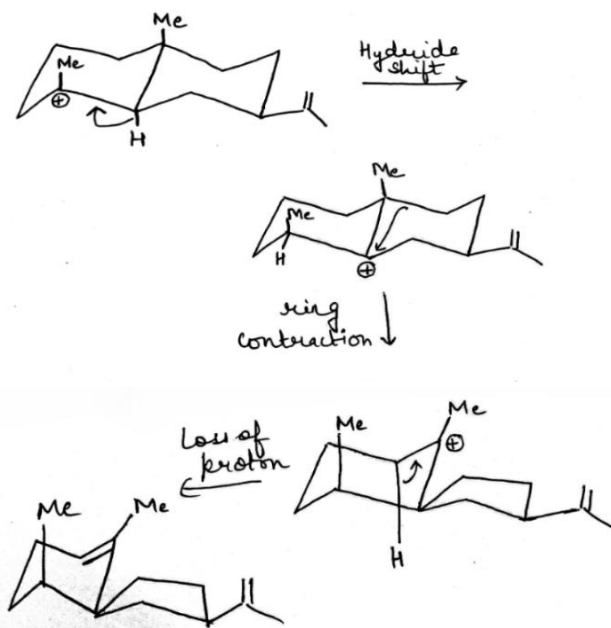
S8. Ans.(b)

Sol. An electrocyclic reaction is the concerted interconversion of a conjugated polyene and a cycloalkene. Electrocyclic reactions are induced either thermally or photochemically.

All electrocyclic reactions are reversible reactions. Open-chain partner of the reaction is always conjugated system whereas cyclic partner may or may not contain conjugated system.

In electrocyclic reactions either a ring is formed with the generation of a new σ bond and the loss of a π bond (*i.e.*, gain of one σ bond and loss of one π bond) or ring is broken with the loss of one σ bond and gain of one π bond.
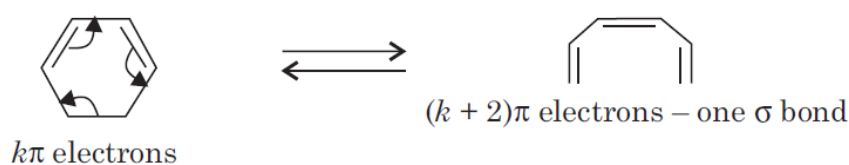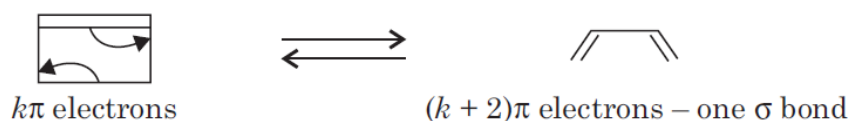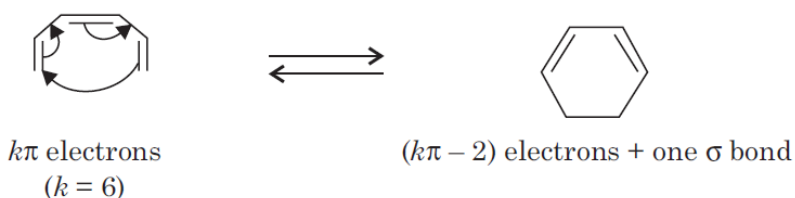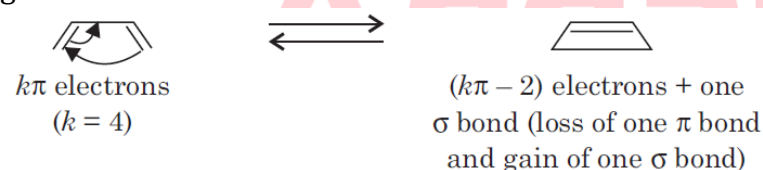
In organic chemistry, an electrocyclic reaction can either be classified as conrotatory or disrotatory based on the rotation at each end of the molecule. In conrotatory mode, both atomic orbitals of the end groups turn in the same direction (such as both atomic orbitals rotating clockwise or counter-clockwise). In disrotatory mode, the atomic orbitals of the end groups turn in opposite directions (one atomic orbital turns clockwise and the other counter-clockwise). The cis/trans geometry of the final product is directly decided by the difference between conrotation and disrotation.

The most common example of the ring opening reaction is the conversion of cyclobutene to 1, 3-butadiene.

This conversion can only be possible if a σ (*sigma*) bond between $C_3 — C_4$ of cyclobutene must break during the course of the reaction.
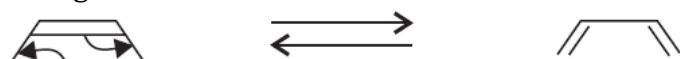
Ring opening reaction

This σ (*sigma*) bond may break in two ways. *First*, the two atomic orbital components of the σ (*sigma*) bond may both rotate in the same direction, clockwise or counter-clockwise. This process is known as conrotatory motion.
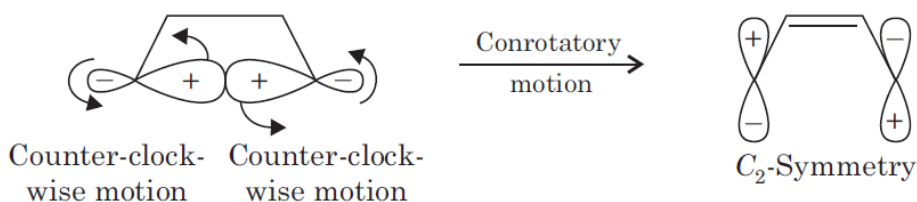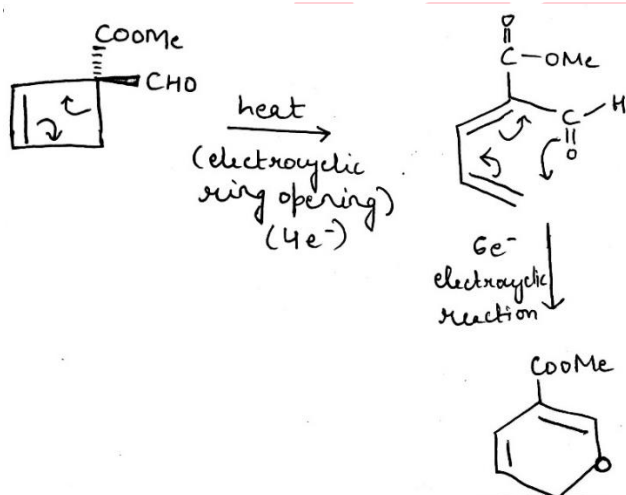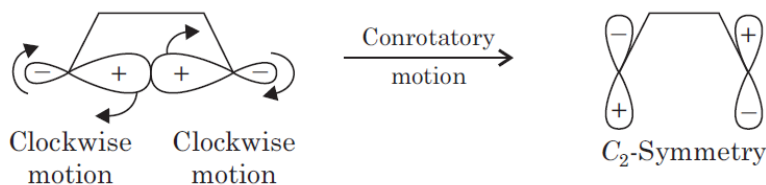
S9. Ans.(a)

Sol. Grignard reagents or Grignard compounds are chemical compounds with the general formula R–Mg–X, where X is a halogen and R is an organic group, normally an alkyl or aryl. Two typical examples are methylmagnesium chloride Cl–Mg–CH$_3$ and phenylmagnesium bromide (C$_6$H$_5$)–Mg–Br. They are a subclass of the organomagnesium compounds.

Grignard compounds are popular reagents in organic synthesis for creating new carbon–carbon bonds. Grignard reagents react with a variety of carbonyl derivatives. Grignard reagents add directly to the carbonyl group of α,β-unsaturated aldehydes and ketones to give allylic alcohols.

Organocopper reagents undergo conjugate addition

The copper works by transmetallating the Grignard reagent to give an organocopper reagent. Organocoppers are softer than Grignard reagents, and add in a conjugate fashion to the softer C=C double bond. Once the organocopper has added, the copper salt is available to transmetallate some more Grignard, and only a catalytic amount is required.

Organocoppers are softer than Grignard reagents because copper is less electropositive than magnesium, so the C–Cu bond is less polarized than the C–Mg bond, giving the carbon atom less of a partial negative charge. Electronegativities: Mg, 1.3; Cu, 1.9.
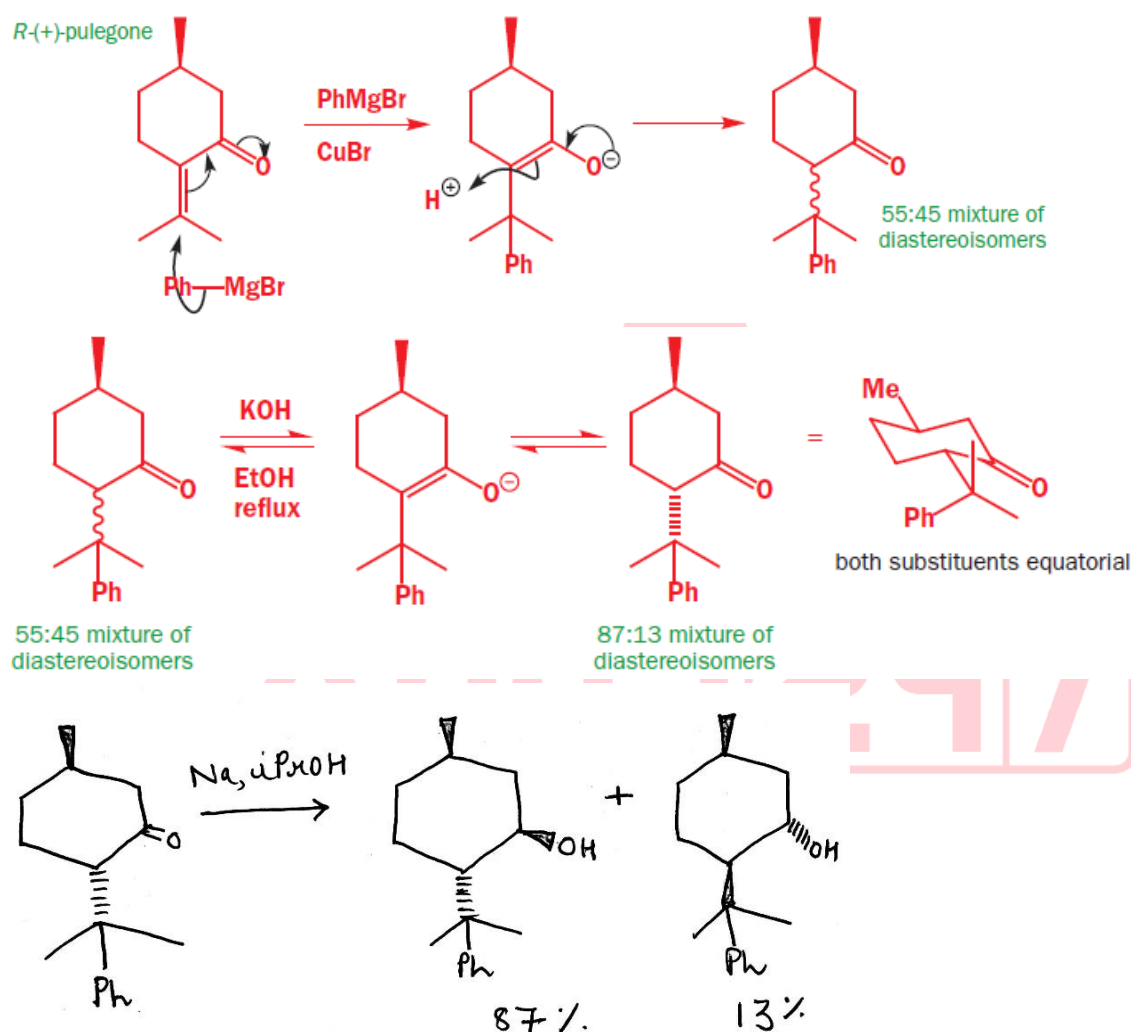
S10. Ans.(a)

Sol. In organic chemistry, a sigmatropic reaction is a pericyclic reaction wherein the net result is one sigma bond (σ-bond) is changed to another σ-bond in an intramolecular reaction. In this type of rearrangement reaction, a substituent moves from one part of a π-system to another part with simultaneous rearrangement of the π-system.

The most important sigmatropic rearrangement are the [3, 3] process involving carbon-carbon bond. The thermal rearrangement of 1, 5-dienes by [3, 3] sigmatropy is called Cope rearrangement.

This particular reaction is called a [3, 3] sigmatropic rearrangement because the new σ bond has a 3, 3 relationship to the old σ (*sigma*) bond.

The Cope rearrangement usually proceeds through the chair like transition state. The stereochemical features of the reaction can usually be predicted and analysed on the basis of a chair transition state that minimizes steric interactions between substituents.

Meso form

TS

Cis-trans 99.7%

Trans-trans (90%)
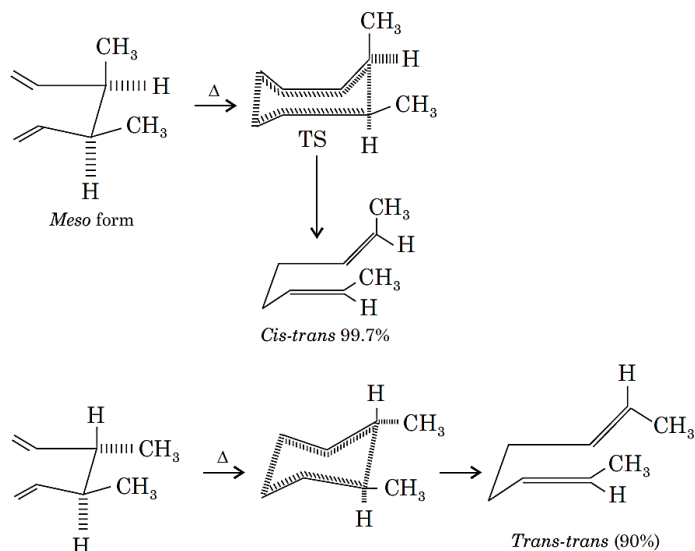
Preparation of Carbonyl Compounds from Cope Rearrangement

1, 5-Hexadiene-3-ol on heating undergoes Cope rearrangement with formation of unsaturated carbonyl compounds. Cope rearrangement given by such compounds is known as oxy-Cope rearrangement.

Enol

Unsaturated carbonyl compound

heat ↓

[TS]
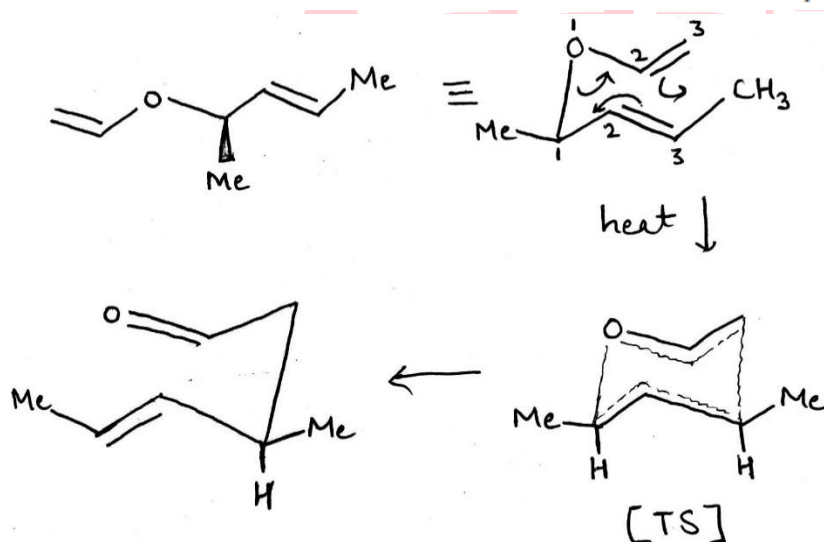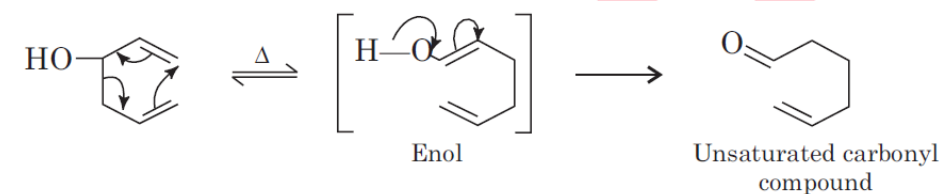
S11. Ans.(b)

Sol. Pyridine can be oxidized to pyridine *N*-oxide with reagents such as *m*-CPBA or just H_2O_2 in acetic acid. These *N*-oxides are stable dipolar species with the electrons on oxygen delocalized round the pyridine ring, raising the HOMO of the molecule.

pyridine → pyridine N-oxide
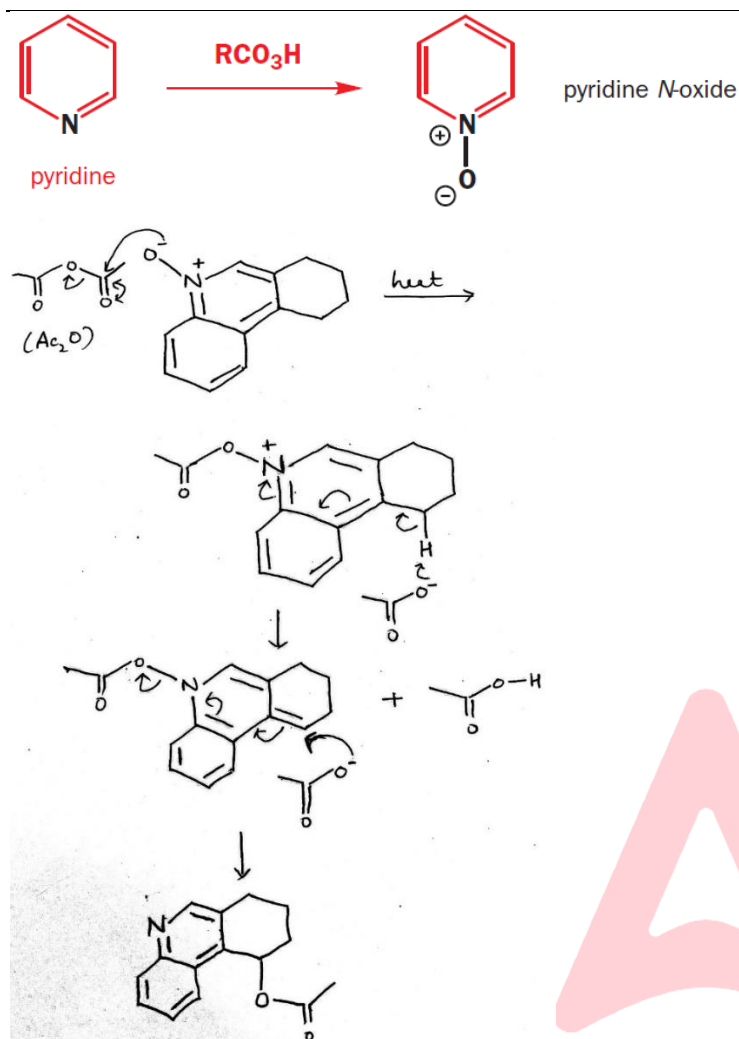
S12. Ans.(c)
Sol. Neighbouring group participation
Neighbouring group participation (NGP, also known as anchimeric assistance) is defined as the interaction of a reaction centre with a lone pair of electrons in an atom or the electrons present in a sigma or pi bond contained within the parent molecule but not conjugated with the reaction centre.

neighbouring group participation of a sulfide

three-membered ring intermediate
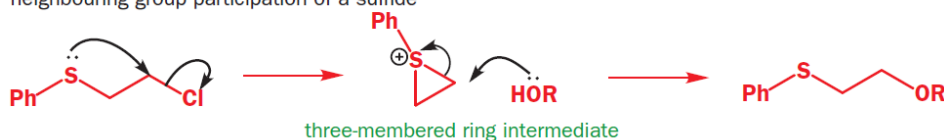
When NGP is in operation it is normal for the reaction rate to be increased. It is also possible for the stereochemistry of the reaction to be abnormal (or unexpected) when compared with a *normal* reaction.
Absolute Configuration
The Cahn–Ingold–Prelog (CIP) sequence rules are a standard process to completely and unequivocally name a stereoisomer of a molecule. The purpose of the CIP system is to assign an *R* or *S* descriptor to each stereocenter.
1. Compare the atomic number (Z) of the atoms directly attached to the stereocenter; the group having the atom of higher atomic number Z receives higher priority (i.e. number 1).

2. If there is a tie, the atoms at distance 2 from the stereocenter have to be considered: a list is made for each group of further atoms bonded to the one directly attached to the stereocenter. Each list is arranged in order of decreasing atomic number Z. Then the lists are compared atom by atom; at the earliest difference, the group containing the atom of higher atomic number Z receives higher priority.
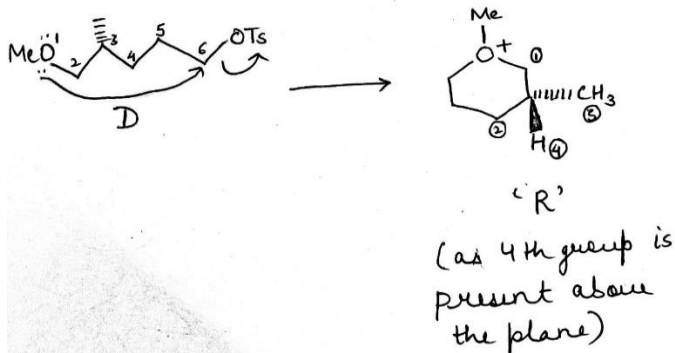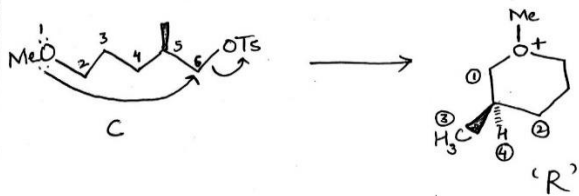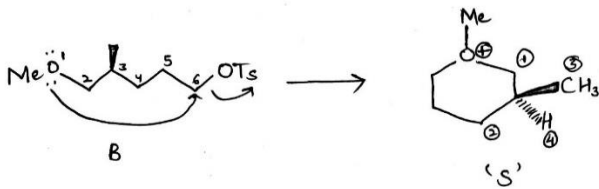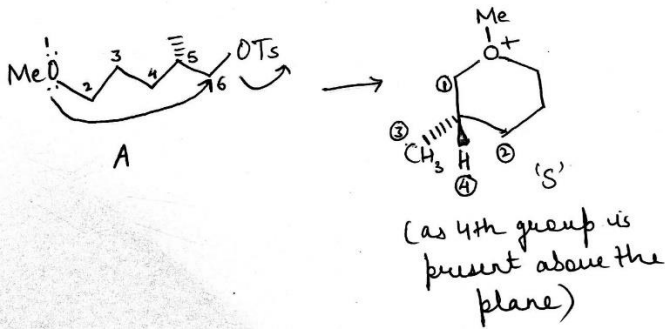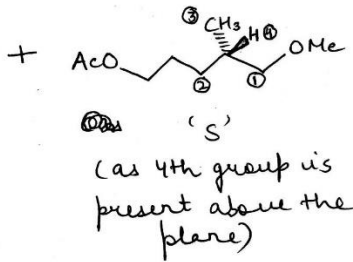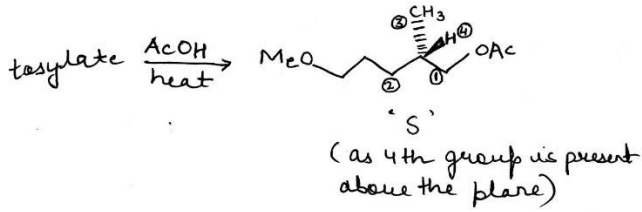
S13. Ans.(b)

Sol. A useful, mild reagent for the oxidation of primary and secondary alcohols to carbonyl compounds is manganese dioxide. This reagent has found most use as a highly specific oxidant for allylic and benzylic hydroxy groups, and reaction takes place under mild conditions (room temperature) in a neutral solvent (e.g. water, petroleum, acetone, DMF, CH_2Cl_2 or $CHCl_3$). It avoids some of the problems of chromium reagents, which may promote epoxidation of the allylic alcohol or isomerization (*Z* to *E* geometry) of the double bond. For maximum activity it is best to prepare the manganese dioxide immediately prior to use. The best method appears to be by reaction of manganese (II) sulfate with potassium permanganate in alkaline solution; the hydrated manganese dioxide obtained is highly active.

p-Toluenesulfonic acid[1]
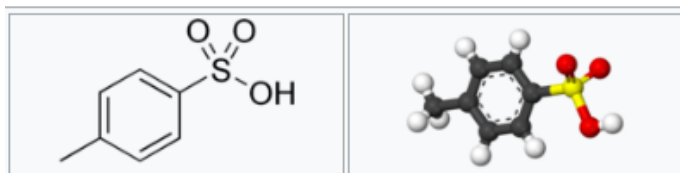
Pyridinium chlorochromate (PCC) is a yellow-orange salt with the formula $[C_5H_5NH]^+[CrO_3Cl]^-$. It is a reagent in organic synthesis used primarily for oxidation of alcohols to form carbonyls. In particular, it has proven to be highly effective in oxidizing primary and secondary alcohols to aldehydes and ketones, respectively.
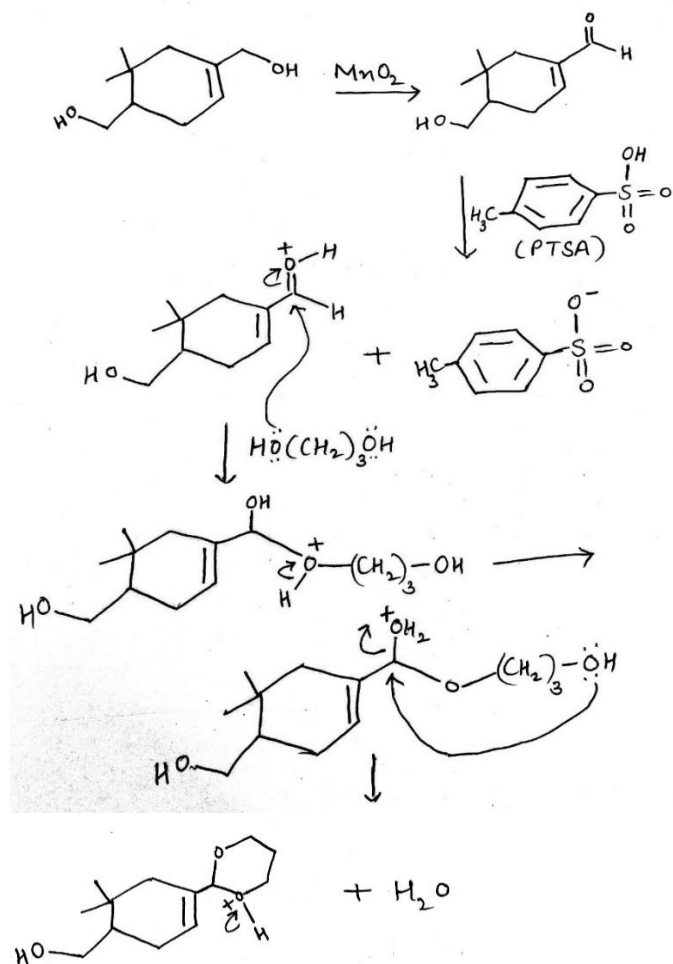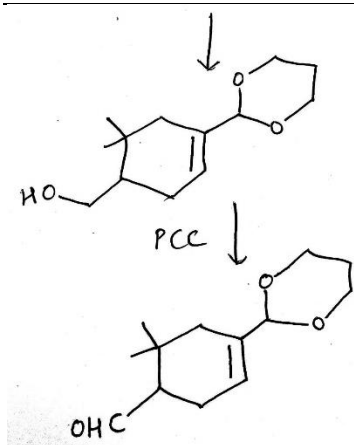
S14. Ans.(c)

Sol. Step 1:

Group 1 metals, such as sodium or lithium, readily give up their single outer-shell electron as they dissolve in solvents such as liquid ammonia or ethanol. Electrons are the simplest reducing agents, and they will reduce carbonyl compounds, alkynes, or aromatic rings—in fact any functional group with a low-energy π* orbital into which the electron can go.

The dissolving metal reduction of aromatic rings is known as the Birch reduction.

The first thing to note is that when lithium or sodium dissolve in ammonia they give an intense blue solution. Blue is the colour of solvated electrons: these group 1 metals ionize to give Li$^+$ or Na$^+$ and e$^-$ (NH$_3$) $_n$-the gaps between the ammonia molecules are just the right size for an electron. With time, the blue colour fades, as the electrons reduce the ammonia to (NH$_2$)$^-$ and hydrogen gas.

Birch reductions use those blue solutions, with their solvated electrons, as reducing agents. The reduction of NH$_3$ to (NH$_2$)$^-$ and H$_2$ is quite slow, and a better electron acceptor will get reduced in preference. The electrons go into benzene's lowest lying antibonding orbital (its LUMO).

The radical anion is very basic, and it picks up a proton from the ethanol that is in the reaction mixture. The molecule is now no longer anionic, but it is still a radical. It can pick up another electron, which pairs with the radical to give an anion, which is quenched again by the proton source (ethanol).

Further questions of regioselectivity arise when there are substituents around the aromatic ring.

Electron-withdrawing groups promote *ipso, para* reduction while electron-donating groups promote *ortho, meta* reduction. The explanation must lie in the distribution of electron density in the intermediate radical anions. Electron-donating groups stabilize *ortho* and *meta* electron density.
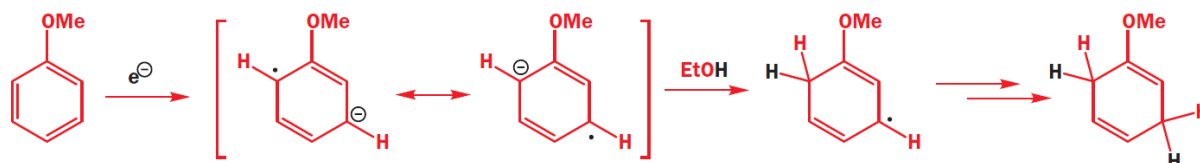
Step 2:

One of the most studied catalytic systems is the Rh(I) complex [RhCl (PPh$_3$)$_3$], which is often referred to as **Wilkinson's catalyst**. This useful catalyst hydrogenates a wide variety of alkenes and alkynes at pressures of hydrogen close to 1 atm or less at room temperature. The dominant cycle for the hydrogenation of terminal alkenes by Wilkinson's catalyst is shown
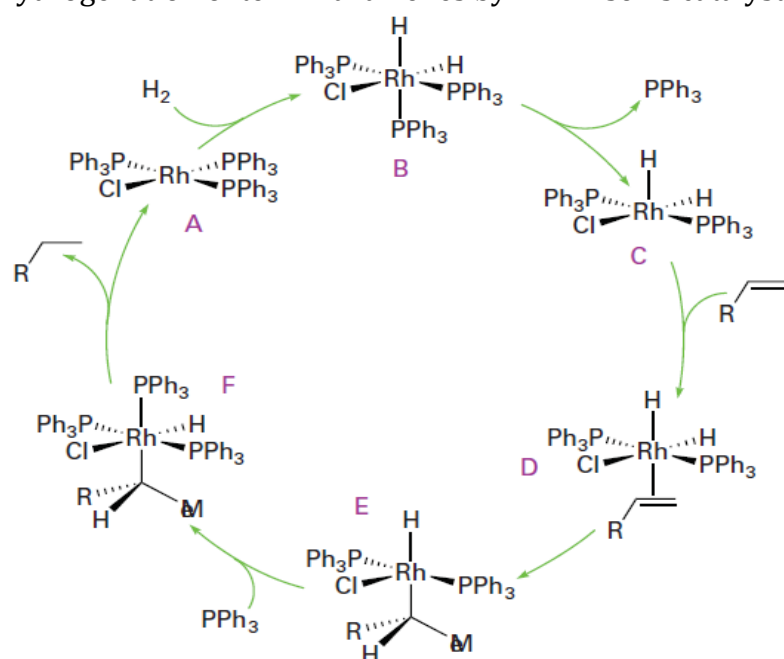
The catalytic cycle for the hydrogenation of terminal alkenes by Wilkinson's catalyst.

It involves the oxidative addition of H$_2$ to the 16-electron complex [RhCl (PPh$_3$)$_3$] (A), to form the 18-electron dihydrido complex (B). The dissociation of a phosphine ligand from (B) results in the formation of the coordinatively unsaturated complex (C), which then forms the alkene complex (D). Hydrogen transfer from the Rh atom in (D) to the coordinated alkene yields a transient 16-electron alkyl complex (E). This complex takes on a phosphine ligand to produce (F), and hydrogen migration to carbon results in the reductive elimination of the alkane and the reformation of (A), which is set to repeat the cycle. A parallel but slower cycle (which is not shown) is known in which the order of H$_2$ and alkene addition is reversed. Another cycle is known, based around the 14-electron intermediate [RhCl(PPh$_3$)$_2$]. Even though there is very little of this species present, it reacts much faster with hydrogen than [RhCl(PPh$_3$)$_3$] and makes a significant contribution to the catalytic cycle. In this cycle, (E) would eliminate alkane directly, regenerating [RhCl(PPh$_3$)$_2$], which rapidly adds H$_2$ to give (C).

Wilkinson's catalyst is highly sensitive to the nature of the phosphine ligand and the alkene substrate. The alkene must be just the right size: highly hindered alkenes or the sterically unencumbered ethene are not hydrogenated by the catalyst, presumably because the sterically crowded alkenes do not coordinate and ethene forms a strong complex that does not react further.

Step 3:

Hydroboration–oxidation reaction is a two-step hydration reaction that converts an alkene into an alcohol. The process results in the syn addition of a hydrogen and a hydroxyl group where the double bond had been. Hydroboration–oxidation is an anti-Markovnikov reaction, with the hydroxyl group attaching to the less-substituted carbon.

The general form of the reaction is as follows:
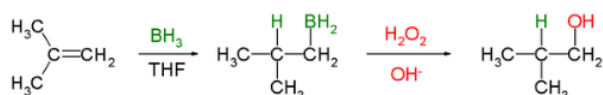
Hydroboration step: In the first step, borane (BH_3) adds to the double bond, transferring one of the hydrogen atoms to the carbon adjacent to the one that becomes bonded to the boron. This hydroboration is repeated two additional times, successively reacting each B–H bond so that three alkenes add to each BH_3. The resulting trialkylborane is treated with hydrogen peroxide in the second step. This process replaces the B-C bonds with HO-C bonds. The boron reagent is converted to boric acid.

Hexanol synthesis
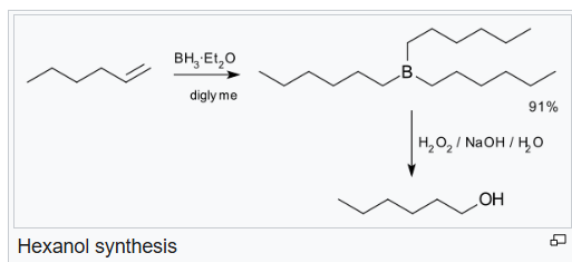
Oxidation step: In the second step of the reaction sequence, the nucleophilic hydroperoxide anion attacks the boron atom. Alkyl migration to oxygen gives the alkyl borane with retention of stereochemistry (in reality, the reaction occurs via the trialkyl borate $B(OR)_3$, rather than the monoalkyl borinic ester BH_2OR).

Hydroboration–oxidation mechanism
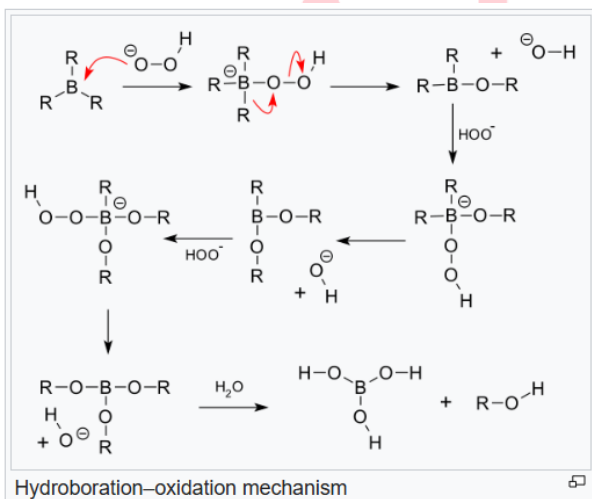
The 'H' atom in the reaction comes from B_2H_6, the 'O' atom comes from hydrogen peroxide (H_2O_2) whereas the O attached 'H' atom comes from the solvent (refer mechanism).

S15. Ans.(d)
Sol. Unpaired electrons are desperate to be paired up again. This means that radicals usually have a very short lifetime; they don't survive long before undergoing a chemical reaction.

Electron spin resonance, or **ESR** (also known as EPR, electron paramagnetic resonance) not only confirms that radicals do exist, but it can also tell us quite a lot about their structure. ESR tells us that the methyl radical is planar: the carbon atom must therefore be sp^2 hybridized, with the unpaired electron in a p orbital. We can represent this in an energy level diagram.

energy level diagram for the methyl radical

E

unoccupied σ*(C–H) orbitals

singly occupied p orbital

doubly occupied σ(C–H) orbitals

$CH_3\bullet$ (like all radicals) has an orbital containing one electron, which we call a Singly Occupied Molecular Orbital (SOMO).

As with all molecules, it is the energy of the electrons in the molecular orbitals of the radical that dictate its stability. Any interaction that can decrease the energy levels of the filled molecular orbitals increases the stability of the radical (in other words, decreases its reactivity).
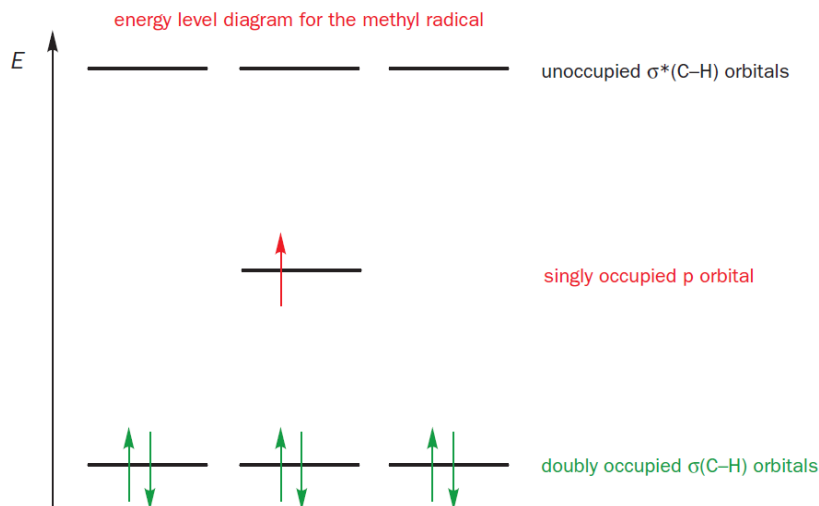
Radicals are stabilized by conjugating, electron-withdrawing, and electron donating groups

Let us consider first what happens when a radical centre finds itself next to an electron-withdrawing group. Groups like C=O and C≡N are electron-withdrawing because they have a low-lying empty π* orbital. By overlapping with the (usually p) orbital containing the radical (the SOMO), two new molecular orbitals are generated. One electron (the one in the old SOMO) is available to fill the two new orbitals. It enters the new SOMO, which is of lower energy than the old one, and the radical experiences stabilization because this electron drops in energy.

radical stabilized by electron-withdrawing group

π* orbital of electron-withdrawing group

SOMO of radical (p orbital)

energy of radical drops because electron is in a lower-energy orbital

new SOMO is of lower energy
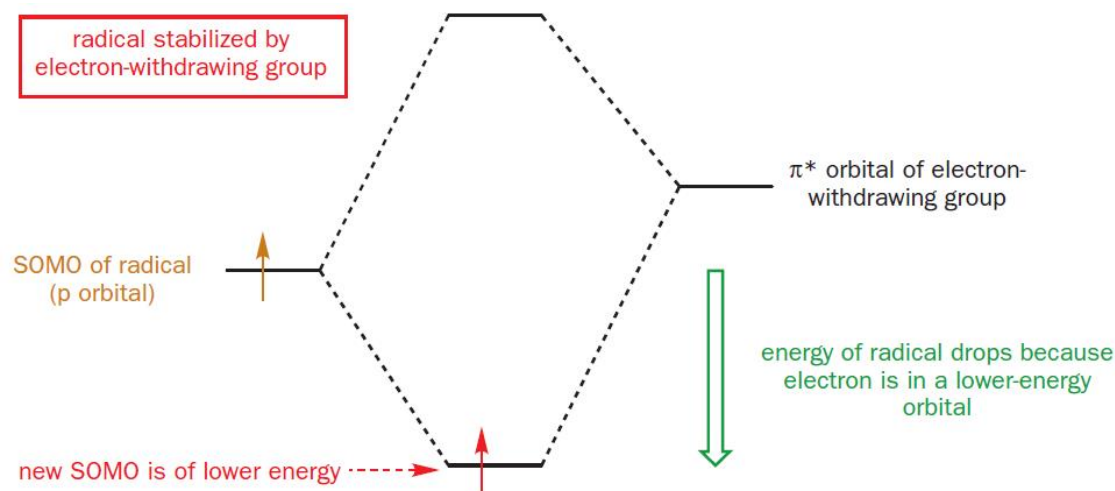
We can analyse what happens with electron-rich groups, such as RO groups, electron-donating groups (including alkyl groups with C–H s bonds), in a similar way.

Ether oxygen atoms have relatively high-energy filled n orbitals, their lone pairs. Interacting this with the SOMO again gives two new molecular orbitals. Three electrons are available to fill them. The SOMO is now higher in energy than it was to start with, but the lone pair is lower. Because two electrons have dropped in energy and only one has risen, there is an overall stabilization of the system, even though the new SOMO is of higher energy than the old one.
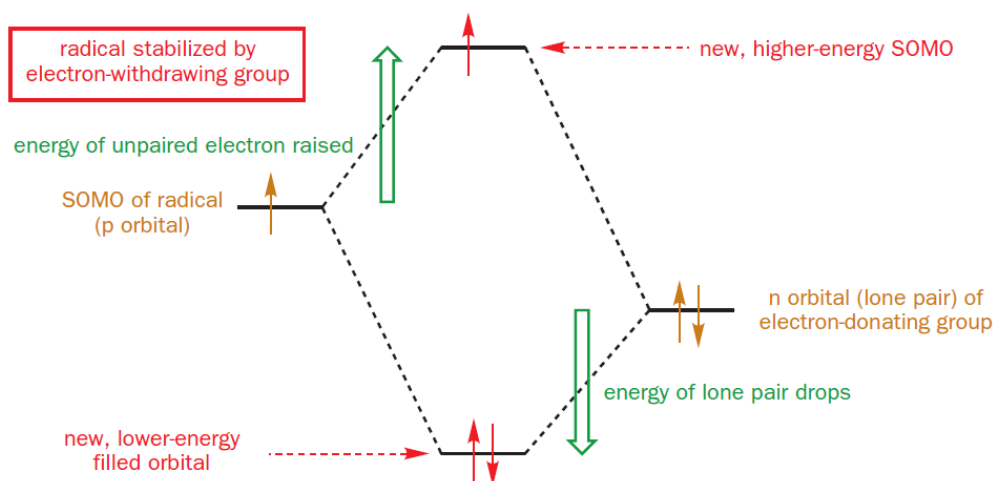
Electron deficient radical will react with electron rich substituted alkene and electron rich radical will react with electron deficient substituted alkene.

S16. Ans.(b)
Sol. Nuclear magnetic resonance (NMR) spectroscopy is a resonance technique involving absorption of radiofrequency energy. The magnetic environment of a nucleus affects its resonance frequency and allows structural information to be deduced.

Structural assignment is often helped by the observation of the spin–spin coupling, which gives rise to multiplets in the spectrum due to interactions between nuclear spins. Spin–spin coupling arises when the orientation of the spin of a nearby nucleus affects the energy of another nucleus and causes small changes in the location of the latter's resonance. A multiplet of 2I+1 lines is obtained when a spin-1/2 nucleus (or a set of symmetry-related spin-1/2 nuclei) is coupled to a nucleus of spin I. The coupling of the nuclear spins of different elements is called heteronuclear coupling. Homonuclear coupling between nuclei of the same element is detectable when the nuclei are in chemically inequivalent locations.

J-couplings are mediated through chemical bonds connecting two spins. It is an indirect interaction between two nuclear spins that arises from hyperfine interactions between the nuclei and local electrons. In NMR spectroscopy, J-coupling contains information about relative bond distances and angles. Most importantly, J-coupling provides information on the connectivity of chemical bonds. The J coupling (always reported in Hz) is field-independent (i.e. J is constant at different external magnetic field strength), and is mutual (i.e. $J_{AX} = J_{XA}$).

In a typical hydrocarbon, the spin of a hydrogen nucleus in one C-H bond is coupled to the spins of those hydrogens in adjacent C-H bonds. These H-C-C-H couplings are usually called vicinal couplings because the hydrogens are on neighboring carbon atoms (Latin *vicinus* = "neighbor"). Vicinal couplings are three-bond couplings and have a coupling constant designated as [3]J.

In the first case, H_b will first couple with three H_c protons to give a quartet. After that, H_b will couple with H_a to give a doublet.

In the second case, H_b will couple with H_a and three H_c protons to give a quintet.
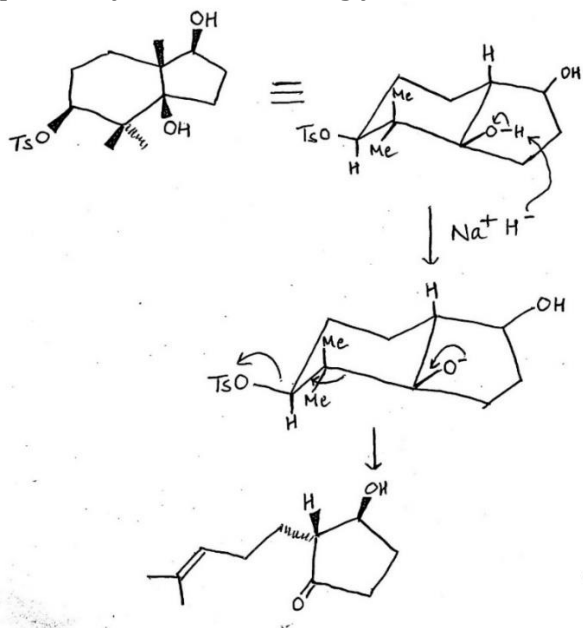
S17. Ans.(b)

Sol. Fragmentation reactions, which are similar to β-elimination reactions, can be useful for the formation of alkenes, particularly from carbocyclic compounds. Fragmentation reactions occur most easily from conformationally locked 1,3-difunctionalized compounds, in which the breaking C-X and C-C bonds (highlighted) are aligned antiperiplanar.
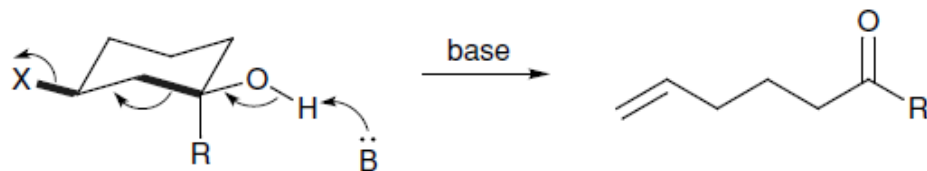
X = leaving group, *e.g.* OSO_2Me

Fragmentation reactions may be used to prepare cyclic or acyclic alkenes from cyclic precursors. The stereochemistry of the alkene can be set up by controlling the relative stereochemistry of the cyclic substrate, a process that is normally relatively easy.
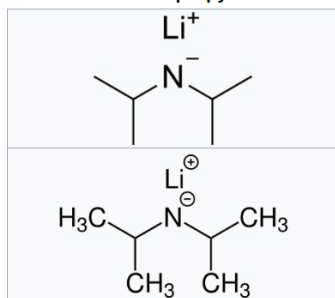
Sodium hydride is the chemical compound with the empirical formula NaH. This alkali metal hydride is primarily used as a strong yet combustible base in organic synthesis.
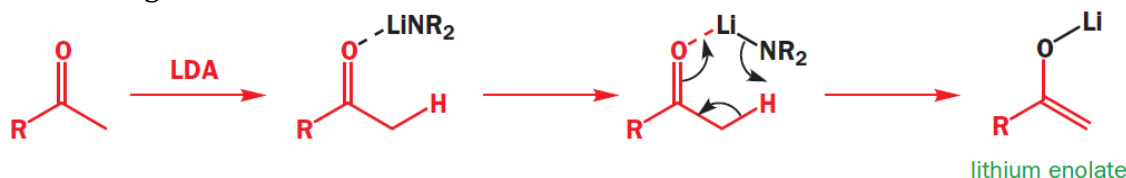

S18. Ans.(c)

Sol. Lithium diisopropylamide (commonly abbreviated LDA) is a chemical compound with the molecular formula $LiN(CH(CH_3)_2)_2$. It is used as a strong base and has been widely utilized due to its good solubility in non-polar organic solvents and non-nucleophilic nature.

Lithium enolates are usually made at low temperature in THF with a hindered lithium amide base (often LDA) and are stable under those conditions because of the strong O–Li bond. The formation of the enolate begins with Li–O bond formation before the removal of the proton from the a position by the basic nitrogen atom.

LDA is too hindered to attack C=O, so it attacks C–H instead. And, if there is a choice of C–H bonds, it will attack the least hindered possible. It will also prefer to attack more acidic C–H bonds, and C–H bonds on less substituted carbons are indeed more acidic.

The central carbon in 1,3-dicarbonyl compound is known as an activated methylene group. This is because, owing to the structure, the carbon is especially acidic and can easily be deprotonated to form a methylene group.

The Robinson annulation is a chemical reaction used in organic chemistry for ring formation. It was discovered by Robert Robinson as a method to create a six membered ring by forming three new carbon–carbon bonds. The method uses a ketone and a methyl vinyl ketone to form an α,β-unsaturated ketone in a cyclohexane ring by a Michael addition followed by an aldol condensation. This procedure is one of the key methods to form fused ring systems.

The mechanism combines two important reactions. The first stage is the formation of the stable enolate and the conjugate addition to the enone. The second stage is the formation of a new enolate on the other side of the ketone from the first. Note that the original enolate, the intermediate in the conjugate addition, can cyclize to give only an unstable four-membered ring so this cyclization would be reversible. The next intermediate, the aldol product, is often isolated from Robinson annelations. The final stage is dehydration of the aldol and an E1cB reaction that involves the carbonyl group as in a standard aldol reaction. Another enolate must form in the same position as the last.

Additional Knowledge

In organic chemistry, the Michael reaction or Michael 1,4 addition is a reaction between a Michael donor (an enolate or other nucleophile) and a Michael acceptor (usually an α,β-unsaturated carbonyl) to produce a Michael adduct by creating a carbon-carbon bond at the acceptor's β-carbon.
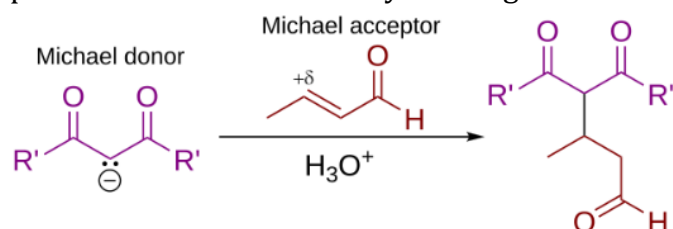
An aldol condensation is a condensation reaction in organic chemistry in which two carbonyl moieties (of aldehydes or ketones) react to form a β-hydroxyaldehyde or β-hydroxyketone (an aldol reaction), and this is then followed by dehydration to give a conjugated enone.

The overall reaction equation is as follows (where the Rs can be H)
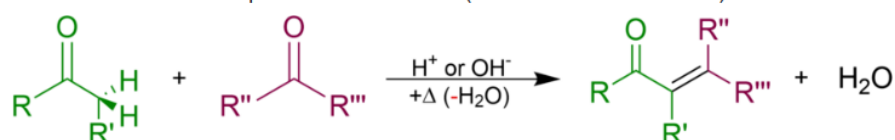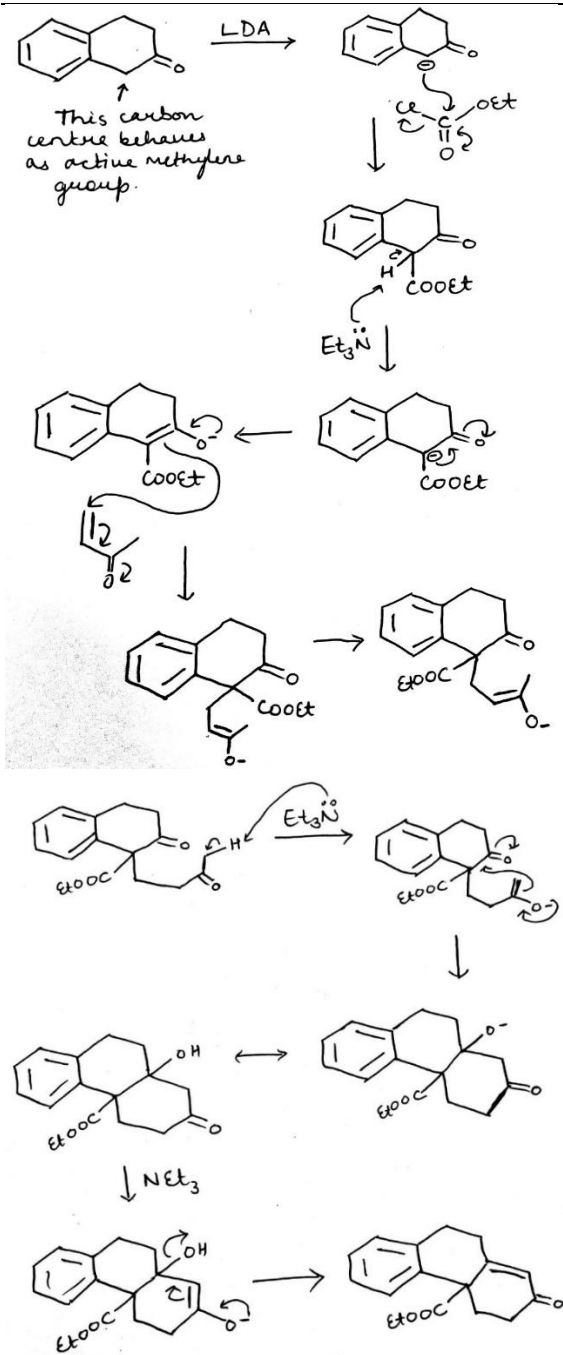
S19. Ans.(d)
Sol. Nuclear magnetic resonance (NMR) spectroscopy is a resonance technique involving absorption of radiofrequency energy. The magnetic environment of a nucleus affects its resonance frequency and allows structural information to be deduced.

Structural assignment is often helped by the observation of the spin–spin coupling, which gives rise to multiplets in the spectrum due to interactions between nuclear spins. Spin–spin coupling arises when the orientation of the spin of a nearby nucleus affects the energy of another nucleus and causes small changes in the location of the latter's resonance. A multiplet of $2I+1$ lines is obtained when a spin-1/2 nucleus (or a set of symmetry-related spin-1/2 nuclei) is coupled to a nucleus of spin I. The coupling of the nuclear spins of different elements is called heteronuclear coupling. Homonuclear coupling between nuclei of the same element is detectable when the nuclei are in chemically inequivalent locations.

Routinely, ^{31}P NMR spectroscopy is used in characterizing P-containing species.

All of the ^{31}P found in chemically identical environments within a molecule are chemically equivalent. On the other hand, a molecule that has sets of protons that are chemically distinct from one another may give rise to a different absorption peak from each set, in which case the sets of protons are chemically nonequivalent.
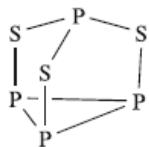
P_4S_3
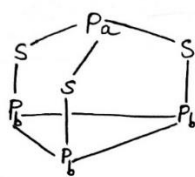
P_a : $2nI + 1 = 2 \times 3 \times \frac{1}{2} + 1 = 4$

P_a will show a quartet due to coupling with three P_b

P_b : $2nI + 1 = 2 \times 1 \times \frac{1}{2} + 1 = 2$

P_b will show a doublet due to coupling with one P_a.
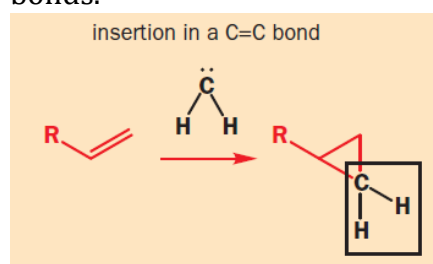
S20. Ans.(d)

Sol. Carbenes are neutral species containing a carbon atom with only six valence electrons. Carbenes have six electrons: two in each bond and two nonbonding electrons, which are often represented as :CR$_2$.
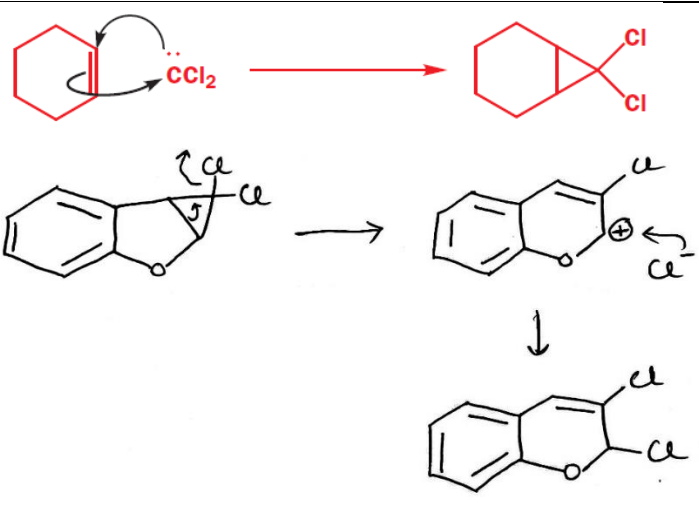
Carbenes are usually formed from precursors by the loss of small, stable molecules.

Decarboxylation of sodium trichloroacetate happens at about 80 °C in solution.
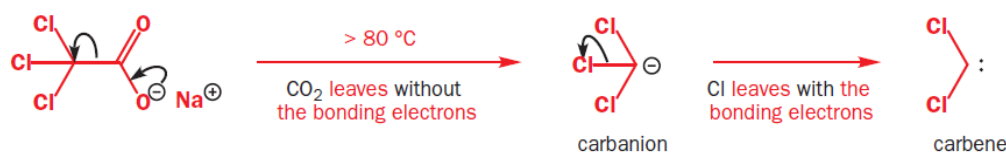
Carbenes are extremely reactive species. They are trapped by alcohols to make ethers, but more importantly they will react with alkenes to make cyclopropanes, and they will also insert into C–H bonds.