

Target IIT-JAM-2017

Test Series-2

ORGANIC CHEMISTRY
[SOLUTIONS]

Booklet Code: **B**

Duration: 2:00 Hours

CHEMISTRY-CY

Date: 08-01-2017

Maximum Marks: 100

Read the following instructions carefully:

- 1 Attempt all the questions.
- 2 **Section-A** contains **30** Multiple Choice Questions (MCQ). Each question has 4 choices (a), (b), (c) and (d), for its answer, out of which **ONLY ONE** is correct. From **Q.1 to Q.10** carries 1 Marks and **Q.11 to Q.30** carries 2 Marks each.
- 3 **Section-B** contains **10** Multiple Select Questions (MSQ). Each question has 4 choices (a), (b), (c) and (d) for its answer, out of which **ONE or MORE than ONE** is/are correct. For each correct answer you will be awarded **2 marks**.
- 4 **Section-C** contains **20** Numerical Answer Type (NAT) questions. From **Q.41 to Q.50** carries **1 Mark** each and **Q.51 to Q.60** carries **2 Marks** each. For each NAT type question, the value of answer in between 0 to 9.
- 5 In all sections, questions not attempted will result in zero mark. In Section-A (MCQ), wrong answer will result in negative marks. For all **1 mark** questions, **1/3 marks** will be deducted for each wrong answer. For all **2 marks** questions, **2/3 marks** will be deducted for each wrong answer. In Section-B (MSQ), there is no negative and no partial marking provision. There is no negative marking in Section-C (NAT) as well.

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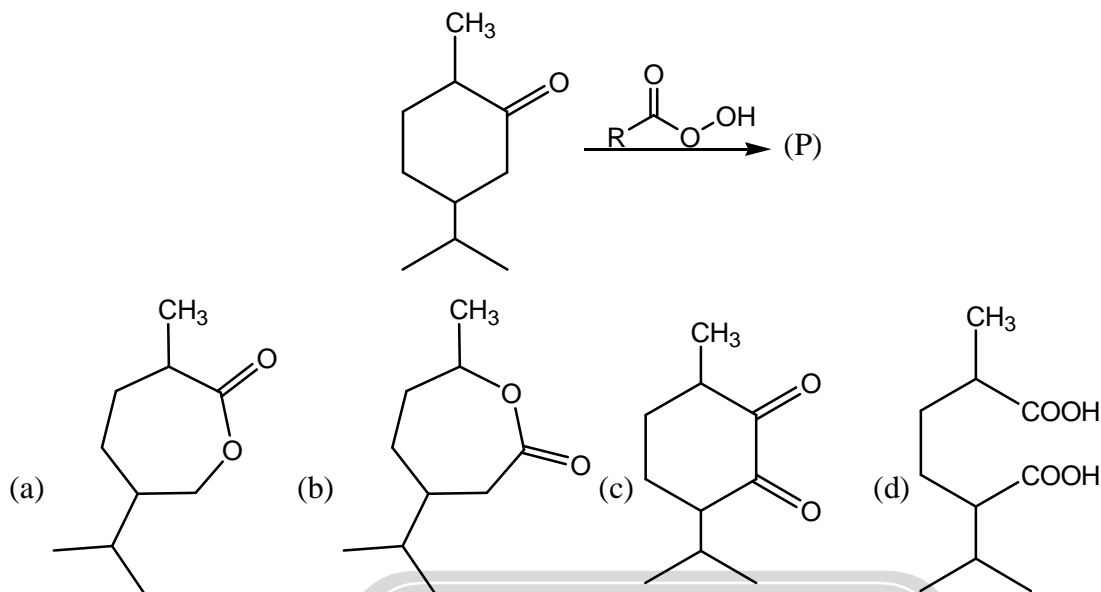
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Section-A : Multiple Choice Questions (MCQ)

Q.1 to Q.10: Carry 1 Mark each.

1. The major product (P) formed will be



Soln. It is an example of Baeyer villiger oxidation and 2° alkyl group has more migrating aptitude as compare to 1° alkyl group.

Correct option is (b)

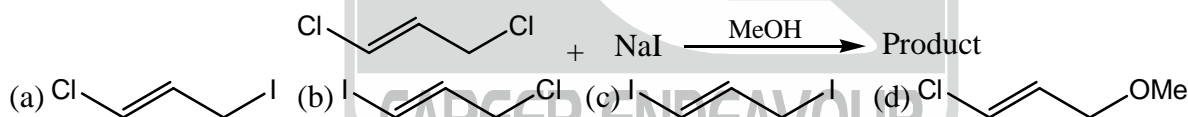
2. Which of the following is most reactive as a nucleophile

- (a) PhO^- (b) PhS^- (c) $\text{Ph}-\text{CH}_2-\text{O}^-$ (d) $\text{Ph}-\text{CH}_2-\ddot{\text{N}}\text{H}_2$

Soln. Basicity and Nucleophilicity move anti-parallel in a group from up to down.

Correct option is (b).

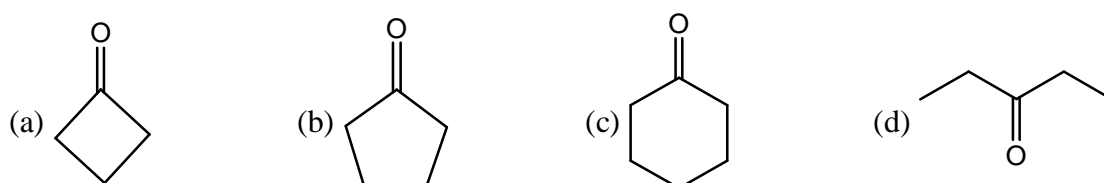
3. Which compound is the major product of the following reaction



Soln. This reaction with a powerful nucleophile I^- , will be by the $\text{S}_{\text{N}}2$ mechanism. In substrate, an allylic chloride and a vinylic chloride, allylic system are very reactive by the $\text{S}_{\text{N}}2$ mechanism and vinylic systems are unreactive.

Correct option is (a).

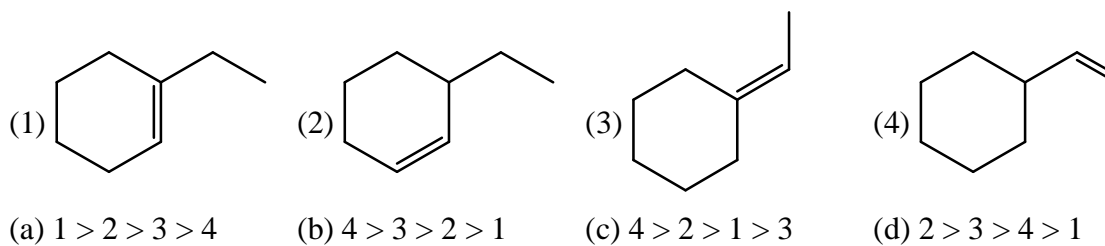
4. Which ketone has the largest equilibrium constant for hydration



Soln. The carbonyl carbon changes from sp^2 to sp^3 hybridisation in the conversion of a ketone of its hydrate, so there is a relief of ring strain upon the hydration of cyclobutanone.

Correct option is (a).

5. Decreasing order of heat of hydrogenation in the following Alkenes.



Soln. Heat of hydrogenation $\propto \frac{1}{\alpha\text{-hydrogen}}$

Correct option is (c)

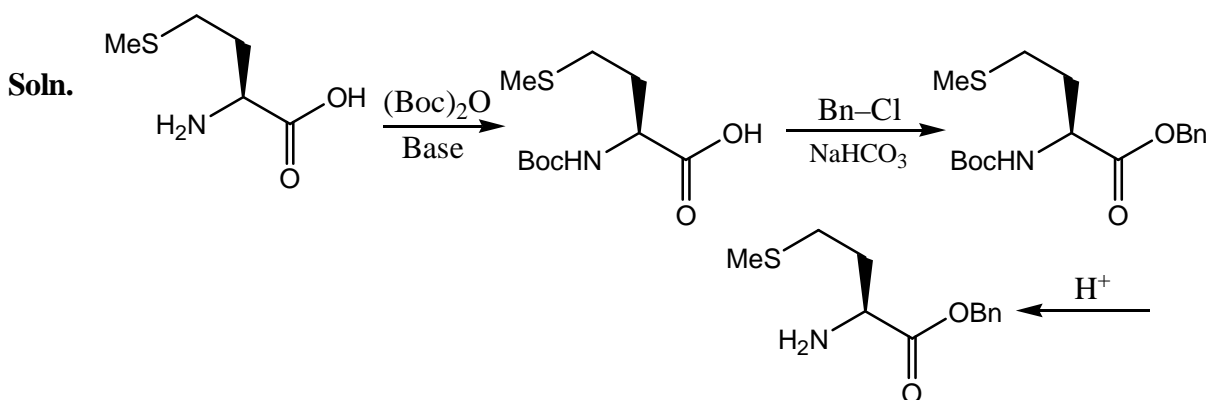
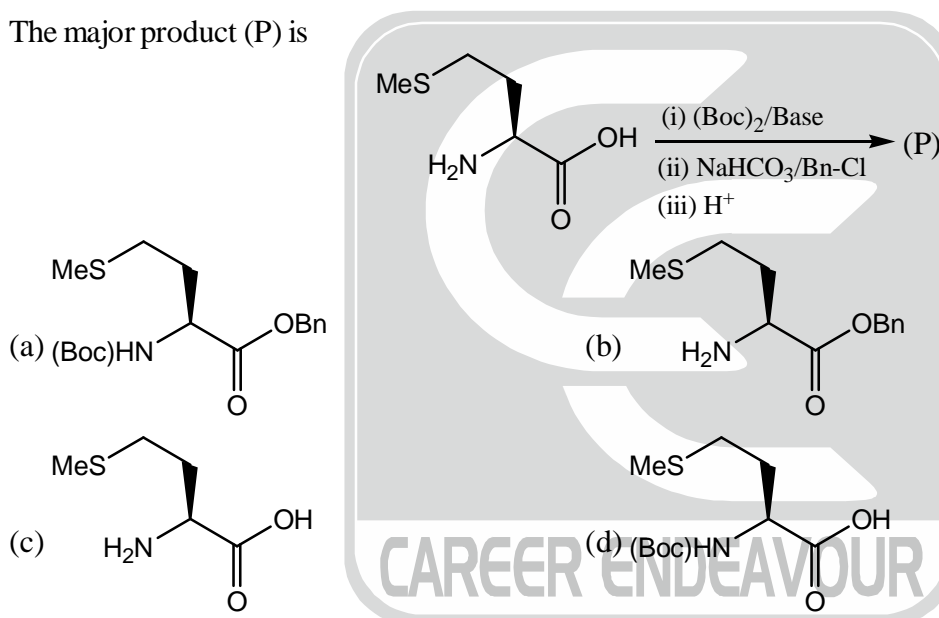
6. The incorrect statement(s) about the furan is/are

- (a) Furan gives electrophilic substitution reaction faster than benzene
 (b) Furan is less aromatic than benzene
 (c) Furan gives poly bromination with Br_2 in non-alcoholic solvents.
 (d) Furan does not give Diels-Alder reaction

Soln. Furan gives Diels-Alder reaction, act as Diene.

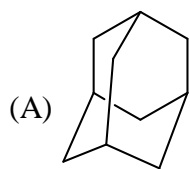
Correct option is (d)

7. The major product (P) is

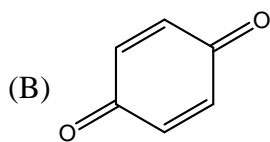


Correct option is (b)

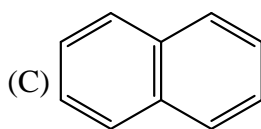
8. How many signals would you expect in the ^{13}C NMR of the following compounds, respectively



(a) 3, 2, 3



(b) 2, 2, 3



(c) 3, 4, 2

(d) 2, 4, 3

Soln. ^{13}C NMR in

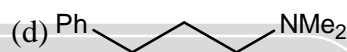
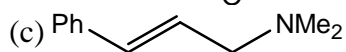
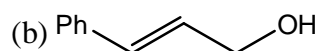
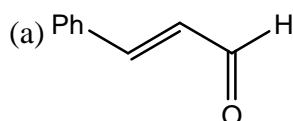
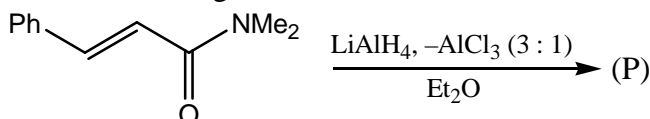
A = 2 signal

B = 2 signal

C = 3 signal

Correct option is (b)

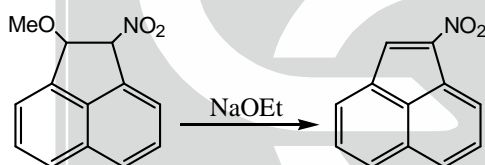
9. The major product formed in the following reaction



Soln. Reduction with lithium aluminium hydride-aluminium chloride (3 : 1) provide a good route from α, β unsaturated carbonyl compounds to unsaturated amines.

Correct option is (c).

10. The reaction given below is an example of



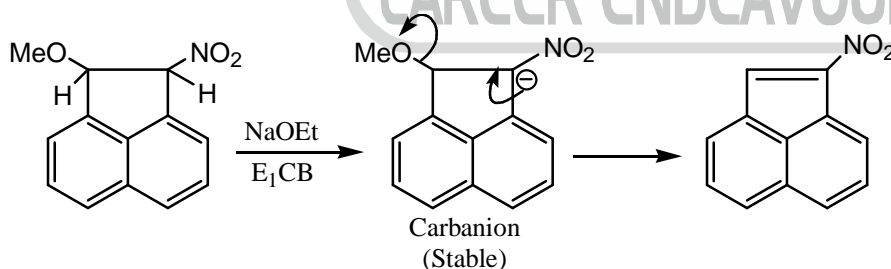
(a) E_2 -elimination

(b) E_1 -elimination

(c) syn-elimination

(d) E_1CB -elimination

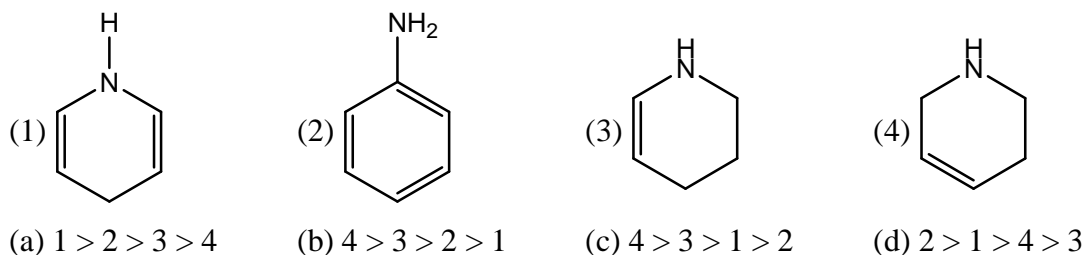
Soln. Chemical reaction involved in the above transformation can be illustrated as



Correct answer: (d)

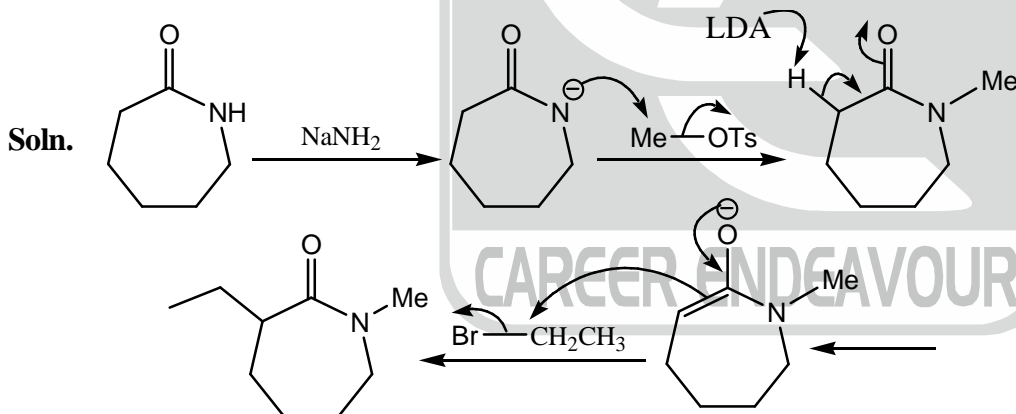
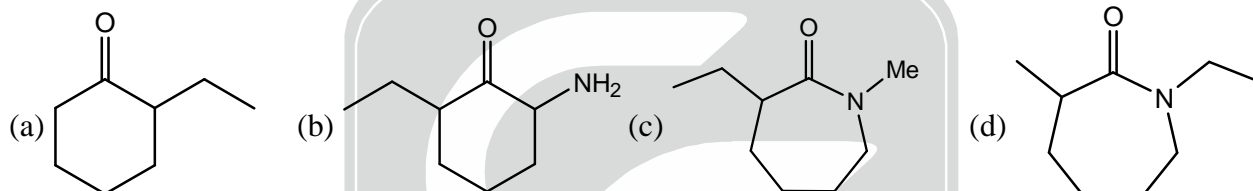
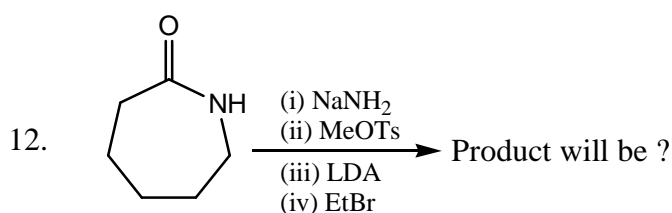
Q.11 to Q.30: Carry 2 Marks each.

11. Order of basicity in following compound will be



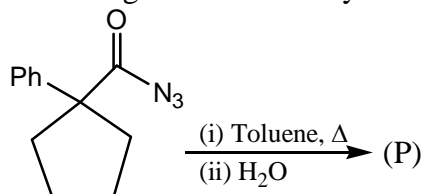
Soln. If the lonepair of N involves in resonance than basicity of N is decrease. Hence, in the compound (4) lone pair of nitrogen atom does not involve in the resonance, so most basic in nature.

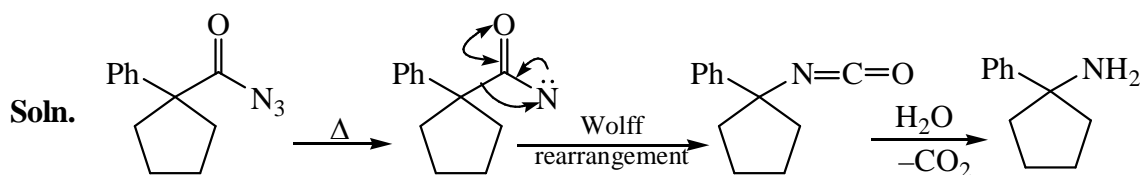
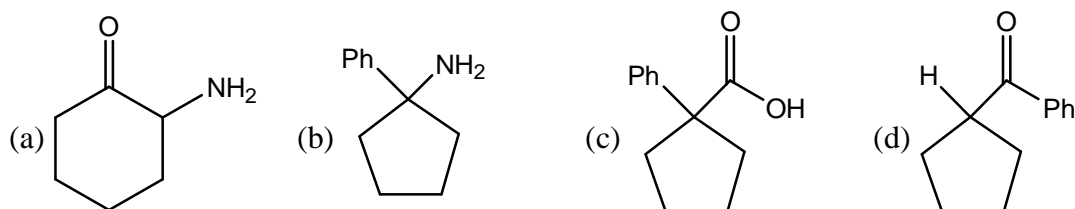
Correct option is (c)



Correct option is (c)

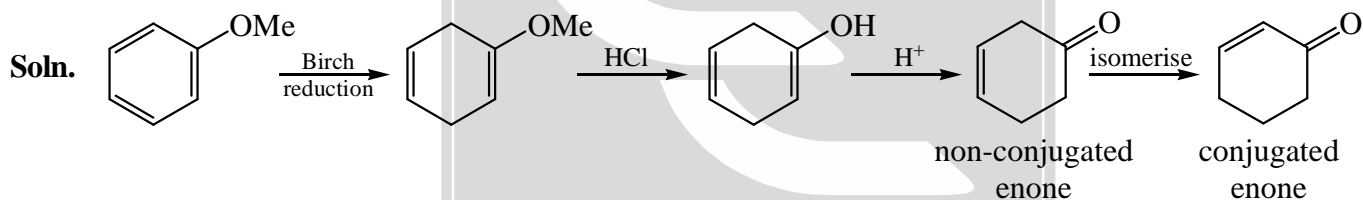
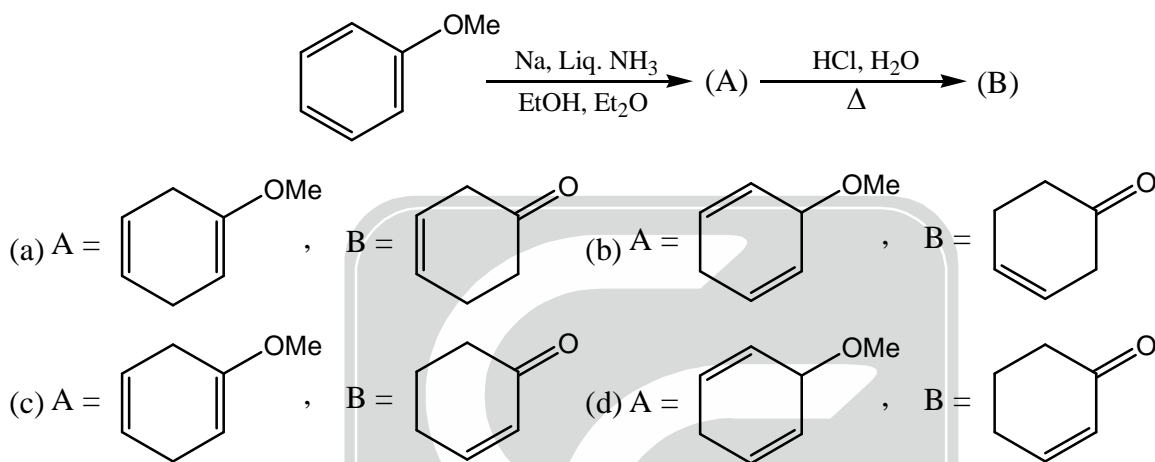
13. Which is the major product of the following reaction of an acyl azide?





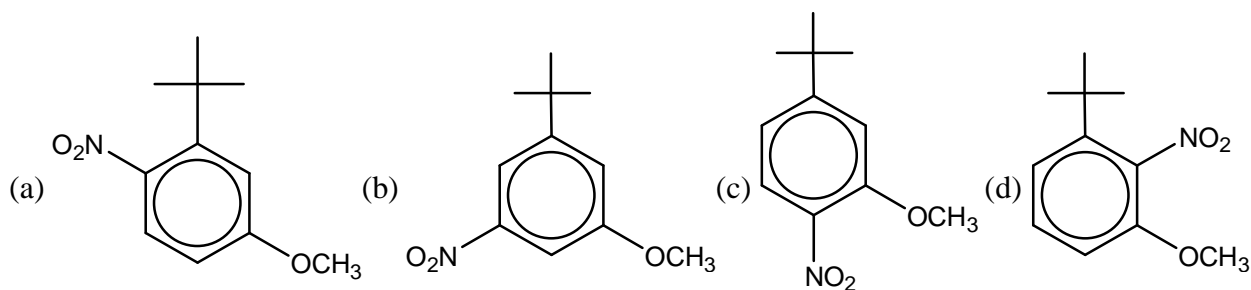
Correct option is (b).

14. Which combination of compounds in a-d identifies A and B in the following reaction



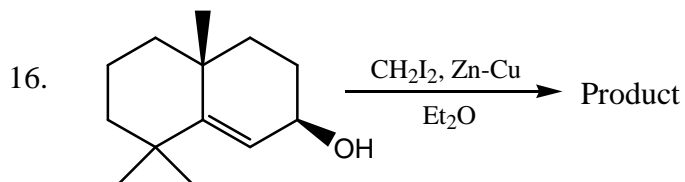
Correct option is (c).

15. Which is obtained as the main product upon reaction of m-t-butylanisole (1-t-butyl-3-methoxybenzene) with conc. ($\text{HNO}_3 + \text{H}_2\text{SO}_4$)

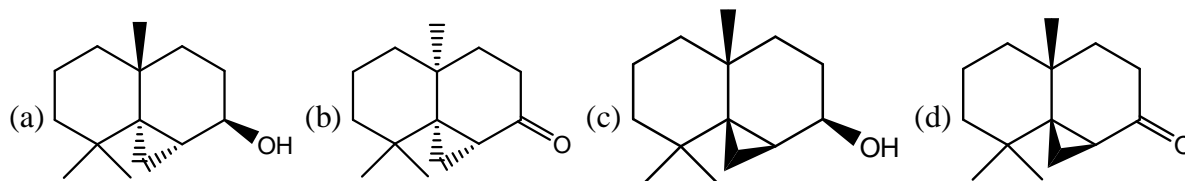


Soln. In between t-butyl group and methoxy group, OCH_3 is strong activating group and $-\text{NO}_2$ group occupy to its ortho position.

Correct option is (c)

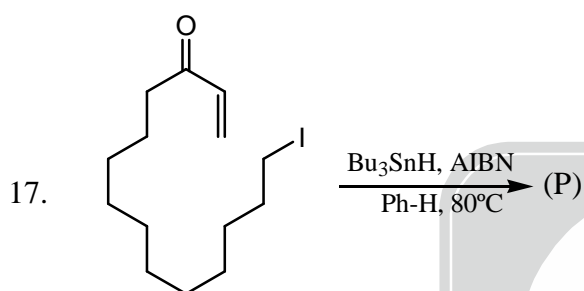


The major product formed will be

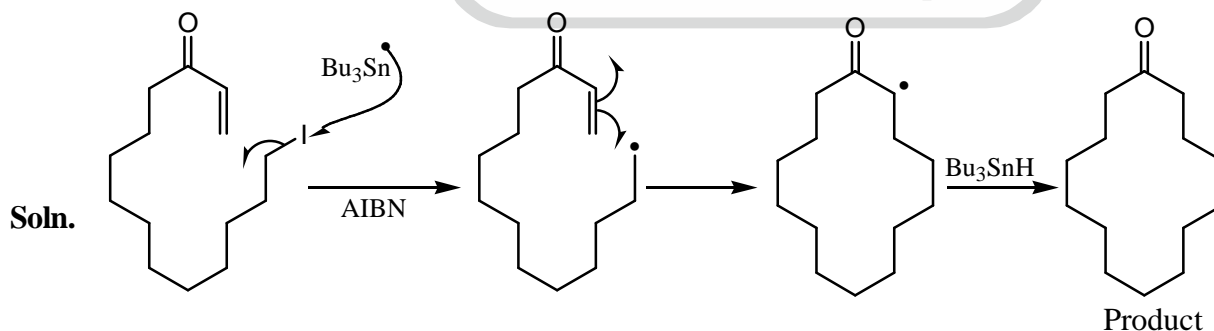
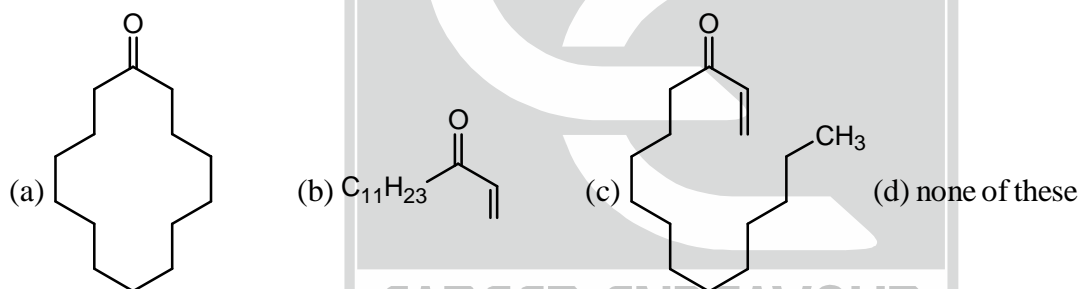


Soln. Since $-\text{OH}$ is polar group. So, Simmons smith reagent will attack from the same side of $-\text{OH}$ group due chelation between O and Zn metal.

Correct option is (c)

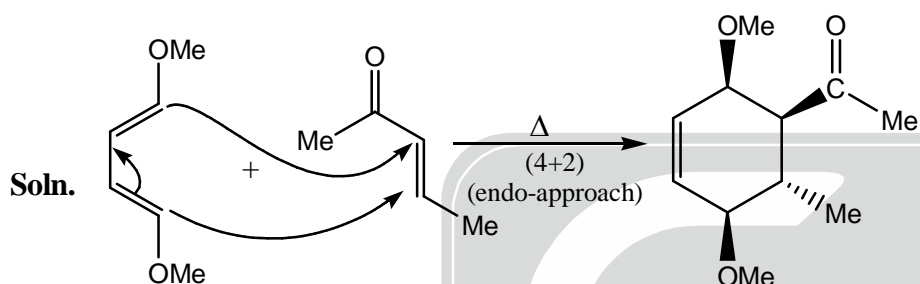
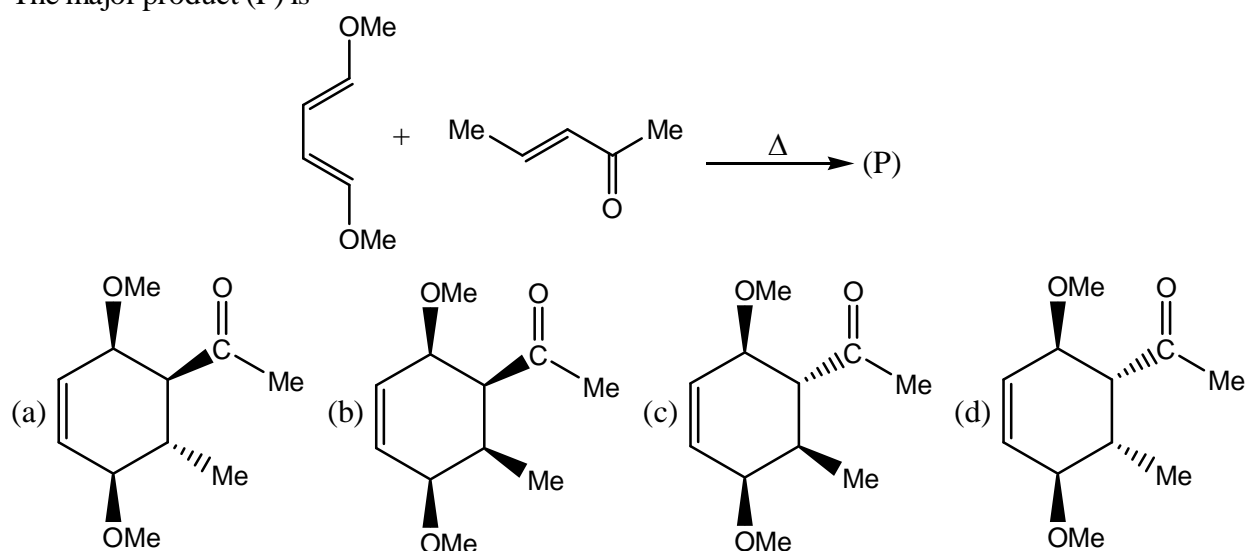


The major product formed in the above reaction is



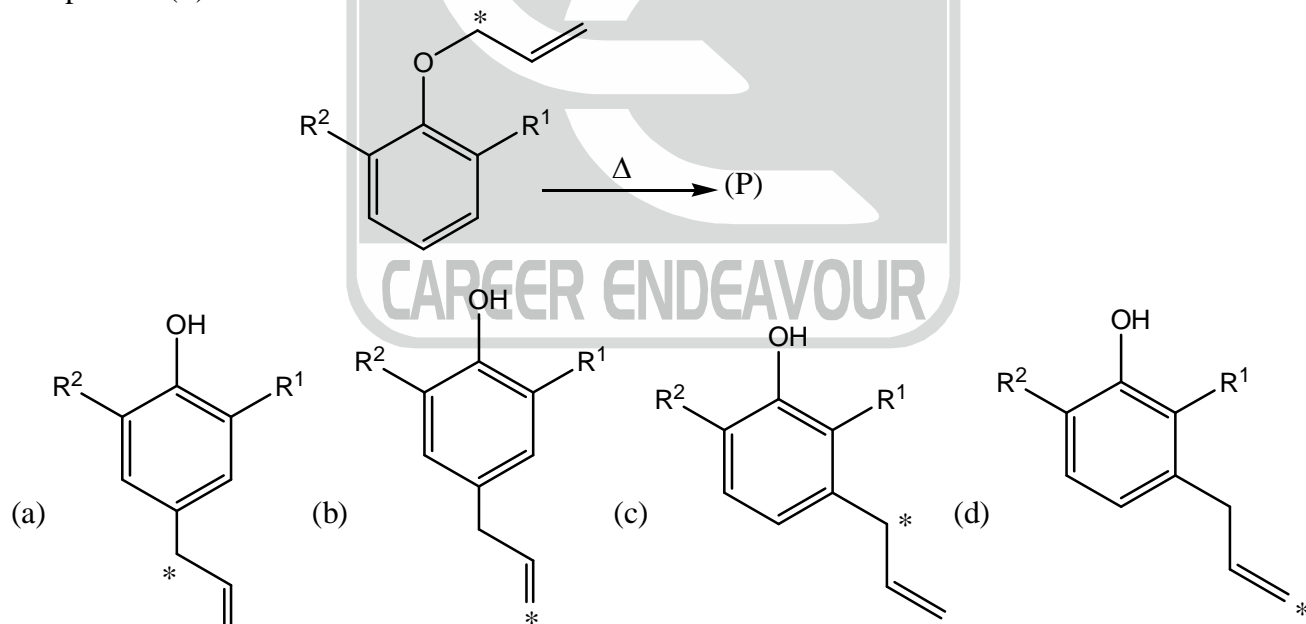
Correct option is (a)

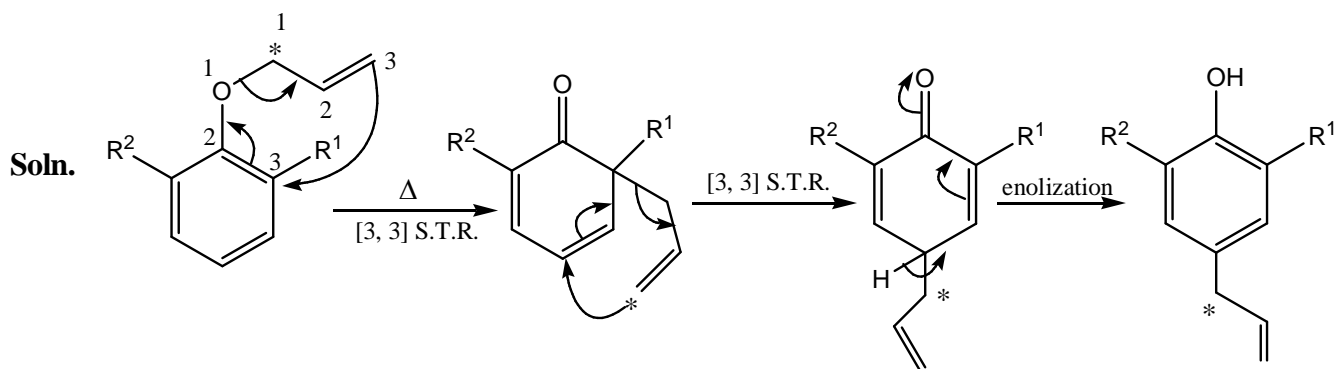
18. The major product (P) is



Correct option is (a)

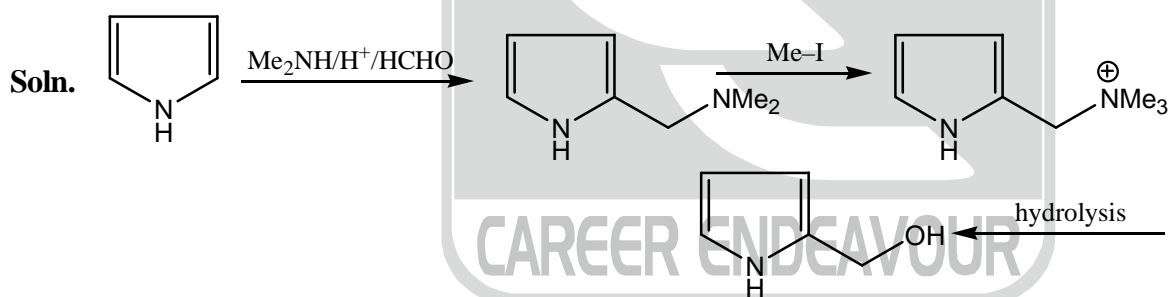
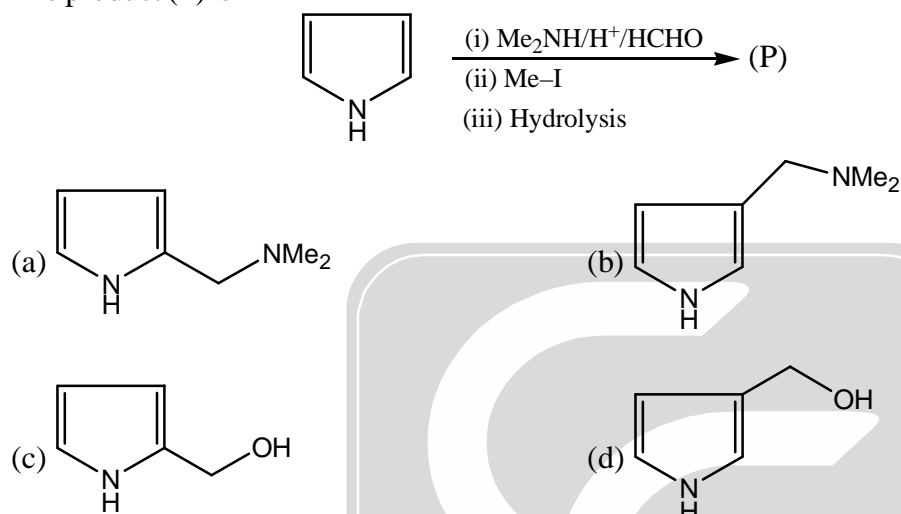
19. The product (P) is





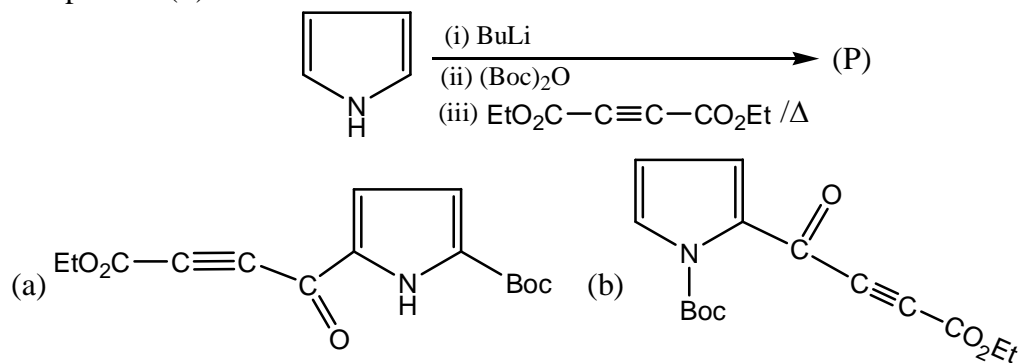
Correct option is (a)

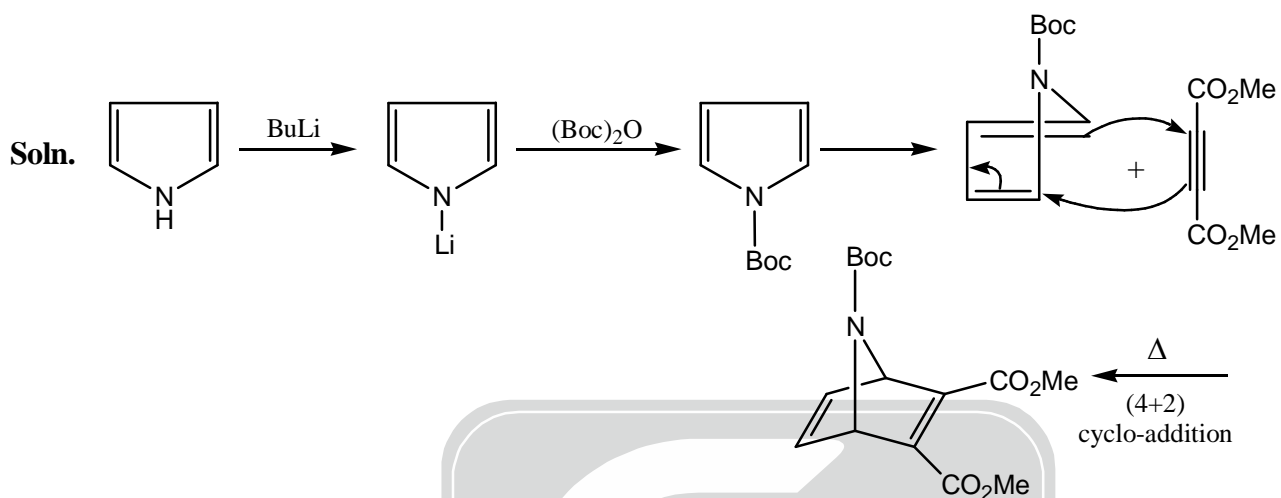
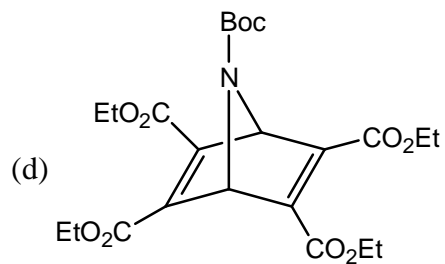
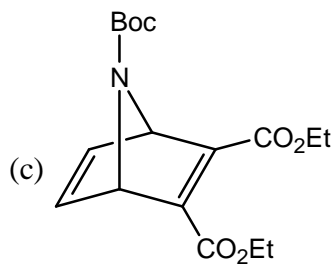
20. The product (P) is



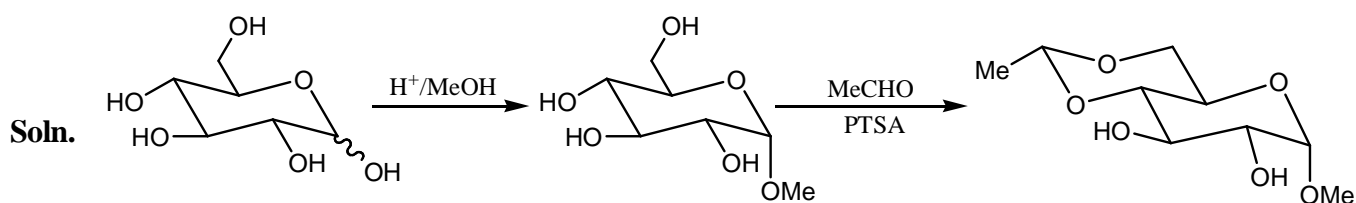
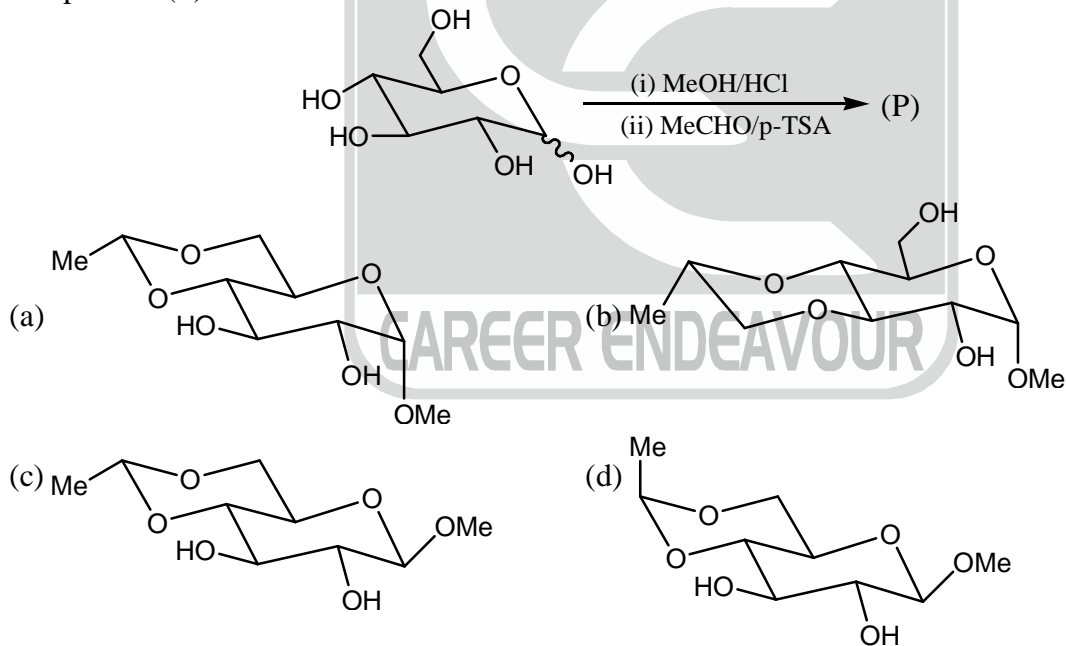
Correct option is (c)

21. The product (P) is



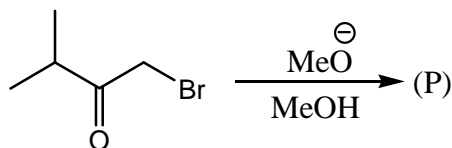


22. **Correct option is (c)**
The product (P) is



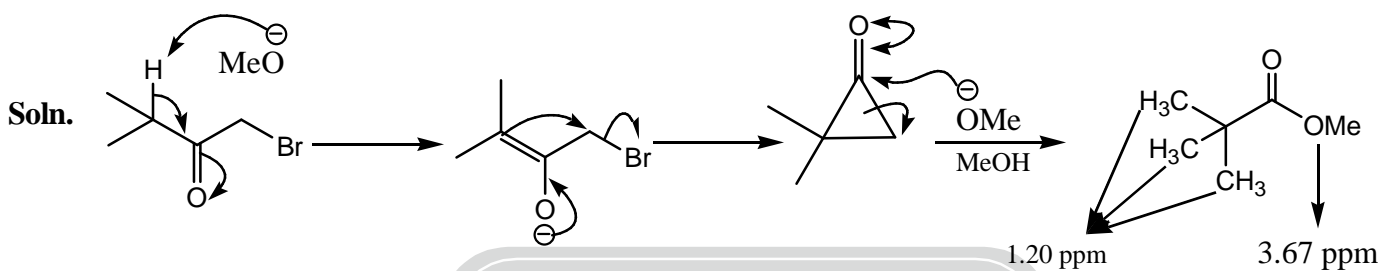
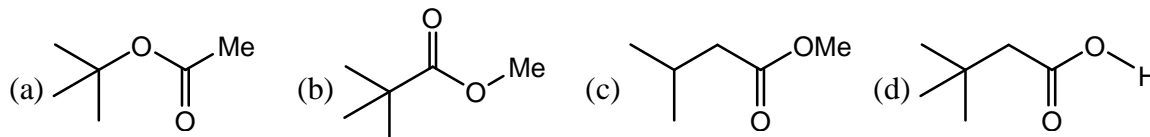
Correct option is (a)

23. Suggests structure for the products of these reactions, interpreting the spectroscopic data



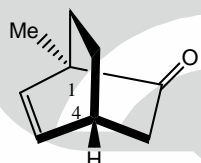
Molecular formula : $\text{C}_6\text{H}_{12}\text{O}_2$

ν_{max} (cm^{-1}) 1745 ; δ_{C} (ppm) : 179, 52, 39, 27 ; δ_{H} (ppm) , 1.20 (9H, s) , 3.67 (3H, s)

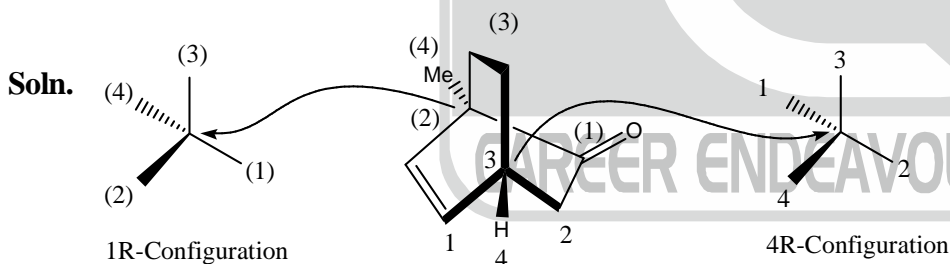


Correct option is (b)

24. The configuration at the two stereocentres in the compound given below are

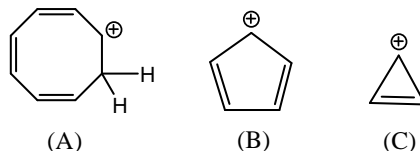


- (a) 1R, 4R (b) 1R, 4S (c) 1S, 4R (d) 1S, 4S

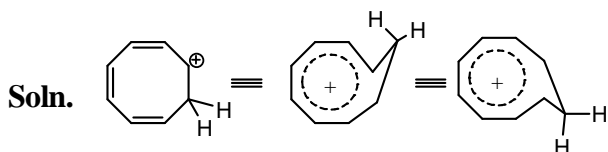


Correct answer: (a)

25. Among the carbocations given below

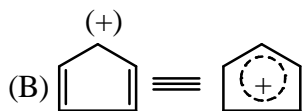


- (a) A is homoaromatic, B is antiaromatic and C is aromatic.
 (b) A is aromatic, B is antiaromatic and C is homoaromatic.
 (c) A is antiaromatic, B is aromatic and C is homoaromatic.
 (d) A is homoaromatic, B is aromatic and C is antiaromatic.



(A) Homoaromatic character

(Aromatised by bypassing the sp^3 -carbon atom)



- Delocalisation
- sp^2 - carbons (planar)
- $4n = 4$ (π -electron)
n = 1
- Antiaromatic character.

Correct answer: (a)



- Delocalisation
- $(4n+2) = 2$ (π -electron)
n = 0
- Aromatic character.

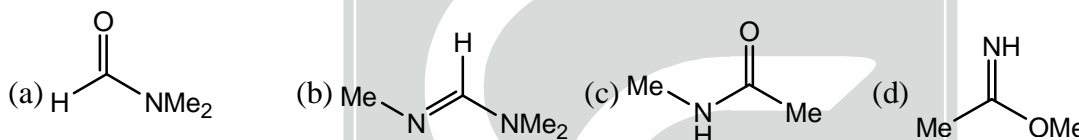
26. The order of carbonyl stretching frequency in the IR spectra of ketone, amide and anhydride is:
 (a) Anhydride > amide > ketone (b) Ketone > amide > anhydride
 (c) Amide > anhydride > ketone (d) Anhydride > ketone > amide

Soln. Because ν_{C-O} of anhydride = $1800-1900\text{ cm}^{-1}$.

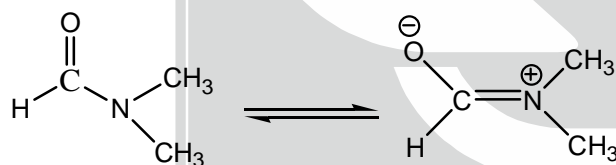
ν_{C-O} of ketone = 1720 cm^{-1} . ν_{C-O} of amide = $1600-1700\text{ cm}^{-1}$.

Correct answer: (d)

27. In the $^1\text{H NMR}$ spectrum recorded at 293 K, an organic compound ($\text{C}_3\text{H}_7\text{NO}$), exhibited signals at δ 7.8 (1H, s), 2.8 (3H, s) and 2.6 (3H, s). The compound is



Soln. DMF appears in two forms as shown below



Form-1 at higher temperature

Form-2 at 293 K

At lower temperature DMF remains in form-2 preferentially

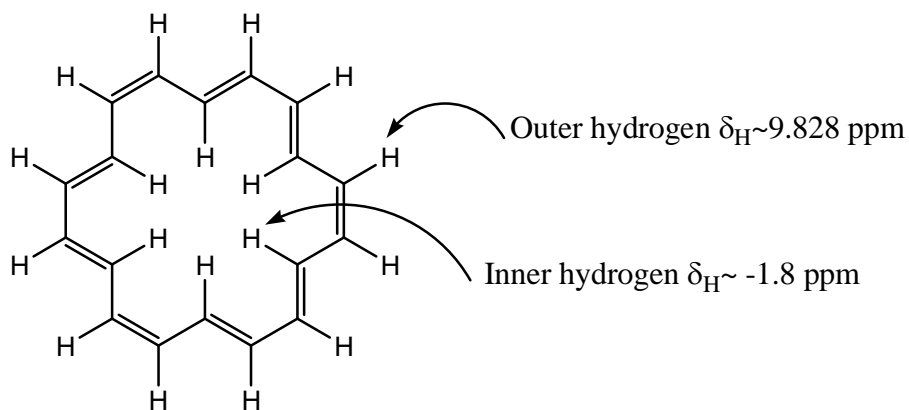
In form-2 methyl groups are chemically non-equivalent and they appears as singlets at 2.8 and 2.6 ppm. Singlet at 7.8 ppm appears due to olefinic proton of form-2.

Correct answer is (a)

28. Consider the following statements for [18]-annulene
 (A) It is aromatic
 (B) The inner protons resonate at δ 9.28 in its $^1\text{H NMR}$ spectrum
 (C) There are six protons in the shielded zone.
 (a) A, B, C (b) A and B only (c) B and C only (d) A and C only

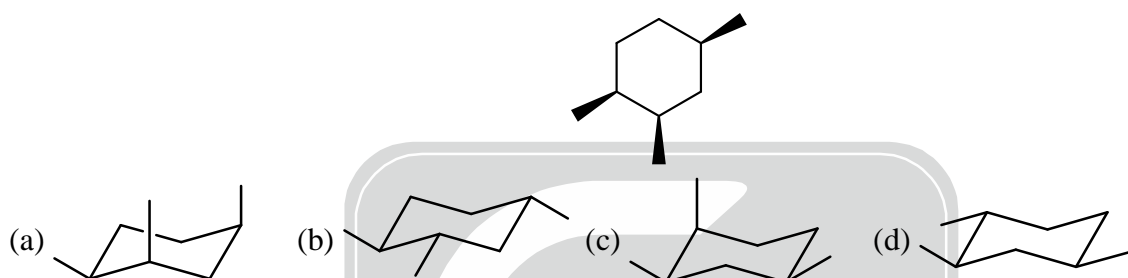
Soln. [18] annulene is aromatic compound and shows ring current

- The ring current produces strong induced magnetic field.
 - Outer 12 protons appears at 8.9 ppm because they remains in deshielding zone.
- Inner six protons appears at -1.8 ppm because they remains in shielding zone (up-field)
 Hence, statement A and C are correct.



Correct answer is (d).

29. Among the structures given below, the most stable conformation for the following compound is



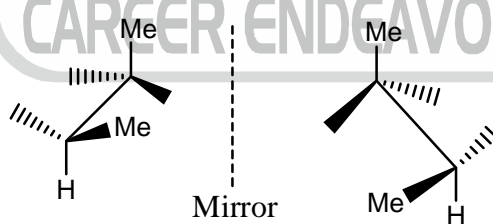
Soln. In conformation, all methyl group in same direction. A and C having all group in same side. But in case (A) 1-3, diaxial interaction occur. So, (C) is more stable as compare to (A).

Correct option is (c).

30. The gauche conformation ($\phi = 60^\circ$) of n-butane possesses

- (a) plane of symmetry; and is achiral (b) C_2 -axis of symmetry; and is chiral
 (c) centre of symmetry; and is achiral (d) plane of symmetry; and is chiral

Soln. The Gauche conformations of n-Butane are non-superimposable mirror image of each other, thus Gauche conformation is chiral.



If contains neither plane nor centre of symmetry.

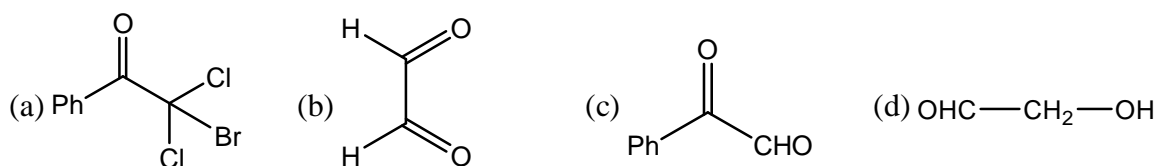
A C_2 axis passes through the mid-point of C_2-C_3 bond and bisecting the dihedral angle between the two methyls.

Correct answer is (b).

Section-B : Multiple Select Questions (MSQ)

Q.31 to Q.40: Carry 2 Marks each.

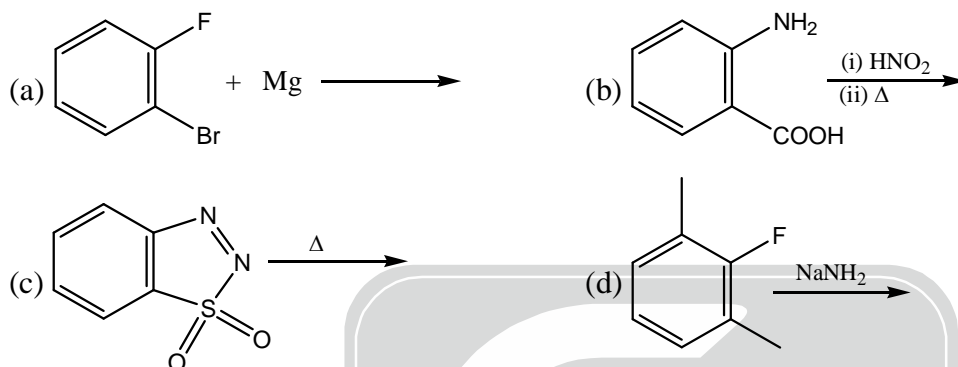
31. Select the compounds undergoing inter or intra molecular Cannizaro reaction



Soln. Compound in which α -hydrogen atoms are absent, give Cannizaro reaction.

Correct options are (a), (b) and (c)

32. In which reactions benzyne will be formed as intermediate



Soln. In structure, (a), (b) and (c) formed Benzyne intermediate.

Correct options are (a), (b) and (c).

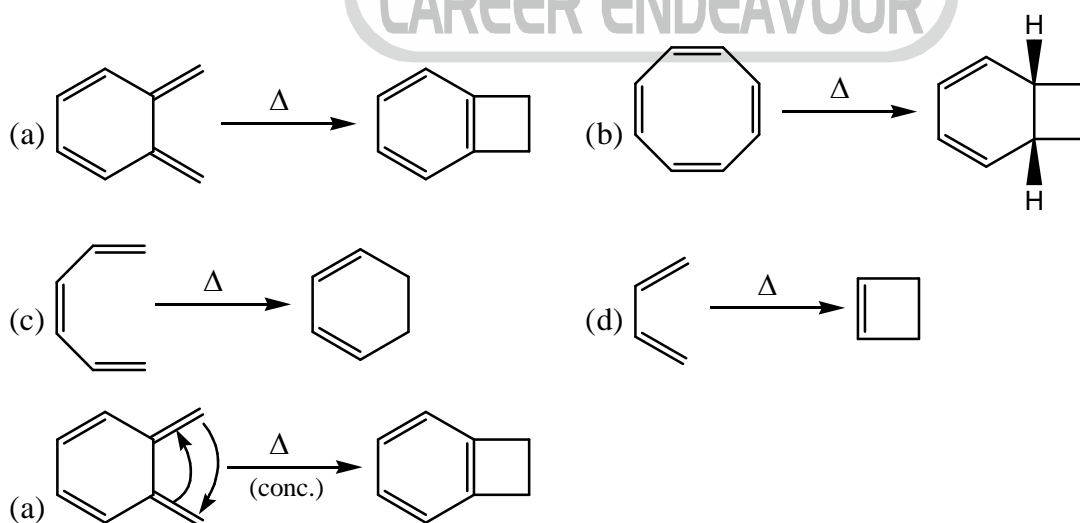
33. The incorrect statement(s) about the heterocyclic compounds is/are

- (a) Pyrrole gives electrophilic substitution reaction while as pyridine give nucleophilic substitution reactions
 (b) Pyrrole does not act as base while as pyridine does.
 (c) Furan and thiophene gives electrophilic substitution reactions with equal rate
 (d) Pyrrole gives nucleophilic addition reaction with Grignard reagent.

Soln. 3rd and 4th statement are incorrect.

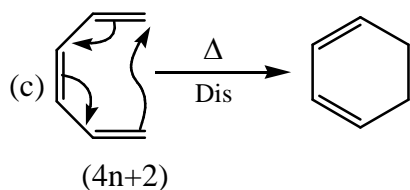
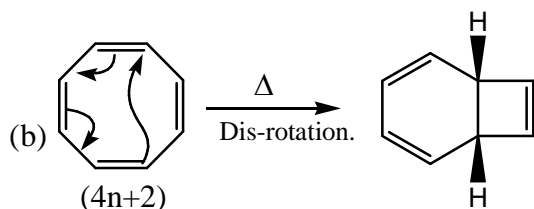
Correct option (c) and (d).

34. In which the product is formed through dis-rotation



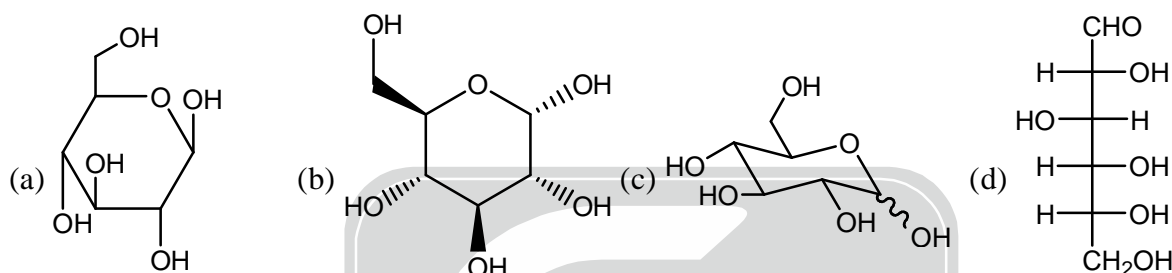
Soln.

(4n)



Correct option is (b) and (c)

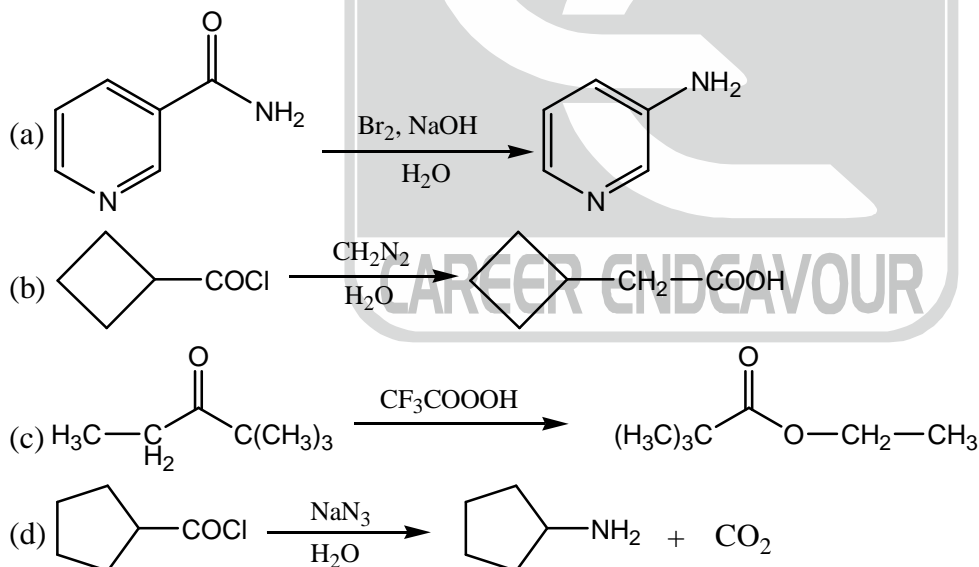
35. The correct structure of the D-glucose is/are



Soln. All forms are the correct structures of D-glucose.

Correct option is (a), (b), (c) and (d)

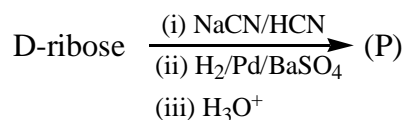
36. Which of the following equation shown as correct product



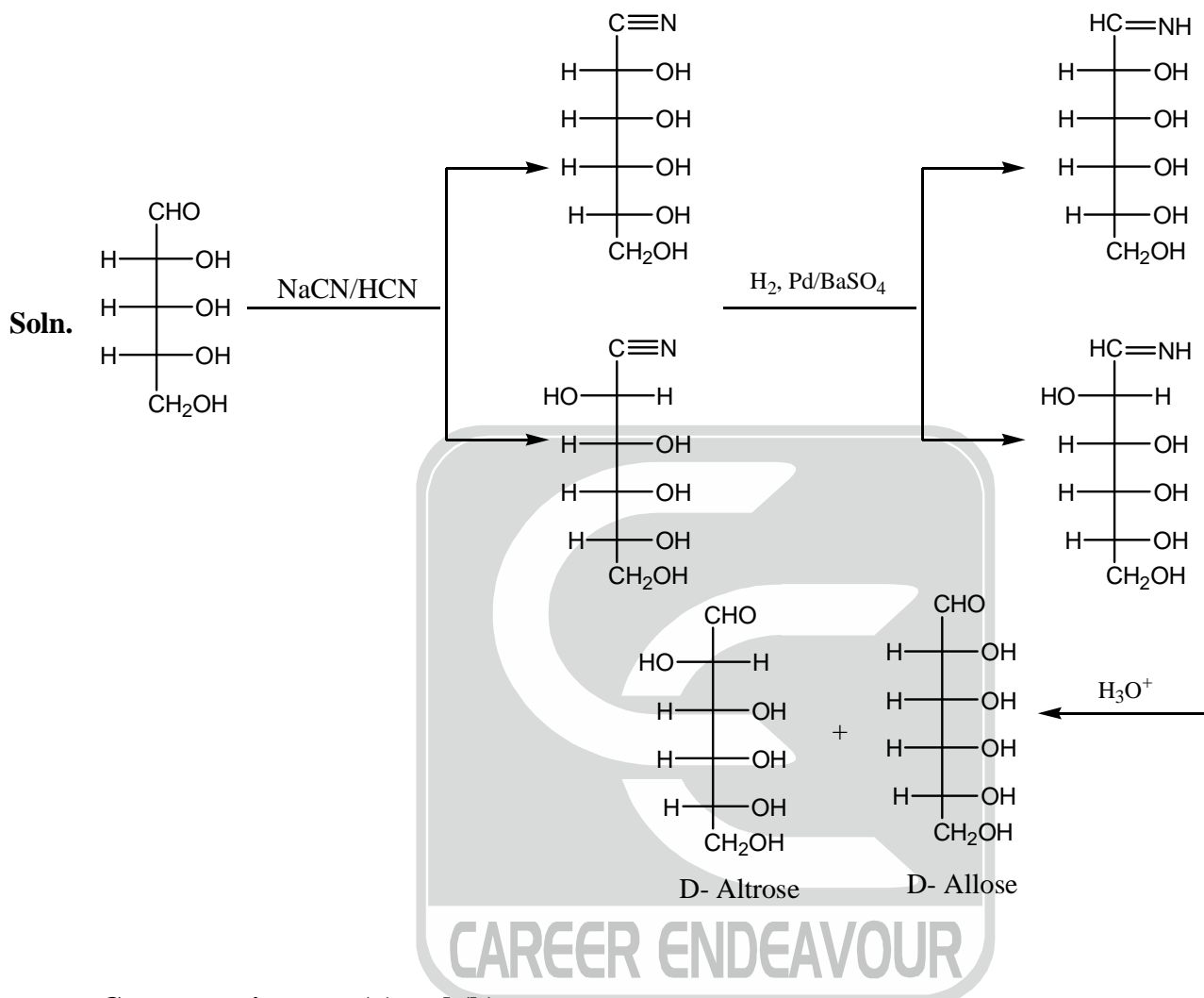
Soln. The reaction include (a) Hoffmann rearrangement, (b) a wolff rearrangement, (d) curtius rearrangement. Reaction (c) is possible Baeyer-villiger oxidation, but t-butyl has a higher migratory aptitude than ethyl to give the alternative ester as the major product.

Correct options are (a), (b) and (d).

37. The products formed in the following reaction is/are



- (a) D-Allose (b) D-Altrose (c) D-Glucose (d) D-Mannose



Correct options are (a) and (b)

38. The correct statement(s) about the Diels-Alder reaction is/are

- (a) electron donating groups on diene increases, the rate of Diels-Alder reaction
 (b) electron donating groups on Dienophile decreases, the rate of Diels-Alder reaction
 (c) Anthracene gives Diels-Alder reaction while as benzene does not give
 (d) Aromatic character is directly proportional to the reactivity of Diels-Alder reactions

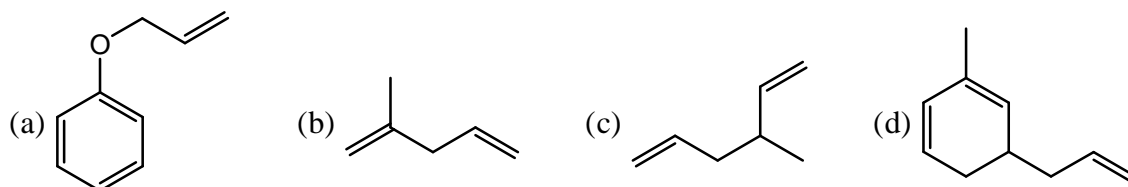
Soln. In presence of electron donating group on the Diene, the energy of HOMO increases while electron withdrawing group on Dienophile decreases the energy of LUMO. Hence, HOMO-LUMO gap decreases and rate of reaction increases.

Anthracene gives the Diels-Alder reaction because it is less aromatic.

Statements (1), (2) and (3) are correct.

Correct options are (a), (b) and (c).

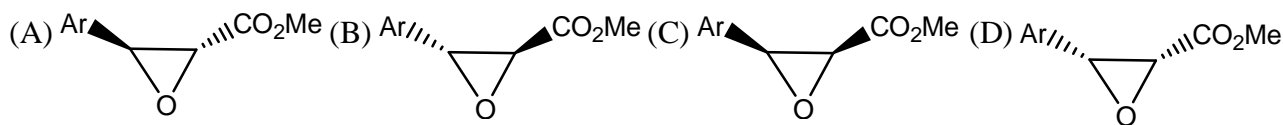
39. The number of compounds which undergo [3, 3] sigmatropic shift



Soln. Compound first, third and fourth undergoes [3, 3] sigmatropic rearrangement and for [3, 3] sigmatropic rearrangement compound should be in 1, 5-hexadiene form.

Correct options are (a), (c) and (d).

40. The correct statement(s) about the given compounds



(a) A and B are enantiomers

(b) B and D are diastereomers

(c) B and C are homomers

(d) C and D are enantiomers

Soln. A and B → Enantiomers

B and D → Diastereoisomers

B and C → Diastereoisomers

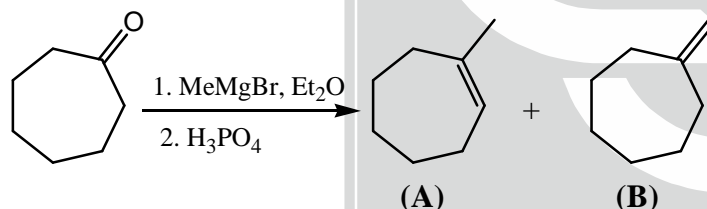
C and D → Enantiomers

Correct options are (a), (b) and (d).

Section-C : Numerical Answer Type (NAT)

Q.41 to Q.50: Carry 1 Mark each.

41. Among the following, how many incorrect statements for the following reaction is/are _____



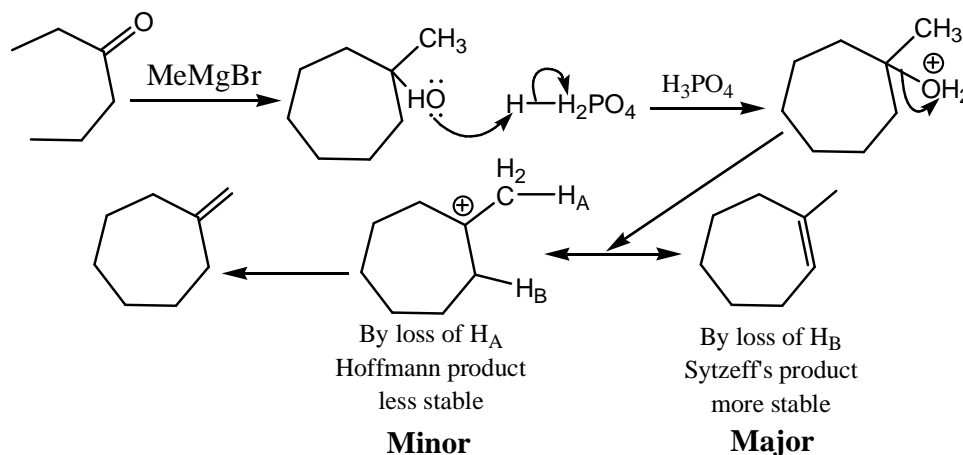
(1) A is the major product and it will have five signals in the proton decoupled ^{13}C NMR spectrum

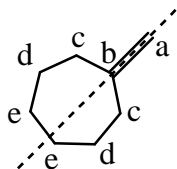
(2) A is the minor product and it will have eight signals in the proton decoupled ^{13}C NMR spectrum

(3) B is the major product and it will have five signals in the proton decoupled ^{13}C NMR spectrum

(4) B is the minor product and it will have five signals in the proton decoupled ^{13}C NMR spectrum

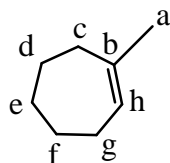
Soln. Chemical reaction involved in the above transformation can be illustrated as





Five distinct carbon atoms, thus five signals in proton decoupled ^{13}C NMR spectrum.

Plane of symmetry



Eight distinct carbon atoms, thus eight signals in proton decoupled NMR spectrum.

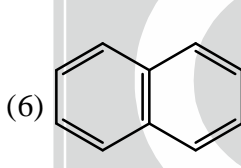
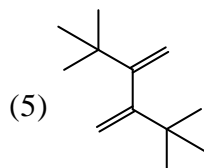
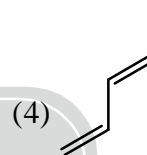
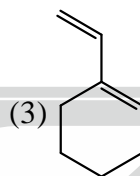
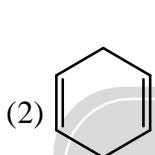
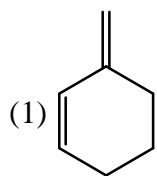
Correct answer is (3)

42. Nucleophilic substitution reactions of pyridine occurs at which position _____

Soln. Pyridine is π -sink and gives nucleophilic substitution reaction at second position.

Correct answer is (2)

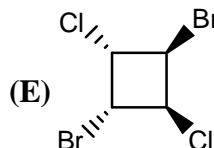
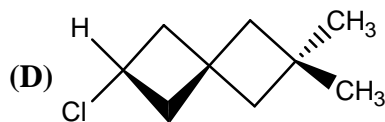
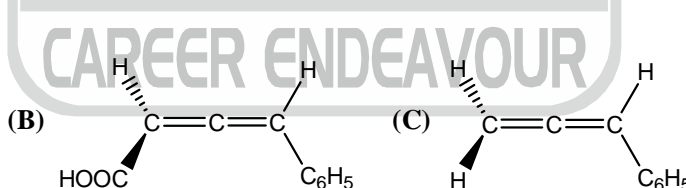
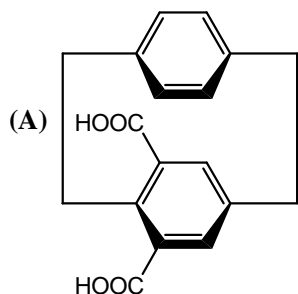
43. The number of compounds which undergoes Diels-Alder reaction



Soln. For Diels-Alder's reaction Diene should be in cisoid form. The naphthalene is highly aromatic, hence does not give the Diels-Alder reaction.

Correct answer is (2)

44. How many in the following molecules are chiral



Soln. (a) Achiral, due to the presence of plane of symmetry

(b) Chiral

(c) Achiral, plane of symmetry present

(d) Achiral, Plane of symmetry present

(e) Achiral, due to the presence of centre of symmetry.

Correct answer is (1)

45. In the IR spectrum of p-nitrophenyl acetate, the carbonyl absorption band appears at _____ cm^{-1}

Soln. C = O structure occurs at cm^{-1} .

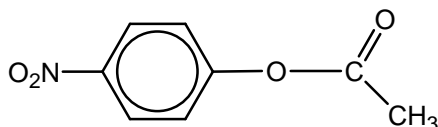
1750 – 1735 cm^{-1} for aliphatic esters.

1740 – 1715 cm^{-1} if C = O conjugated with aromatic.

1765 – 1762 cm^{-1} if oxygen atom is conjugated with alkene or aromatic.

Example: Phenyl acetate 1765 cm^{-1}

p-nitrophenyl acetate 1761 cm^{-1} .



Correct answer is (1755 to 1765)

46. Among the following, how many are polar protic solvents?

- (i) H_2O (ii) CH_3OH (iii) $\text{CH}_3\text{CH}_2\text{OH}$ (iv) NH_3
 (v) Acetone (vi) DMF (vii) Benzene (viii) DMSO (ix) Cyclohexane

Soln. Molecule having polarity with acidic proton known as polar protic solvent. (Proton attached with more electronegative element containing polar molecule).

H_2O , CH_3OH , $\text{CH}_3\text{CH}_2\text{OH}$, NH_3 are polar protic solvent.

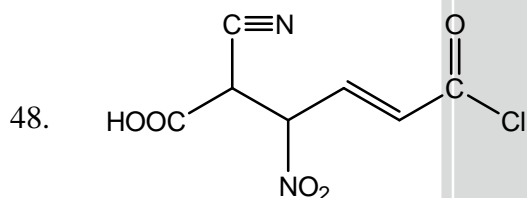
Correct answer is (4)

47. How many of following rearrangements form isocyanate _____

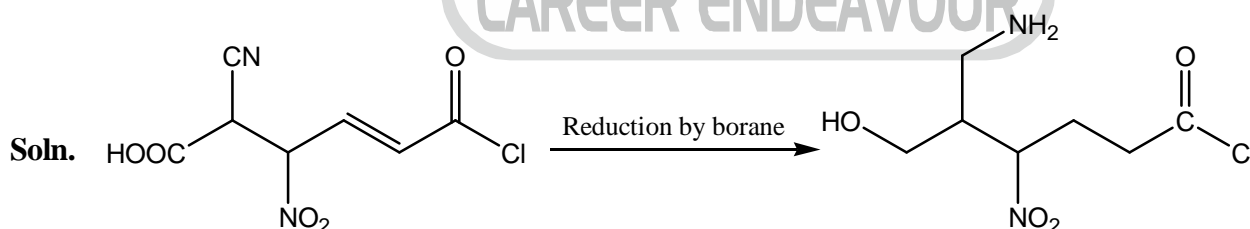
- (1) Wolf rearrangement (2) Hoffmann rearrangement
 (3) Beckmann rearrangement (4) Schmidt rearrangement
 (5) Lossen rearrangement (6) Curtius rearrangement (7) Claisen rearrangement

Soln. In the above rearrangements, Curtius, Hoffman, Lossen and Schmidt form isocyanate intermediate.

Correct answer is (4)



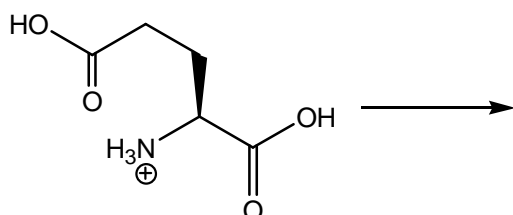
In the above structure, how many functional groups not reduce by borane.

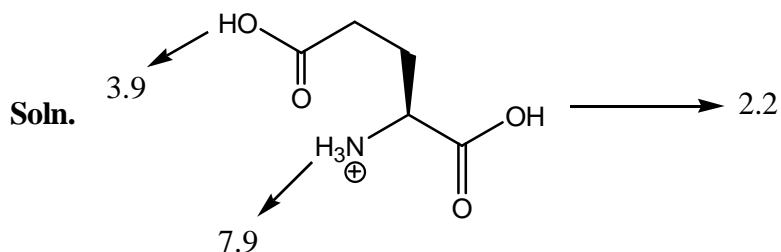


In the above structure, RCOCl and R-NO_2 are not reduce by Borane.

Correct answer is (2)

49. Calculate the pI of the following salt of amino acid having pKa value $x = 2.2$, $y = 3.9$ and $z = 7.9$ respectively.





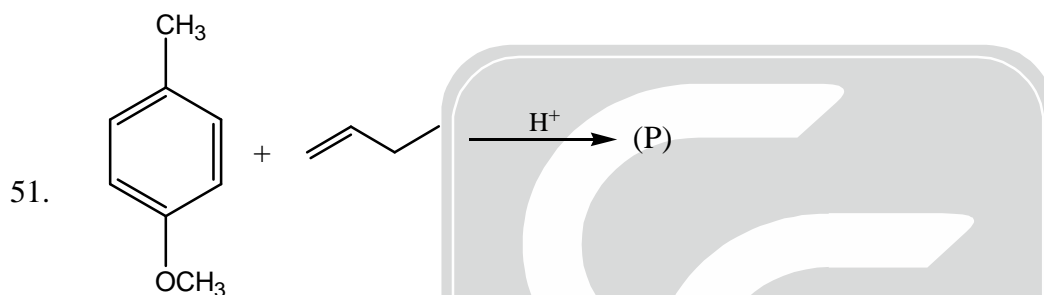
PI of an amino acid having ionizable side chain is the average pK_a values of similarly ionizable groups.

$$\Rightarrow \frac{2.2 + 3.9}{2} = \frac{6.1}{2} = 3.05$$

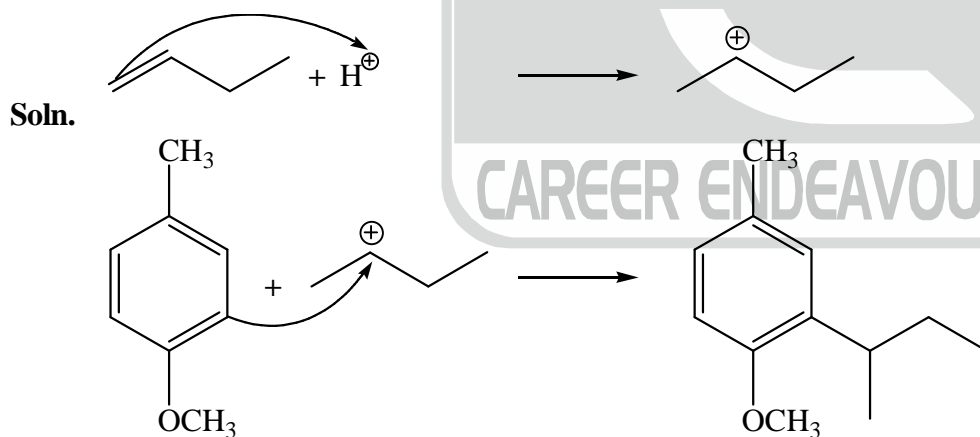
Correct answer is (3.05)

50. How many products will be formed upon the bromination of furan in alcoholic and non-alcoholic solvent.
Soln. Furan upon bromination in alcoholic solvent gives addition product. While as with non-alcoholic solvent gives polybromination products.
Correct answer is (2)

Q.51 to Q.60: Carry 2 Marks each.

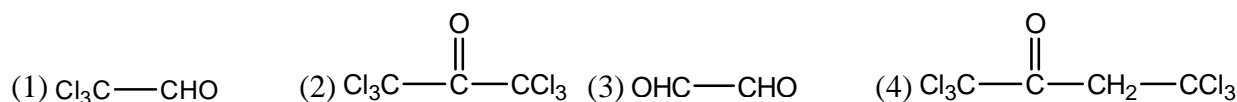


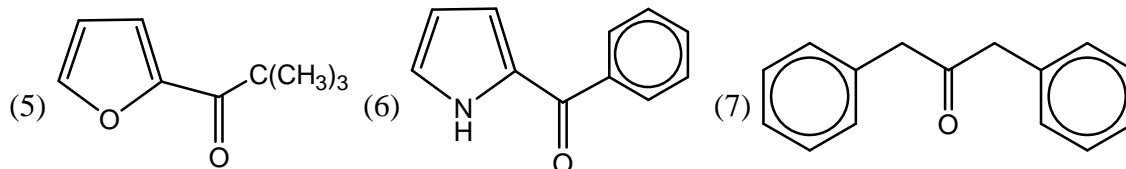
How many product will be formed in above reaction.



Correct answer is (1)

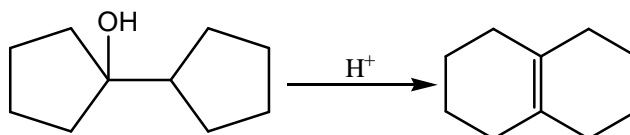
52. How many compounds gives cannizaro reaction



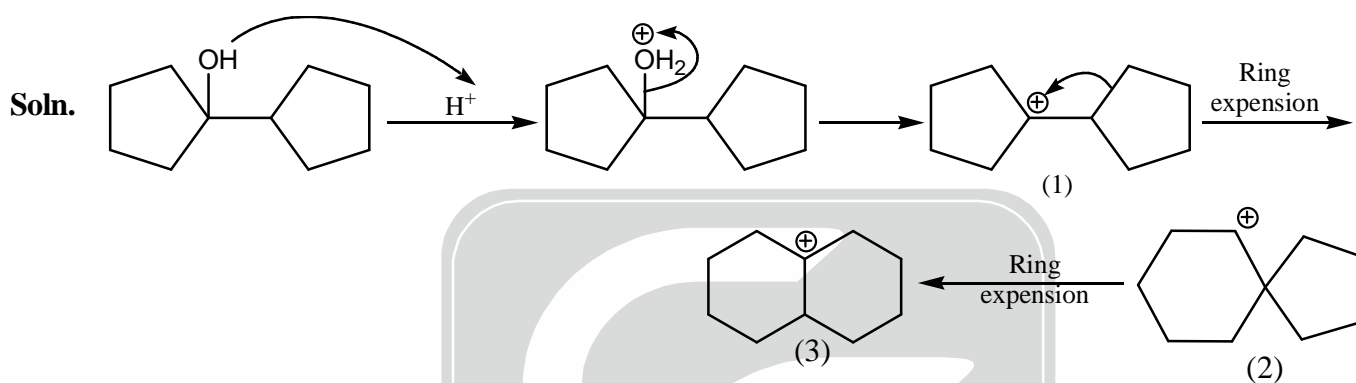


Soln. Compounds in which α -hydrogen atoms are absent give cannizaro reaction.
Correct answer is (5)

53. Reaction,

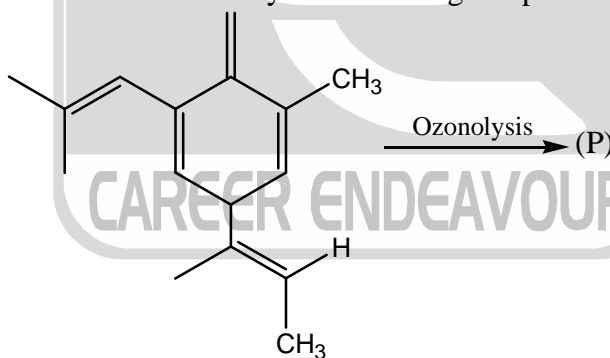


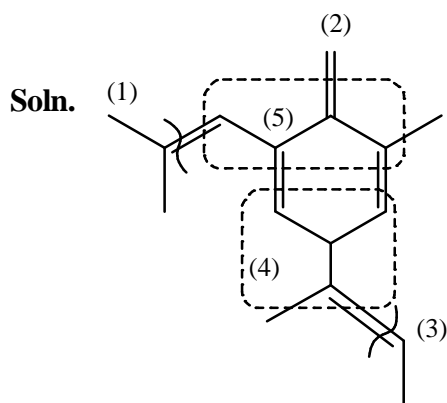
How many intermediate (carbocations) will be form in above conversion.



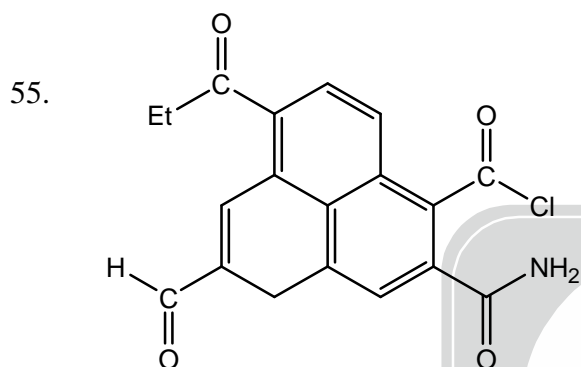
Total carbocation is (3)
Correct answer is (3)

54. How many products will be formed on ozonolysis of following compound





Correct answer is (5)



Number of moles of CH_3MgBr required to neutral above compound is/are _____

Soln. Acid derivatives reacts two mole of CH_3MgBr and carbonyl compound (aldehyde or ketone) react with one mole of CH_3MgBr .

Correct option is (7).

56. Among the following neutral amino acids is/are
 (1) Lysine (2) Arginine (3) Valine (4) Aspartic acid
 (5) isoleucine (6) Traptophane (7) Leucine

Soln. Lysine, Arginine are the basic amino acids.
 Aspartic acid is the acidic amino acid.
 Valine, isoleucine, Traptophane and Leucine are the neutral amino acids.

Correct answer is (4)

57. The $[\alpha]_D$ of a 90% optically pure 2-arylpropanoic acid solution is $+135^\circ$. On treatment with a base at RT for one hour, $[\alpha]_D$ changed to $+120^\circ$. The optical purity is reduced to 40% after 3 hours. If so, its specific rotation after 3 hours would be _____ degree.

Soln. • Optically purity also known as enantiomeric excess a compound of 90% B.E. shows 135° specific rotation.

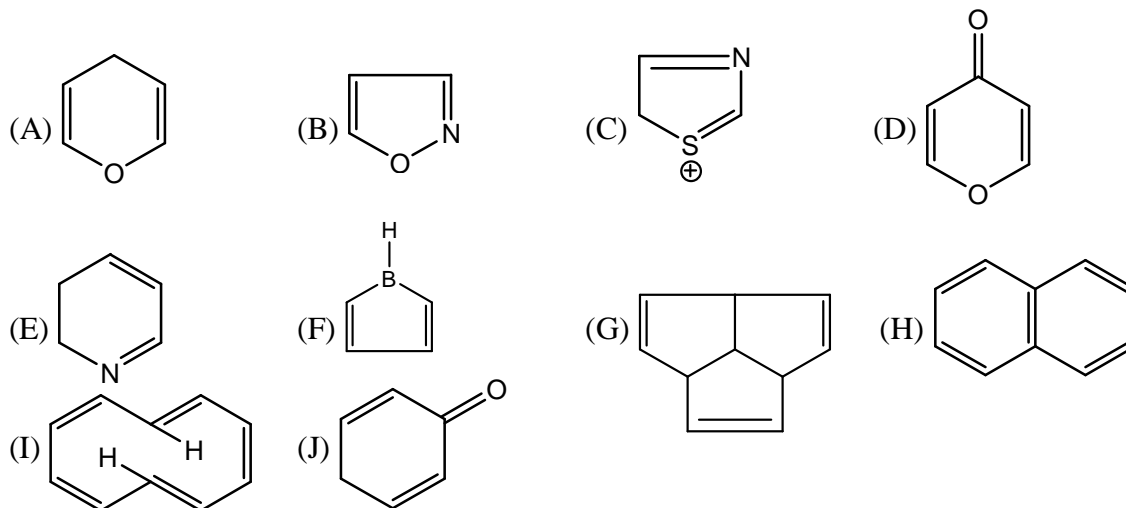
So, its 100% optically pure isomer will show $\frac{135}{90} \times 100 = 150^\circ$ specific rot.

• At one hour the specific rotation reduced to 120° . So, E.E, or optical purity = $\frac{120}{150} \times 100 = 80\%$

• At three hours optical purity is 40%. So, specific rotation = $\frac{150}{100} \times 40 = 60^\circ$

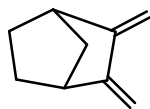
Correct answer is (60)

58. Among the following, how many are aromatic in nature?



Soln. B, D, H aromatic in nature
Correct answer is (3)

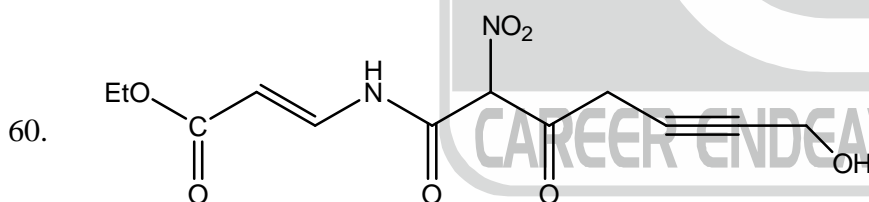
59. For the below compound



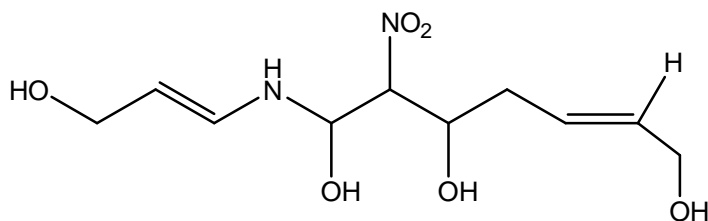
Soln. The λ_{\max} value is _____ $m\mu$

Basic value	= 217 $m\mu$
2-Ring residues	= 10 $m\mu$ (2×5)
2-Exo cyclic double bonds	= 10 $m\mu$
1-bicyclic system	= <u>15 $m\mu$</u>
	= <u>252 $m\mu$</u>

Correct answer is (252)



Soln. In the above structure, how many functional groups are reduced by LiAlH_4 .
 Total number of five functional groups reduced by LiAlH_4 .



Correct answer is (5)



IIT-JAM CHEMISTRY-CY

Date : 08-01-2017

TEST SERIES - 2
(Organic Chemistry)

Booklet : **B**

ANSWER KEY

Section-A : Multiple Choice Questions (MCQ)

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (b) | 2. (b) | 3. (a) | 4. (a) | 5. (c) |
| 6. (d) | 7. (b) | 8. (b) | 9. (c) | 10. (d) |
| 11. (c) | 12. (c) | 13. (b) | 14. (c) | 15. (c) |
| 16. (c) | 17. (a) | 18. (a) | 19. (a) | 20. (c) |
| 21. (c) | 22. (a) | 23. (b) | 24. (a) | 25. (a) |
| 26. (d) | 27. (a) | 28. (d) | 29. (c) | 30. (b) |

Section-B : Multiple Select Questions (MSQ)

- | | | | |
|----------------------|-------------------|-------------|------------------|
| 31. (a),(b), (c) | 32. (a),(b), (c) | 33. (c),(d) | 34. (b), (c) |
| 35. (a),(b),(c), (d) | 36. (a), (b), (d) | 37. (a),(b) | 38. (a),(b), (c) |
| 39. (a), (c), (d) | 40. (a), (b), (d) | | |

Section-C : Numerical Answer Type (NAT)

- | | | | |
|--------------------|---------|-----------|---------|
| 41. (3) | 42. (2) | 43. (2) | 44. (1) |
| 45. (1755 to 1765) | 46. (4) | 47. (4) | 48. (2) |
| 49. (3.05) | 50. (2) | 51. (1) | 52. (5) |
| 53. (3) | 54. (5) | 55. (7) | 56. (4) |
| 57. (60) | 58. (3) | 59. (252) | 60. (5) |

