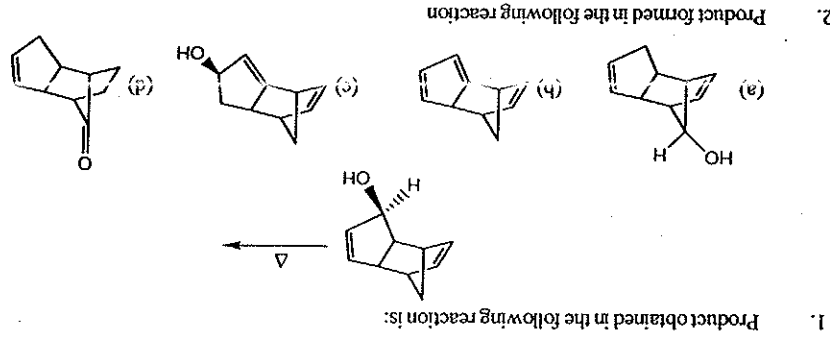
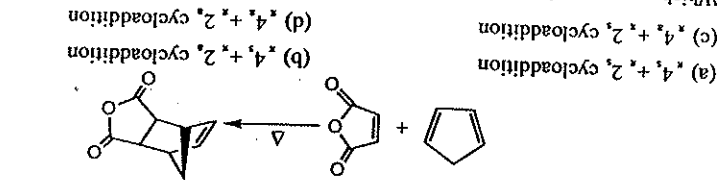


5. Cope rearrangement involves
- (a) [1, 5]-sigmatropic rearrangement
- (b) [4+2]-cycloaddition reaction
- (c) [3, 3]-sigmatropic rearrangement
- (d) 6 π -electrocyclisation reaction



6. The reaction given below is an example of



7. Which one among the dienes A-D will undergo [3, 3]-sigmatropic shift upon heating

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

8. The LUMO of the ground state buta-3-diene is:

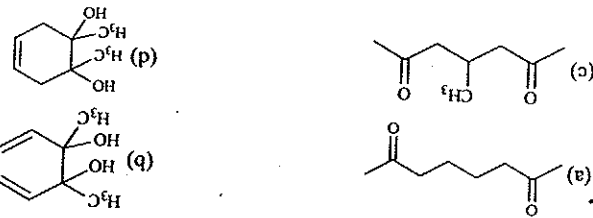
(a) (b) (c) (d)

9. The heterocyclic diene employed in cyclo-addition reaction is:

(a) furan
 (b) pyrrole
 (c) 2,5-dimethylpyrrole
 (d) thiophene

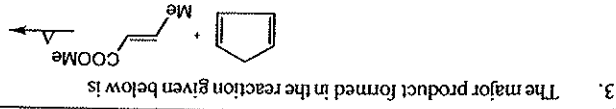
10. On heating undergoes oxy-cope rearrangement to give

(a) (b) (c) (d)



11. The product formed in the reaction given below is

(a) (b) (c) (d)



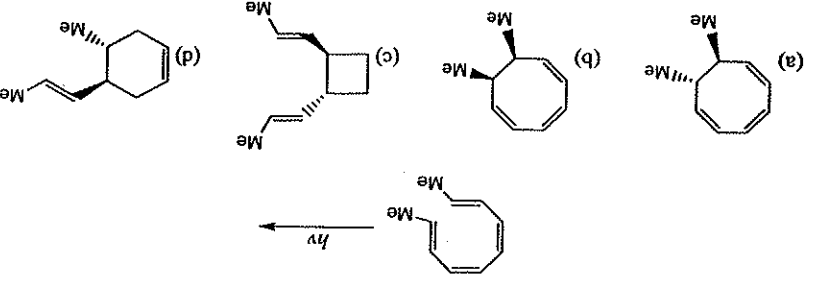
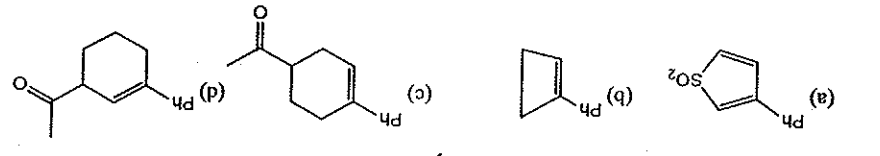
14. Which of the following is true for Cope rearrangement?

(a) [1, 5] shift, intramolecular, uncatalyzed
 (b) [3, 3] shift, intramolecular, uncatalyzed
 (c) [3, 3] shift, intramolecular, catalyzed
 (d) [1, 5] shift, intramolecular, catalyzed

15. Identify the product formed in the reaction.

(i) Heating
 (ii) Methyl vinyl ketone

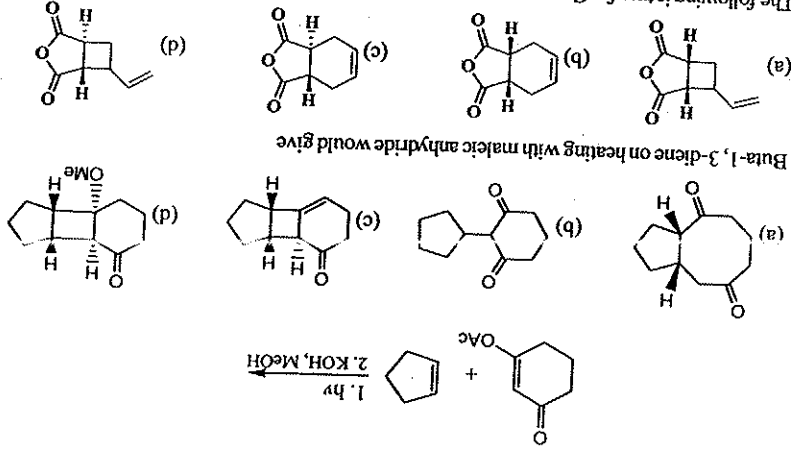
(a) (b) (c) (d)



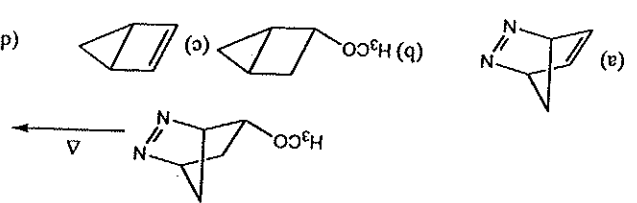
1. (a)
8. (d)
15. (c)
2. (a)
9. (a)
16. (c)
3. (b)
10. (a)
17. (b)
4. (b)
11. (c)
18. (d)
5. (c)
12. (b)
19. (a)
6. (a)
13. (a)
20. (b)
7. (d)
14. (b)
21. (b)

ANSWER KEY

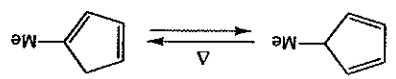
The following is true for Cope reaction
 (a) Occurs at low temp, tertiary amines are reactants, proceeds through SYN pathway
 (b) Occurs at high temp, tertiary amines are reactants, proceeds through SYN pathway
 (c) Occurs at high temp, tertiary amine oxides are reactants, proceeds through ANT pathway
 (d) Occurs at low temp, tertiary amine oxides are reactants, proceeds through ANT pathway



18. The major product formed in the following thermal reaction is



[NET June 2011]

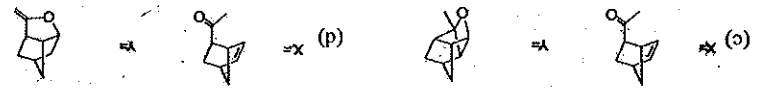
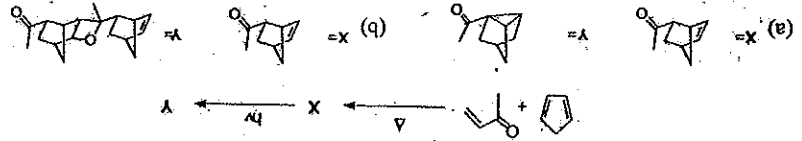


- (a) 1,3-sigmatropic hydrogen shift
 (b) 1,3-sigmatropic methyl shift
 (c) 1,5-sigmatropic hydrogen shift
 (d) 1,5-sigmatropic methyl shift

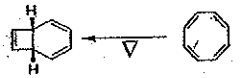
2. The concerted photochemical reaction between two olefins leading to a cyclobutane ring is:

- (a) $\pi_2s + \pi_2s$ cycloaddition
 (b) $\pi_2s + \pi_2s$ cycloaddition
 (c) $\sigma_2s + \sigma_2s$ cycloaddition
 (d) $\pi_2s + \sigma_2s$ cycloaddition

3. The structures of the major products X and Y in the following transformation are

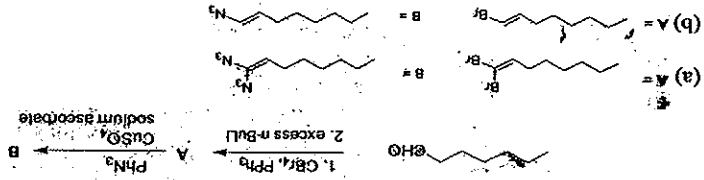


4. In the following concerted reaction, the product is formed by a

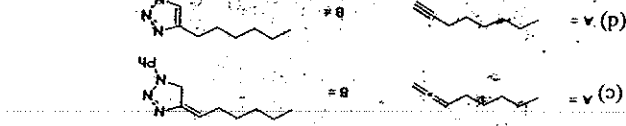


- (a) 6 π - disrotatory electrocyclic ring closure
 (b) 4 π - disrotatory electrocyclic ring closure
 (c) 6 π - conrotatory electrocyclic ring closure
 (d) 4 π - conrotatory electrocyclic ring closure

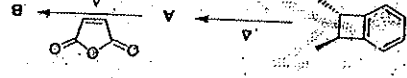
5. The major products A and B in the following reaction sequence are



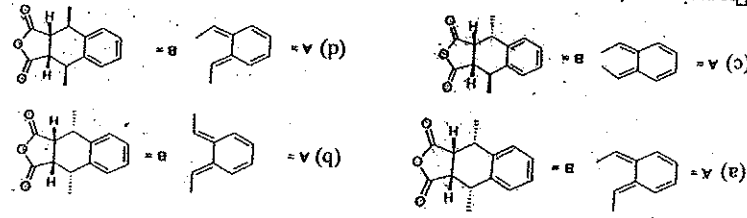
PERICYCLIC REACTIONS



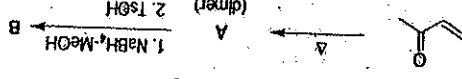
The major products A and B in the following reaction sequence are



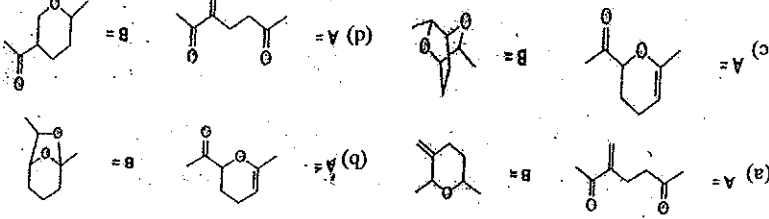
[NET Dec. 2011]



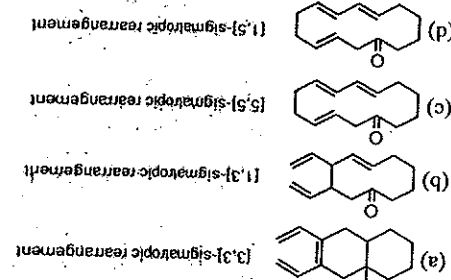
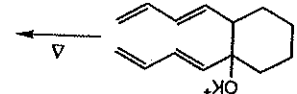
The major products A and B in the following reaction sequence are



[NET Dec. 2011]

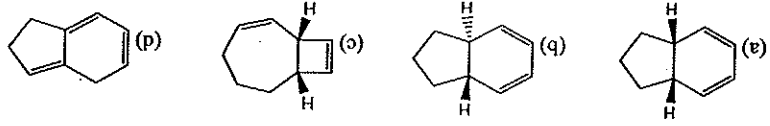
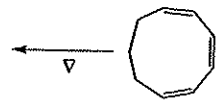


The product formed and the process involved in the following reaction are



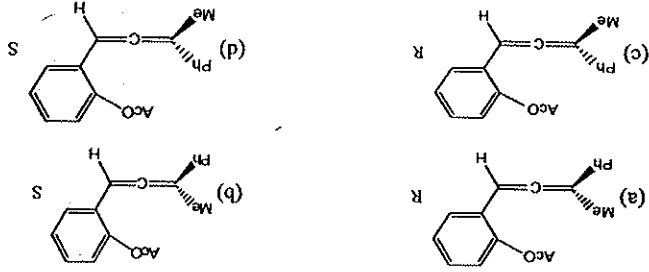
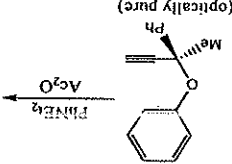
9.

The major product formed in the following concerted reaction is

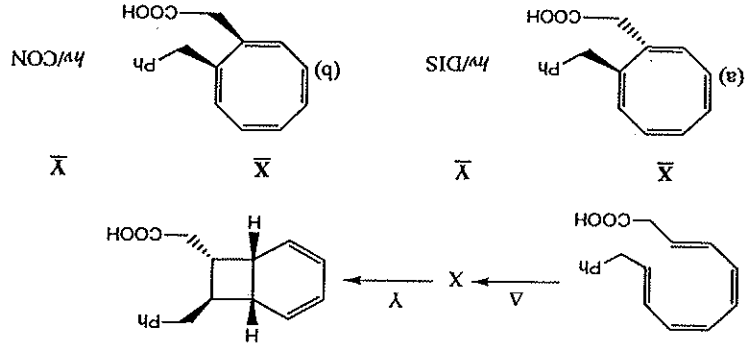


The major product formed when (3R, 4S)-3, 4-dimethylhexa-1, 5-diene is heated at 240° is:
 (a) (2E, 6E)-octa-2, 6-diene
 (b) (2E, 6E)-octa-2, 6-diene
 (c) (2E, 6Z)-octa-2, 6-diene
 (d) (3Z, 5E)-octa-3, 5-diene

In the following pericyclic reaction, the structure of the allene formed and its configuration are



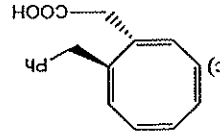
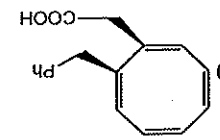
In the following sequence of pericyclic reactions X and Y are



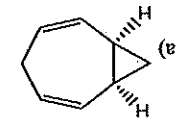
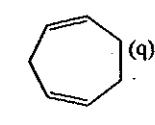
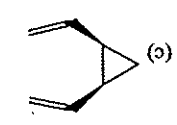
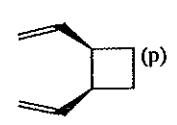
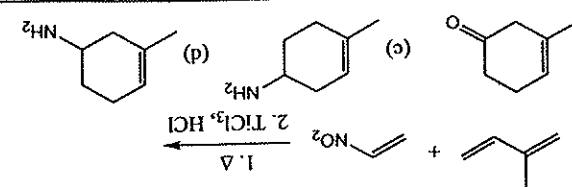
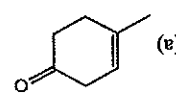
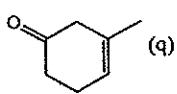
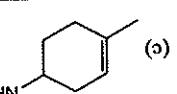
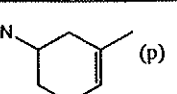
12.

[NET Dec. 2012]

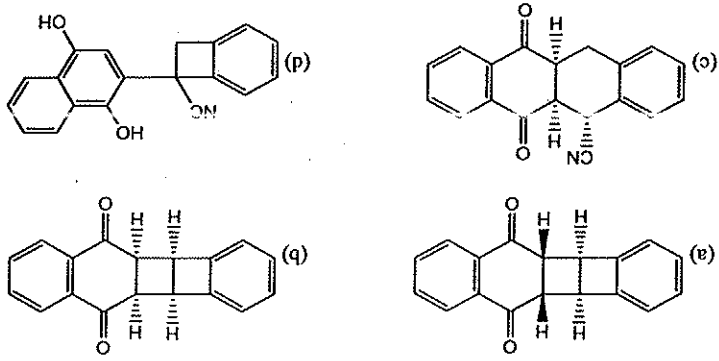
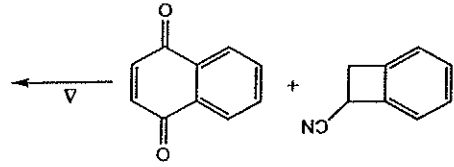
[NET June 2012]

13. The following conversion involves
- (c)  $\xrightarrow{\text{A/DIS}}$ 
- (d)  $\xrightarrow{\text{A/CON}}$ 

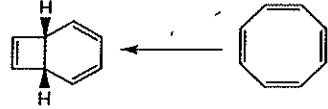
14. The following transformation involves
- (a) a 1,3-dipolar species as reactive intermediate, and a cycloaddition.
 (b) a carbenium ion as reactive intermediate, and a cycloaddition.
 (c) a 1,3-dipolar species as reactive intermediate, and an aza Wittig reaction.
 (d) a carbanion as reactive intermediate, and an aza Cope rearrangement.
- [NET Dec. 2012]

15. Among the following dienes, the one that undergoes a degenerate Cope rearrangement is
- (a)  (b)  (c)  (d) 
- [NET June 2013]
16. The major product formed in the following reaction is
- 
- (a)  (b)  (c)  (d) 
- [NET June 2013]

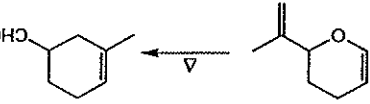
17. The major product formed in the following reaction is



18. The most appropriate mode of cyclisation in the following transformation is

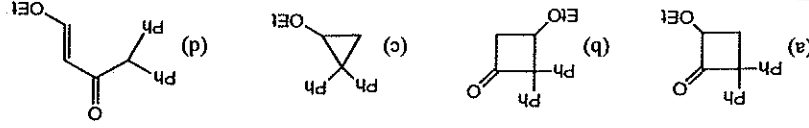
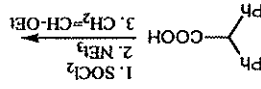


- (a) con-rotatory in photochemical; and dis-rotatory in thermal conditions.
 (b) con-rotatory in thermal; and dis-rotatory in photochemical conditions.
 (c) con-rotatory in thermal; and con-rotatory in photochemical conditions.
 (d) dis-rotatory in photochemical; and dis-rotatory in thermal conditions.



- (a) 1,3-sigmatropic rearrangement
 (c) 3,3-sigmatropic rearrangement
 (b) 2,3-sigmatropic rearrangement
 (d) 3,5-sigmatropic rearrangement

- The major product formed in the following reaction sequence is



- [NET Dec. 2013]

- [NET Dec. 2013]

- [NET June 2013]

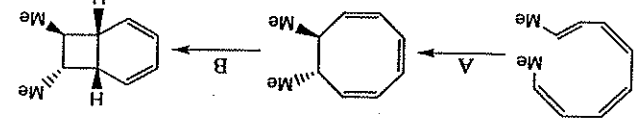
- [NET June 2013]

21. The number of nodes present in the highest occupied molecular orbital of 1,3,5-hexatriene in its ground state

- (a) one (b) two (c) three (d) four

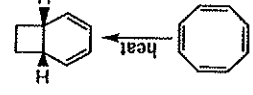
[NET Dec. 2013]

22. The conditions A-B, required for the following pericyclic reactions are



- (a) A-Δ; B-Δ (b) A-hν; B-Δ (c) A-hν; B-hν (d) A-Δ; B-hν

23. The number of π electrons participating and the pericyclic mode in the following reaction are

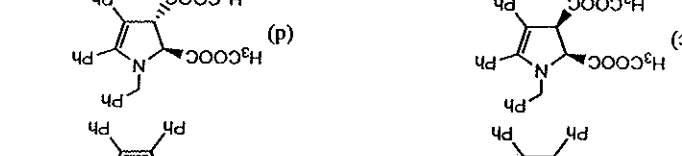
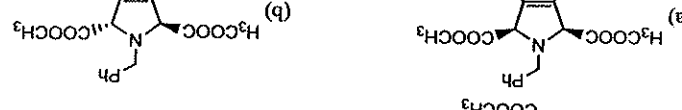
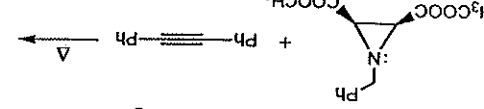


[NET Dec. 2013]

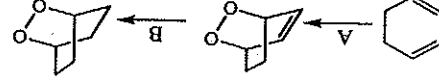
24. In a Diels-Alder reaction, the most reactive diene amongst the following is

- (a) 4E-1,4-hexadiene (b) 4Z-1,4-hexadiene (c) 2E,4E-2,4-hexadiene (d) 2Z,4Z-2,4-hexadiene

25. The major product formed in the following reaction is

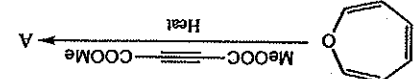


26. The correct combination of reagents for effecting the following sequence of reactions is [NET June 2014]



- (a) A = O₂; B = K⁺-OOC-N=N-COO-K⁺, AcOH
(b) A = O₂; B = K⁺-OOC-N=N-COO-K⁺, AcOH
(c) A = O₂; B = H₂, Pd/C
(d) A = O₂; B = H₂, Pd/C

27. The major product A formed in the following reaction is [NET June 2014]



[NET Dec. 2013]

[NET Dec. 2013]

[NET Dec. 2013]

[NET Dec. 2013]

[NET Dec. 2013]

[NET Dec. 2013]

[NET Dec. 2013]

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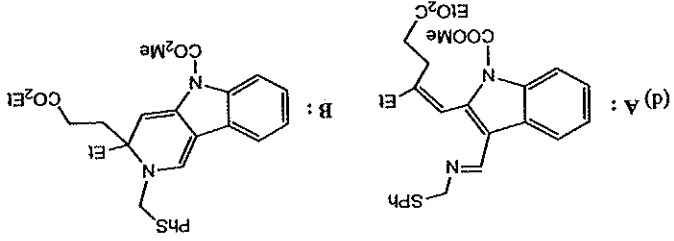
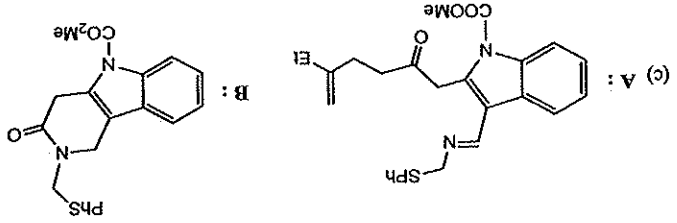
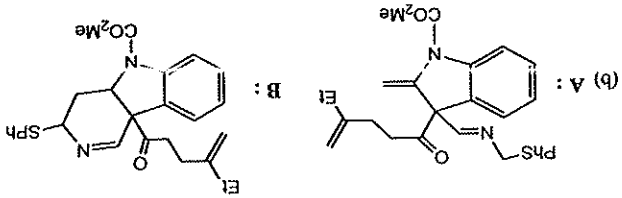
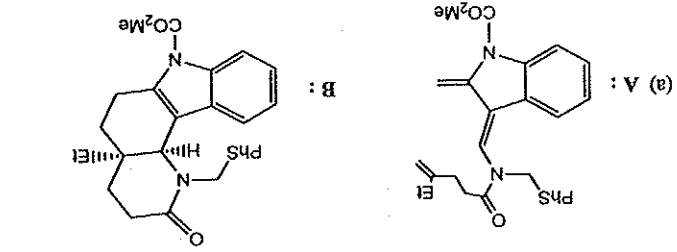
[NET Dec. 2014]

[NET Dec. 2014]

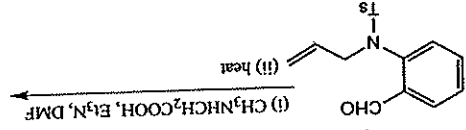
[NET Dec. 2014]

[NET Dec. 2014]

[NET Dec. 2014]



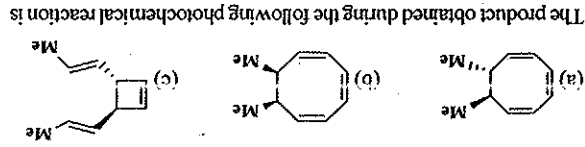
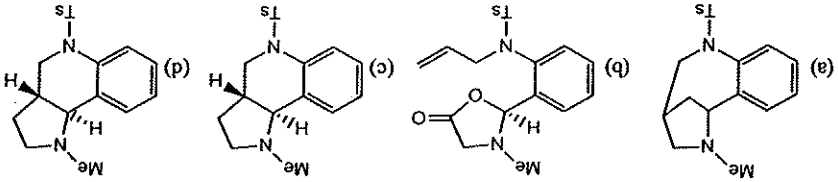
31. The major product of the following reaction is



[NET Dec. 2014]

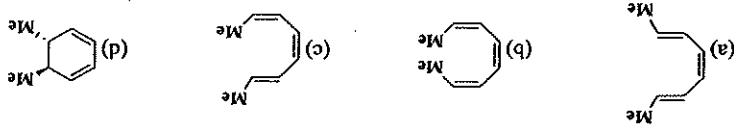
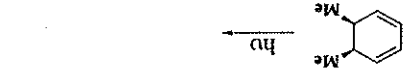
32.

The following tetraene upon photolysis gives



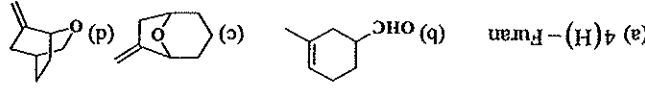
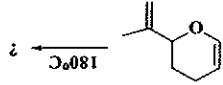
The product obtained during the following photochemical reaction is

[GATE 2001]

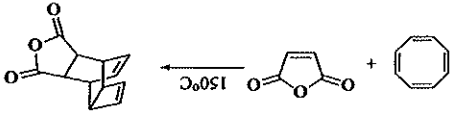


The major product formed in the thermal reaction given below, is

[GATE 2002]



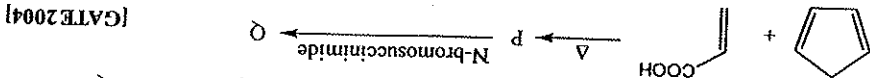
35. The two pericyclic reactions successively involved in the thermal transformation given below are



- (a) 6 π -electrocyclization followed by [4 + 2] π -cycloaddition
 (b) 8 π -cycloaddition followed by [2 + 2] π -electrocyclization
 (c) 6 π -cycloaddition followed by [2 + 2] π -electrocyclization
 (d) 4 π -electrocyclization followed by [4 + 2] π -cycloaddition

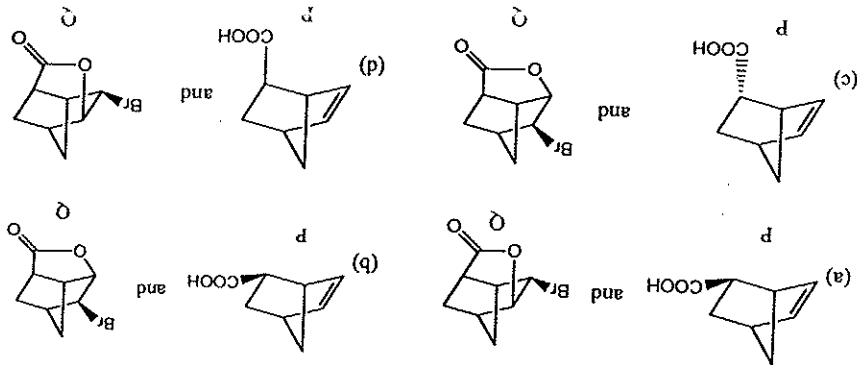
[GATE 2002]

36. In the two step reaction shown below, identify the correct combination of products P and Q.

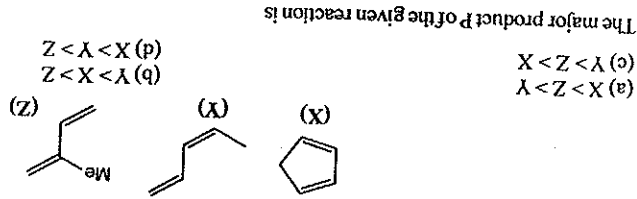


[GATE 2004]

37. Order of reactivity of the following dienes X, Y and Z in Diels-Alder reaction is

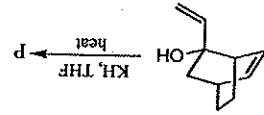


[GATE 2005]

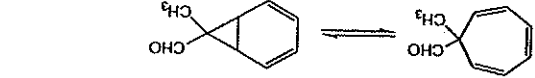


[GATE 2005]

38. The major product P of the given reaction is



39. Select the correct classification in the following reaction from option I to IV gives below. [GATE 2006]



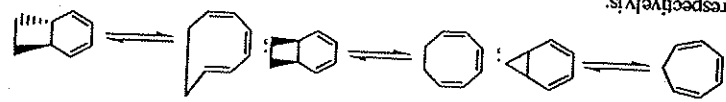
(I) Conrotatory electrocyclic reaction
(II) Disrotatory electrocyclic reaction
(III) Valence isomerization
(IV) $[4s + 2s]$ cycloaddition reaction

(a) I and III
(b) II and IV
(c) II and III
(d) I and IV

The most appropriate starting materials for one step synthesis of the compound (I) are [GATE 2006]

41.

The direction of rotation of the following thermal electrocyclic ring closures.



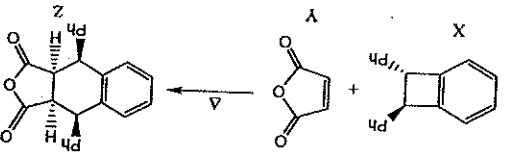
respectively is:

(a) Disrotatory, disrotatory, conrotatory
(b) Conrotatory, conrotatory, conrotatory
(c) Disrotatory, disrotatory, conrotatory
(d) Disrotatory, conrotatory, disrotatory

[GATE 2008]

42.

The reaction between X and Y to give Z proceeds via



(a) 4π - conrotatory opening of X followed by endo Diels-Alder cycloaddition.
(b) 4π - disrotatory opening of X followed by endo Diels-Alder cycloaddition.
(c) 4π - conrotatory opening of X followed by exo Diels-Alder cycloaddition.
(d) 4π - disrotatory opening of X followed by exo Diels-Alder cycloaddition.

The products Y and Z are formed, respectively, from X via

[GATE 2008]

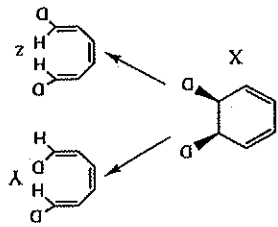
43.



(I) Conrotatory electrocyclic reaction
(II) Disrotatory electrocyclic reaction
(III) Valence isomerization
(IV) $[4s + 2s]$ cycloaddition reaction

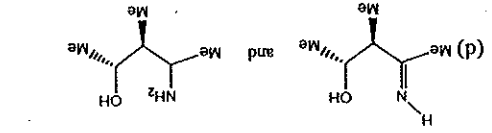
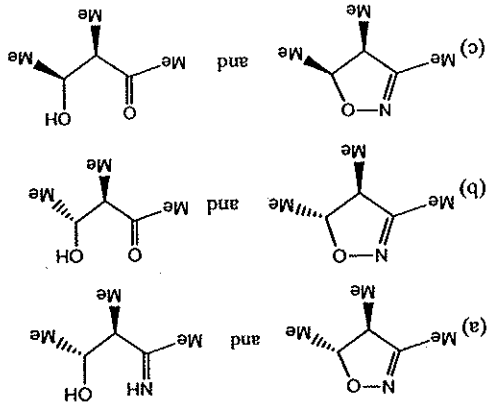
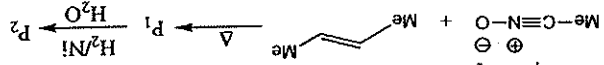
(a) I and III
(b) II and IV
(c) II and III
(d) I and IV

The most appropriate starting materials for one step synthesis of the compound (I) are [GATE 2006]

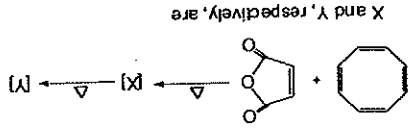


- (a) hv, conrotatory opening and Δ , disrotatory opening.
 (b) hv, disrotatory opening and Δ , conrotatory opening.
 (c) Δ , conrotatory opening and hv, disrotatory opening.
 (d) Δ , disrotatory opening and hv, conrotatory opening.

44. The Major products P_1 and P_2 , respectively, in the following reaction sequence are

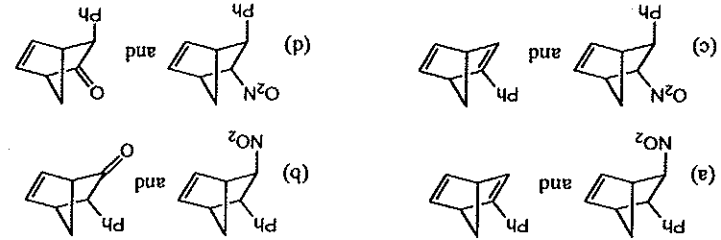


45. In the reaction sequence :

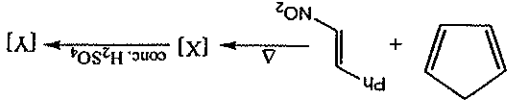


[GATE2009]

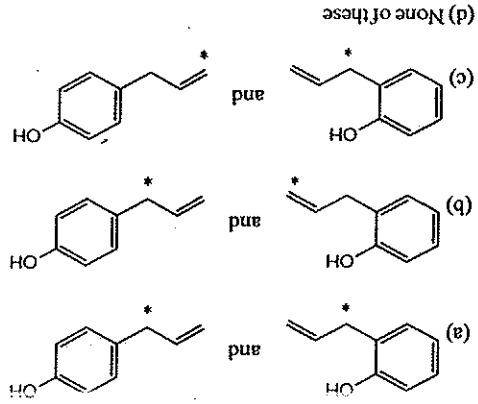
[GATE2008]



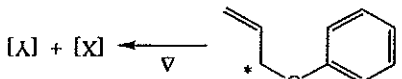
The major products X and Y, respectively are



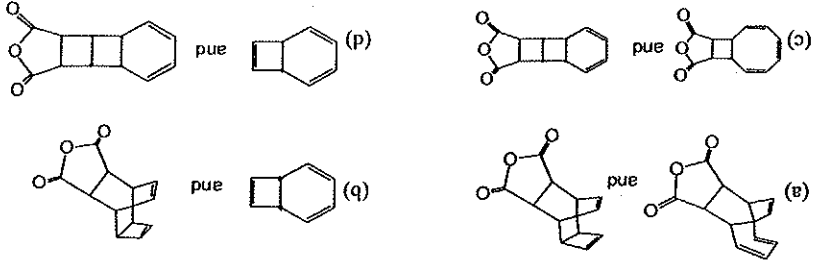
47. In the reaction sequence



the major products X and Y are

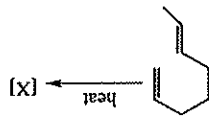


46. In the reaction

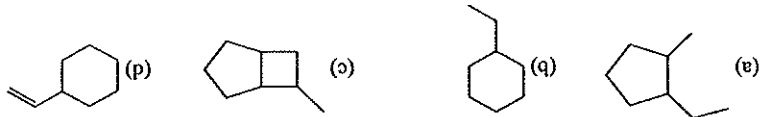


[GATE2009]

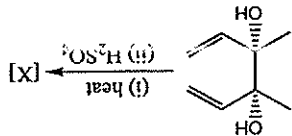
48. In the reaction



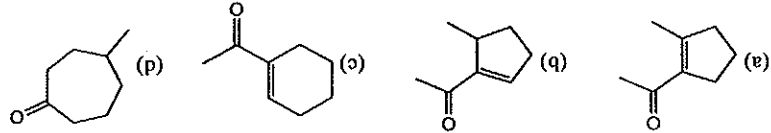
the major product [X] is



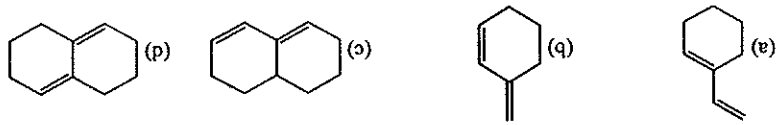
49. In the reaction,



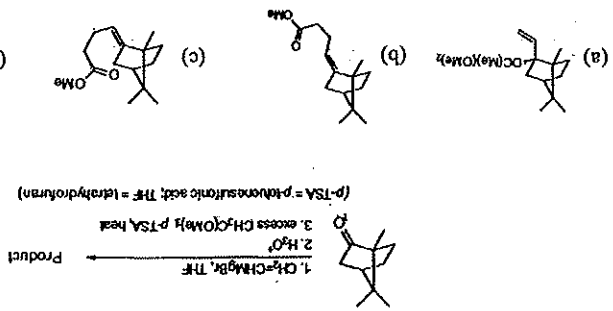
the major product [X] is:



50. The diene which undergoes Diels-Alder reaction with maleic anhydride is



51. In the reaction given below, identify the product

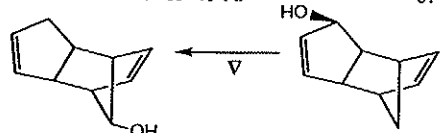


[GATE2012]

[GATE2011]

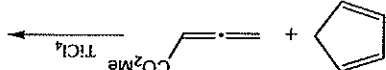
[GATE2010]

52. The pericyclic reaction given below is an example of



(a) [1, 3]-sigmatropic shift
(b) [1, 5]-sigmatropic shift
(c) [3, 5]-sigmatropic shift
(d) [3, 3]-sigmatropic shift

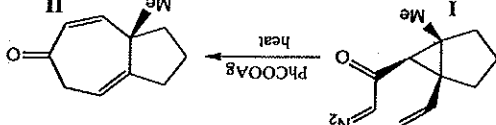
The major product formed in the following reaction is



[GATE2014]

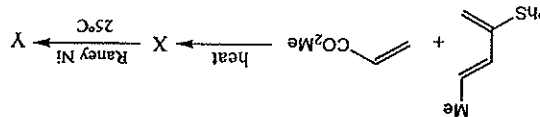
54.

Formation of the ketone II from the diazoketone I involves



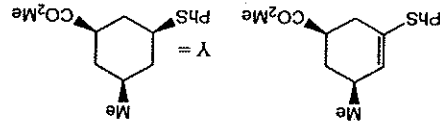
(a) generation of carbene and a [2, 3]-sigmatropic rearrangement
(b) generation of carbene and an electrocyclic ring closing reaction
(c) generation of ketene and a [2+2] cycloaddition
(d) generation of ketene and a [3, 3] sigmatropic rearrangement

The major products X and Y formed in the following reaction sequence are

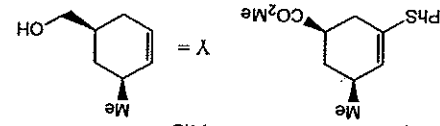


[GATE2014]

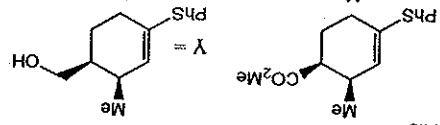
(d) X =



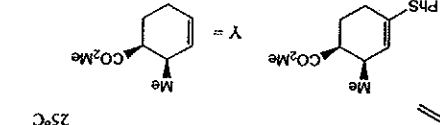
(c) X =



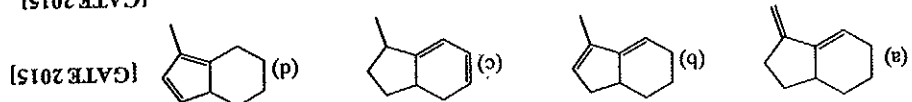
(b) X =



(a) X =

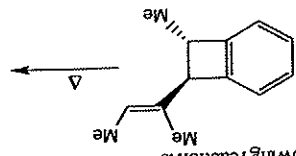


56. Amongst the following the compound that DOES NOT act as a diene in Diels-Alder reaction is



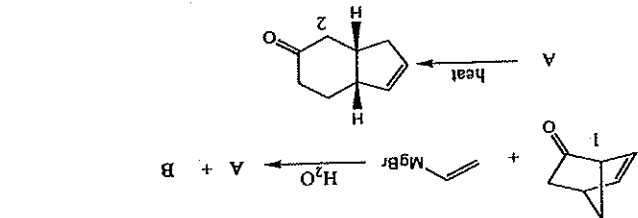
[GATE 2015]

57. The major product formed in the following reaction is

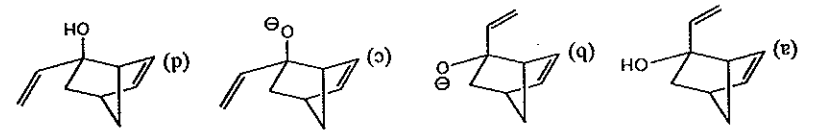


[GATE 2015]

58. Compound 1 reacts with vinyl Grignard reagent to give two compounds A and B after hydrolysis. A gives compound 2 upon heating. Predict the structure of A.

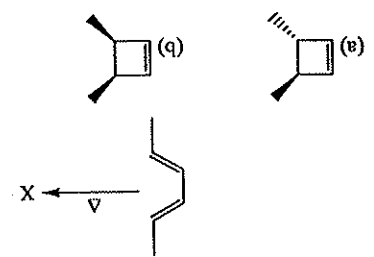


[TIFR]



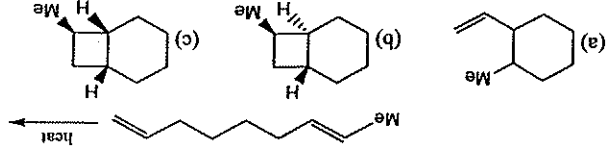
[TIFR]

59. What is the product of the following electrocyclic ring-closing reaction?

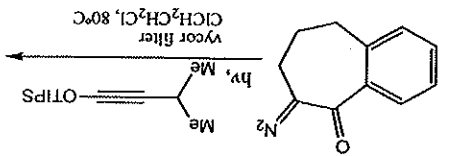


(c) both (a) and (b) (d) none of the above

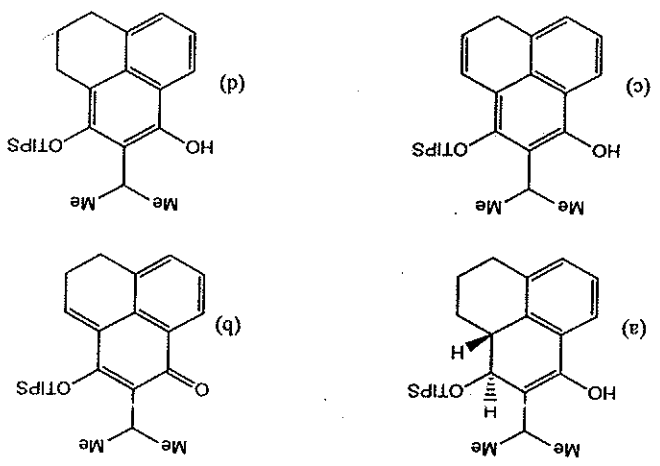
60. The major product formed in the following reaction is



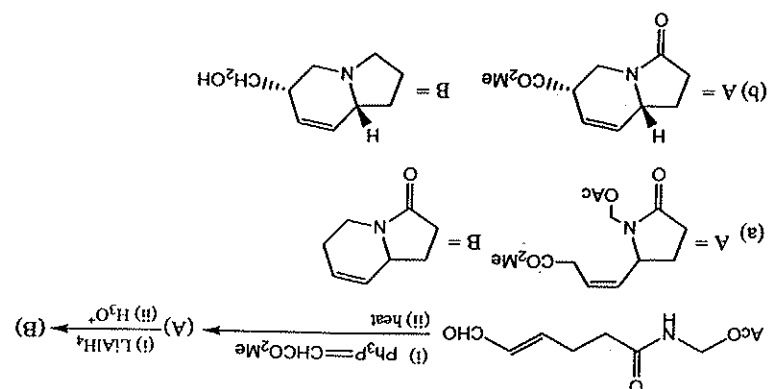
61. The major product in the following reaction sequence is



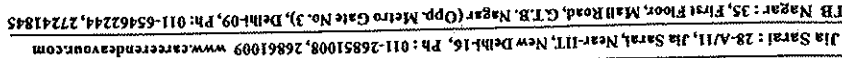
[NET June 2015]



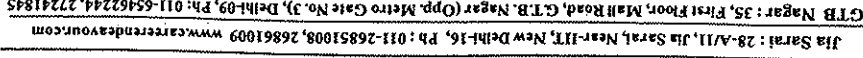
Structures of A and B in the following synthetic sequence are



[NET June 2015]



Jia Sarai : 28-A/11, Jia Sarai, Near-IIT, New Delhi-16, Ph : 011-26851008, 26861009 www.carerendecarevous.com
 JTB Nagar : 35, First Floor, Main Road, G.T.B. Nagar (Opp. Metro Gate No. 3), Delhi-09, Ph: 011-65462244, 27241845



Jia Sarai: 28-A/11, Jia Sarai, Near-IIT, New Delhi-16, Ph: 011-26851008, 26861009 www.careerendeavour.com
GTB Nagar: 35, First Floor, Main Road, GTB Nagar (Opp. Metro Gate No. 3), Delhi-09, Ph: 011-65462244, 27241845

[NET-JRF] GATE / TIFR - Previous Years' Question]

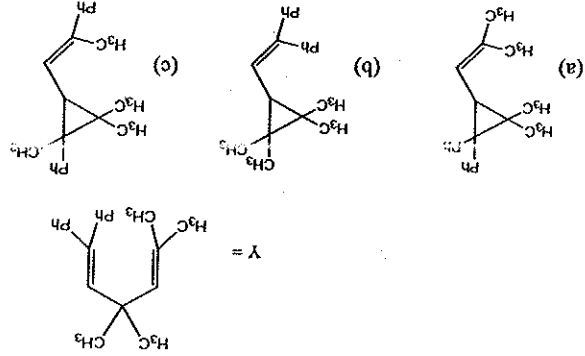
PERICYCLIC REACTIONS

CSIR-UGC-NET/JRF/GATE-CHEMISTRY

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1. The product in the photolysis of Y is:

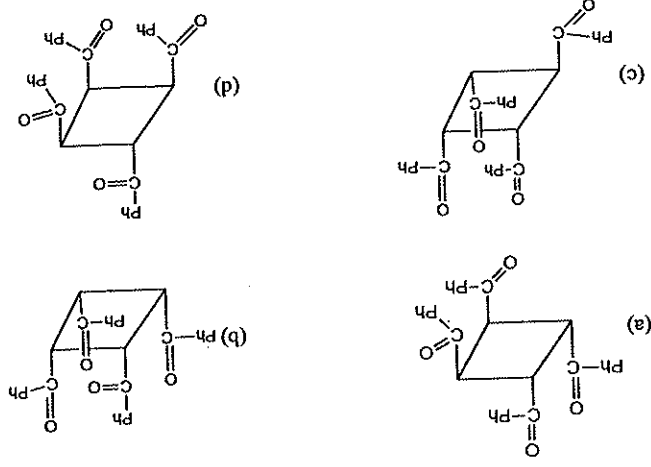
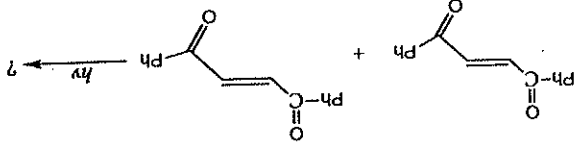
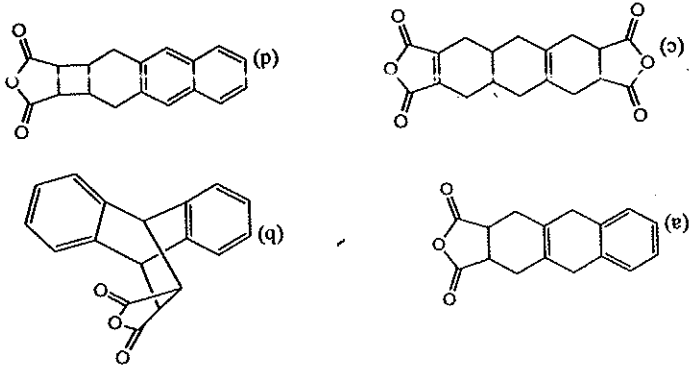
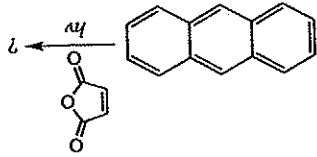


2. o-Methylbenzophenone does not readily undergo photochemical reaction when irradiated in isopropyl alcohol because
- (a) It does not undergo photoexcitation
(b) Of photoionization
(c) The reduction potential is higher than that of acetone
(d) Of steric hindrance of the ortho methyl group.

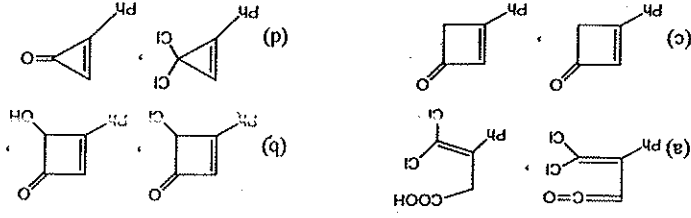
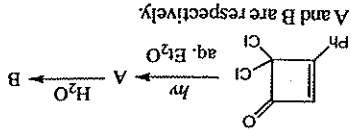
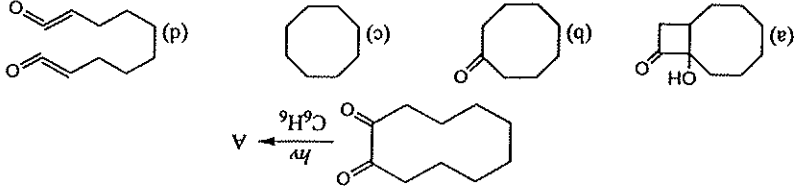


- (a) Norrish type I
(b) Norrish type II
(c) Beta-cleavage
(d) Grob fragmentation
4. During the photolysis of ketones in Norrish type II cleavage.
- (a) A homolytic fission leads to the formation of a radical intermediate.
(b) CO is produced
(c) Photoexcited carbonyl group abstracts a gamma hydrogen in the primary step
(d) Radical formed dimerize.

5. The photochemical Paterno-Buchi reaction is a cycloaddition between
- (a) Two $C=C$ groups.
(b) A $C=O$ and a $C=C$ groups.
(c) A $C=N-R$ and a $C=C$ groups.
(d) A $C=S$ and a $C=C$ groups.



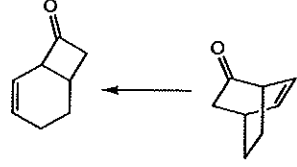
8. The major product (A) is:



10. Laser induced fluorescence is a powerful technique to monitor chemical species that fluorescence. The absorption maximum for a given molecule is at 420 nm. The fluorescence maximum for this molecule could be at:

(a) 23809 cm^{-1} (b) 22000 cm^{-1} (c) 26000 cm^{-1} (d) 2381 cm^{-1}

11. The most suitable method for accomplishing the following conversion is:



(a) hv (b) Δ (c) AIBN (d) H $^+$

12. Phosphorescence is a slower process than fluorescence because

(a) Phosphorescence occurs at longer wavelengths than fluorescence

(b) Spin angular momentum is not conserved in phosphorescence process

(c) Both (a) and (b)

(d) None of the above.

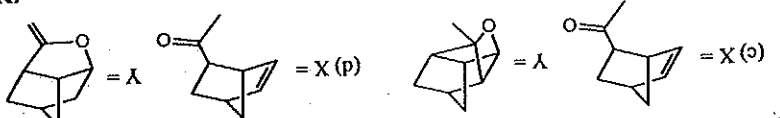
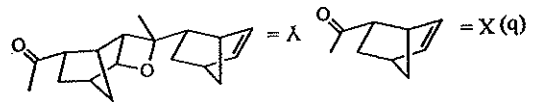
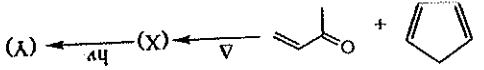
1. (a) 2. (d) 3. (a) 4. (c) 5. (b) 6. (b) 7. (a)
8. (a) 9. (a) 10. (a) 11. (a) 12. (b)

ANSWER KEY

1. The conversion of excited singlet state (S_1) of a molecule to triplet state (T_1) is known as

- (a) fluorescence (b) phosphorescence (c) intersystem crossing (d) internal conversion

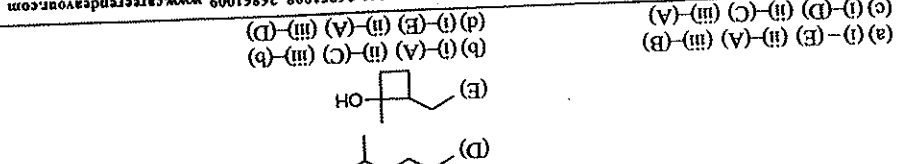
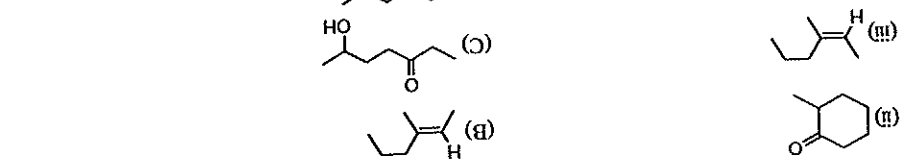
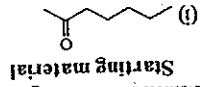
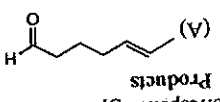
[NET June 2011]



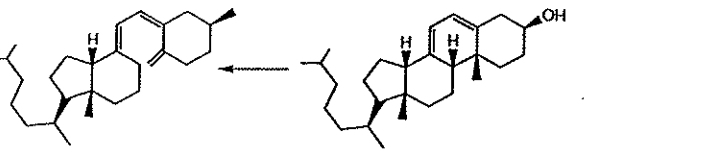
[NET June 2011]

3. Thermolysis of allyl phenyl ether generates
(a) o-allylphenol only
(b) o- and p-allylphenols
(c) o-, m- and p-allylphenols
(d) m-allylphenol only

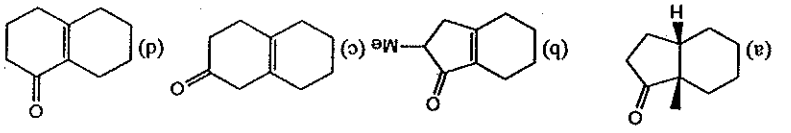
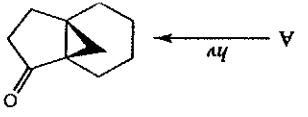
[NET Dec. 2011]



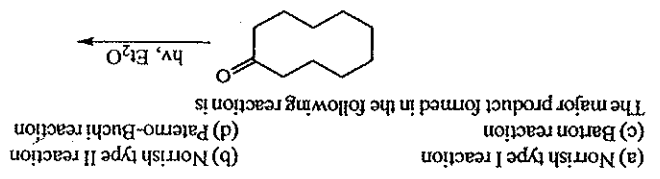
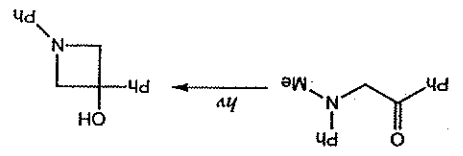
5.



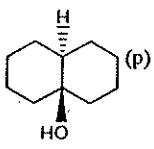
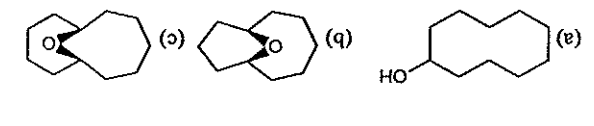
6.



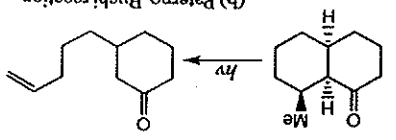
[NET Dec. 2012]



[NET June 2013]

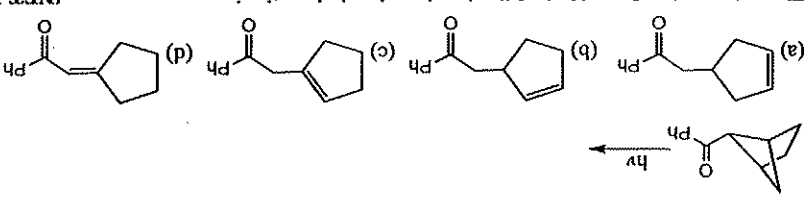


[NET June 2012]



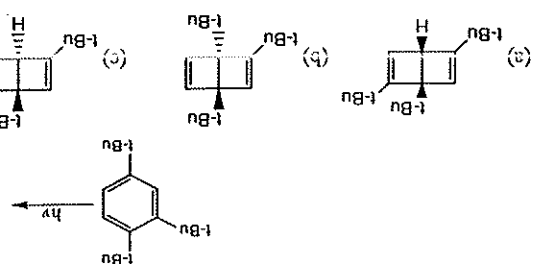
[NET Dec. 2013]

10. The major product formed in the following photochemical reaction is



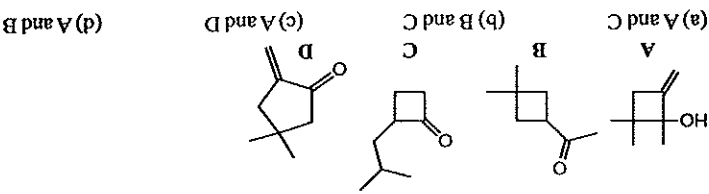
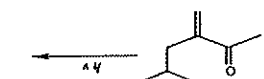
[NET June 2014]

11. The major product formed in the following photochemical reaction is



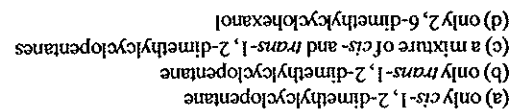
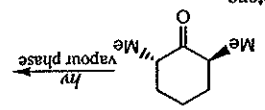
[NET June 2014]

12. Amongst the following, the major products formed in the following photochemical reactions are



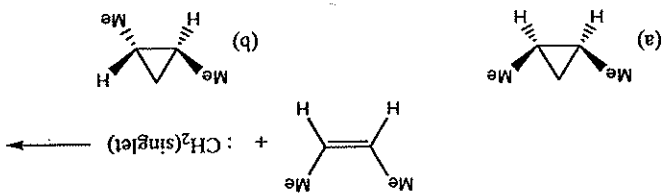
[NET Dec. 2014]

13. The cyclic product(s) of the following photochemical reaction is(are)



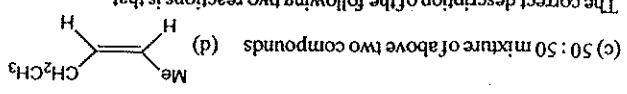
[GATE 2000]

14. The major product formed in the following reaction is:

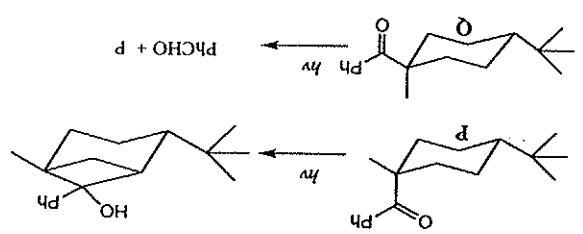


15.

The correct description of the following two reactions is that



[GATE 2003]



(a) Both P and Q undergo α -cleavage reaction

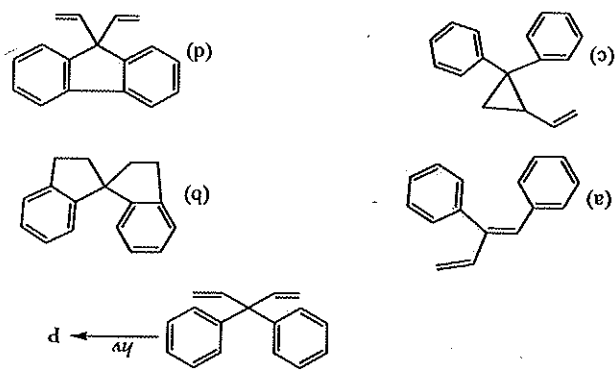
(b) P undergoes only Norrish type II reaction whereas Q undergoes only Norrish type I reaction.

(c) Q gives P by photochemical chair to chair interconversion of the cyclohexane Ring

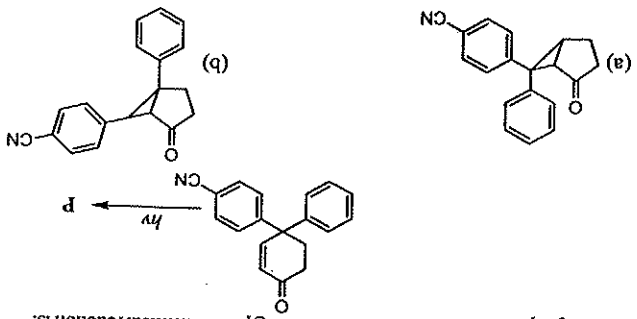
(d) Both P and Q undergo Norrish type I reaction, but only Q gives S through this mechanism.

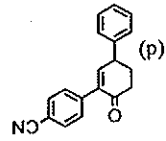
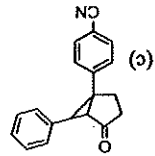
[GATE 2004]

17. The major product P formed in the following photochemical reaction is:

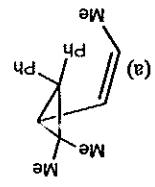
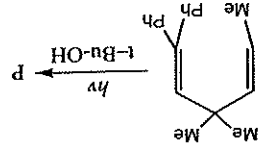


[GATE 2004]

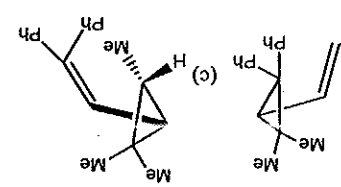




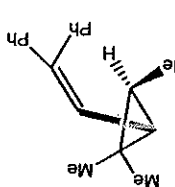
18. Identify the major product P in the following reaction.



(b)

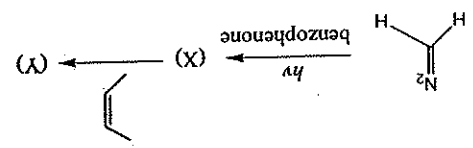


(d)



[GATE 2008]

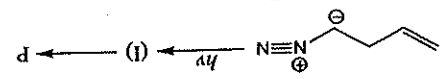
19. In the following reaction



(X) and (Y) respectively are

- (a) 1; CH₂ and cis 1, 2-dimethylcyclopropane.
 (b) 3; CH₂ and cis 1, 2-dimethylcyclopropane.
 (c) 1; CH₂ and a mixture of cis/trans 1, 2-dimethylcyclopropane.
 (d) 3; CH₂ and a mixture of cis/trans 1, 2-dimethylcyclopropane.

20. In the following reaction

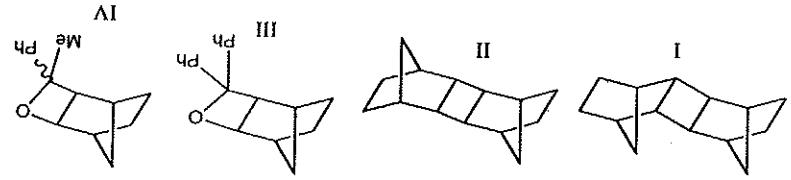


The reactive intermediate I and the product P are

- (a) carbene and
 (b) radical and
 (c) carbene and
 (d) radical and

[GATE 2008]

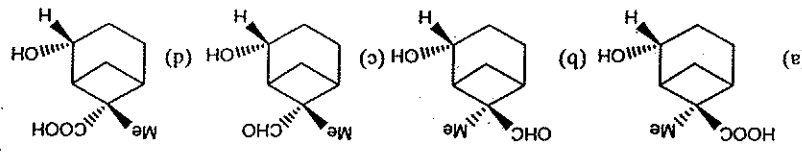
21. Identify the major product P and Q in the following reactions from the list of compounds I to IV.



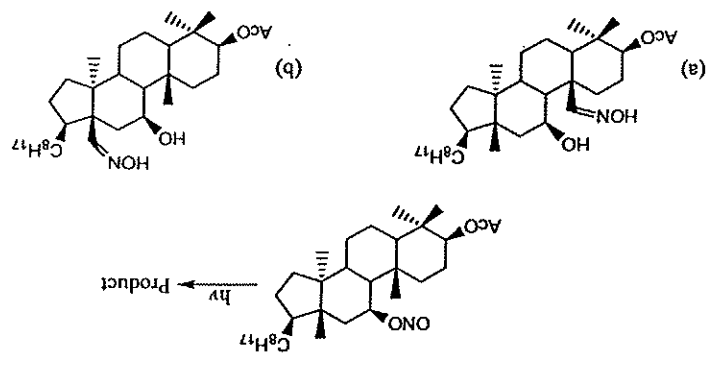
- (a) P:I and Q:II (b) P:II and Q:III (c) P:IV and Q:II (d) P:IV and Q:III

[GATE 2010]

In the following reaction sequence the major product [X] is



23. The product from the following reaction is



[GATE 2012]

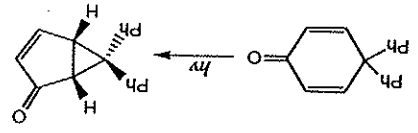
24. Match the compounds in the Column-I with photochemical reactions that they can undergo given in the Column-II: [GATE 2013]
- Column-I

(c)

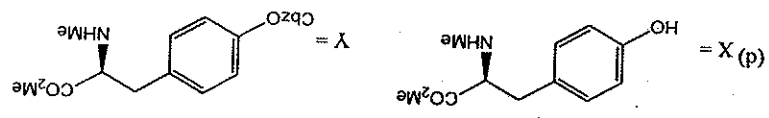
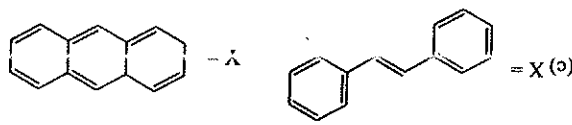
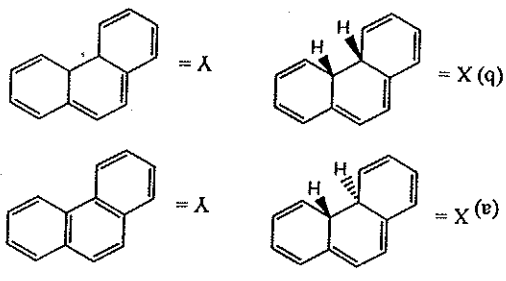
Column-II

(d)

- (i) oxa-di- π -methane rearrangement
 (ii) Paterno-Buchi reaction
 (iii) intramolecular [2+2]-cycloaddition.
- Formation of the product in the following photochemical reaction involves
- (a) di- π -methane rearrangement
 (b) Paterno-Buchi reaction
 (c) [2, 3]-sigmatropic rearrangement
 (d) Norrish type I reaction
- [GATE 2014]



26. The major product X and Y formed in the following reaction sequence are
- cis-stilbene $\xrightarrow{h\nu}$ X $\xrightarrow{C_6H_{12}}$ Y $\xrightarrow{I_2, air}$ Y



The major product formed in the following reaction is [NET June 2015]

