1-50 (2 points for each; wrong answer will deduct 1point)

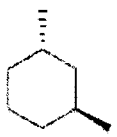
1. On Pluto, where everything is frozen, astronauts discovered two forms of **1,2-dibromoethane**: gauche and anti. Assuming that there are **no rotations** around single bonds, which statement about the two forms is correct?

a) They are enantiomers.
b) They are diastereoisomers.
c) They are meso compounds.
d) The gauche form has two stereogenic centers, and the anti has only one.
e) Both will show optical activity.

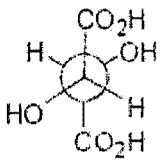
2. What is the best description of the first organic intermediate formed when 2-butyne reacts with HCl?

a) allylic cation b) allylic anion c) chloronium ion d) vinylic cation e) vinylic anion

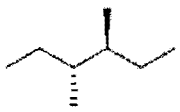
3. Which of the following will show optical activity?



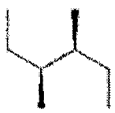
A



B



C



D

E: 50/50 mixture of C and D

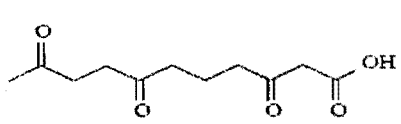
a) **A**, **D**, and **E** b) **B**, **C**, and **D** c) **B**, **C**, and **E** d) **A** and **E** only e) All except **C**

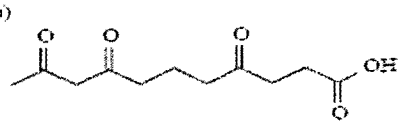
4. One of the two chair conformations of *cis*-1-chloro-3-methylcyclohexane is more stable than the other by 3.70 kcal/mol. What is the energy cost of 1,3-diaxial interaction between a chlorine and a methyl group?

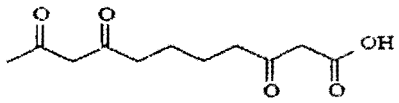
a) 3.95 kcal/mol b) 2.55 kcal/mol c) 2.80 kcal/mol d) 3.05 kcal/mol e) 4.85 kcal/mol

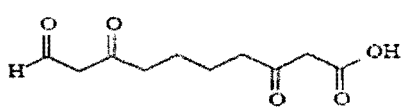
(背面仍有題目,請繼續作答)

5. What is the final product of the following reaction?

a)


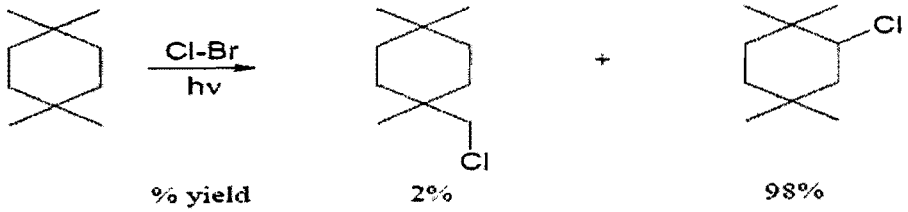
b)


c)


d)


e) None of them

6. Which radical is responsible for the observed selectivity in the chain reaction below?

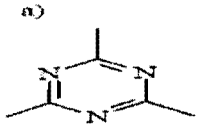


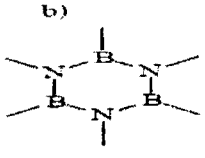
a) Cl• b) Br• c) H• d) 1° alkyl radical e) 2° alkyl radical

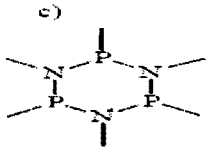
7. What is true about the following equilibrium?

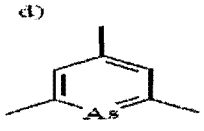
a) It will be almost completely shifted to the left.
b) It will be almost completely shifted to the right.
c) The equilibrium constant is very close to one.
d) The equilibrium constant is zero.
e) None of them

8. Which of the following heterocycles **is not** aromatic? Note that loneelectron pairs are not shown explicitly.

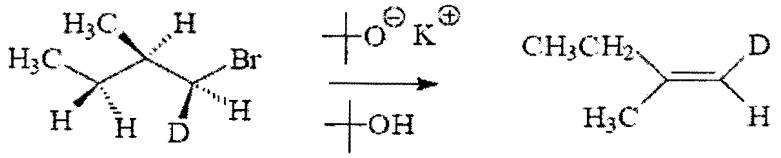
a)


b)


c)


d)


Questions **9** and **10** refer to the following reaction:



9. What is the mechanism of the above reaction?

a) SN1 b) SN2 c) E1 d) E2 e) none of the above

10. What happens to the reaction rate if the concentration of t-butoxide is doubled?

a) no change b) halved c) doubled d) tripled e) quadrupled

11. For the following multistep synthesis, which set of reagents would be more likely to give the desired product?

a) (i) HBr, (ii) O_3 followed by Zn/H+, (iii) Li/NH_3

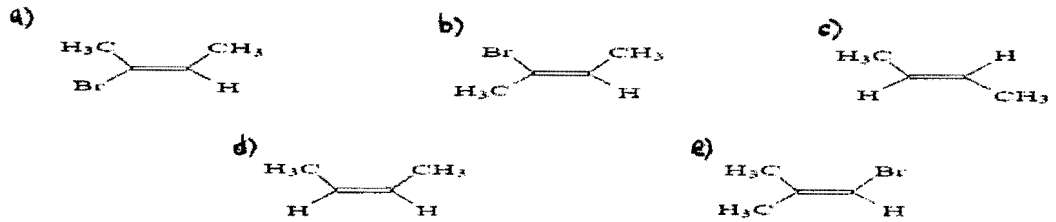
b) (i) $NaNH_2/NH_3$ followed by CH_3CH_2I (ii) Lindlar's catalyst/H_2 (iii) OsO_4 followed by $NaHSO_3$

c) (i) H_2/Pd/C (1 equivalent), (ii) $NaNH_2/NH_3$ followed by CH_3CH_2Br, (iii) $KMnO_4$/ OH/H_2O

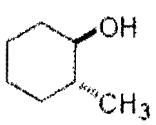
d) (i) $HgSO_4/H_2O/H_2SO_4$, (ii) Lindlar's catalyst/H_2, (iii) OsO_4 followed by $NaHSO_3$

e) None of them

12. What is the product of dehydrohalogenation of (*R*,*R*)-2,3-dibromobutane?



13. Select the **best** method for preparation of the following compound:



a) react cyclohexanone with CH_3Li

b) react 1-methylcyclohexene with $Hg(OAc)_2$ followed by $NaBH_4$

c) react cyclohexene with BH_3; $NaOH/H_2O_2$, followed by CH_3Br

d) react cyclohexene with MCPBA, followed by CH_3MgBr

e) react 1-methylcylohexene with $KMnO_4$/NaOH

(背面仍有題目,請繼續作答)

14. Which is the **best** sequence of reactions for preparation of 2,4-dinitrobenzoic acid from benzene?

a) 1. HNO_3/H_2SO_4 2. $CH_3Br/AlCl_3$ 3. HNO_3/H_2SO_4 4. $KMnO_4/H^+$

b) 1. $CH_3Br/AlCl_3$ 2. HNO_3/H_2SO_4 3. $KMnO_4/H^+$ 4. HNO_3/H_2SO_4

c) 1. $CH_3Br/AlCl_3$ 2. $KMnO_4/H^+$ 3. HNO_3/H_2SO_4 (excess)

d) 1. HNO_3/H_2SO_4 2. $CH_3Br/AlCl_3$ 3. $KMnO_4/H^+$ 4. HNO_3/H_2SO_4

e) 1. $CH_3Br/AlCl_3$ 2. HNO_3/H_2SO_4 (excess) 3. $KMnO_4/H^+$

15. Which of the following series of reactions is the **best** way to convert ***R***-2-pentanol to ***R***-2-ethoxypentane?

a) *p*-TosCl/pyridine; EtOH/NaOH

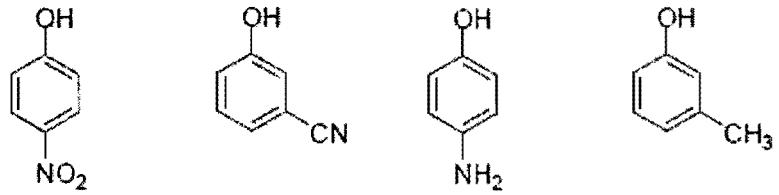
b) *p*-TosCl/pyridine; PBr_3/ether; NaOEt/EtOH

c) PBr_3/ether; NaOEt/DMSO

d) EtOH/NaOH; HCl

e) HBr; NaOEt/EtOH

16. Arrange the following phenols in order of increasing acidity (least to most acidic).

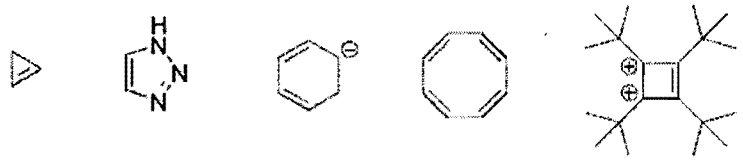


A B C D

a) **A < B < C < D** b) **D < C < A < B** c) **C < D < B < A**

d) **C < D < A < B** e) **D < C < B < A**

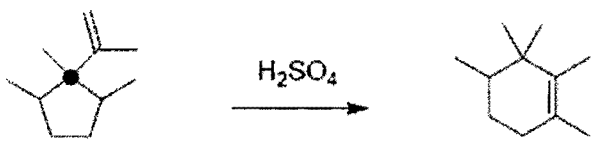
17. Which of the following species are aromatic?



I II III IV V

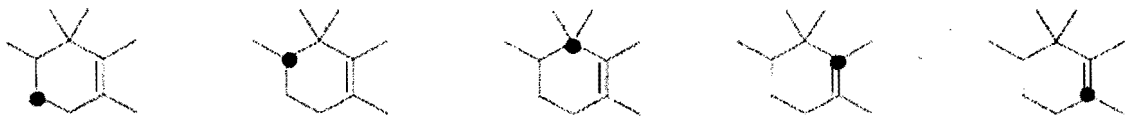
a) **I and II** b) **II and V** c) **IV and V** d) **I, II, and III** e) **II, III, and V**

18. In the reaction shown below, the carbon marked by a dot (•) is 13C isotope that can be distinguished from "normal" carbons (12C) by a special kind of spectroscopy.

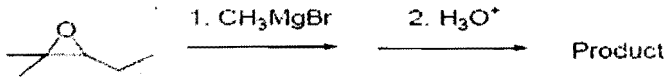


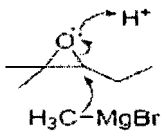
Which structure shows the correct position of ^{13}C in the product of the carbocation rearrangement shown above?

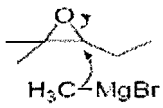
a) b) c) d) e)

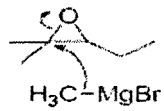


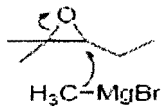
19. What is the correct mechanistic designation for the first step of ring-opening reaction of the epoxide shown below?



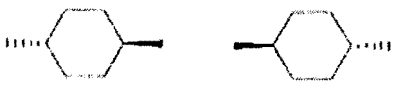
a) 

b) 

c) 

d) 

20. Which of the following statements about A and B is true?



A B

a) They are different conformations of the same molecule.

b) They are constitutional isomers.

c) They are diastereomers.

d) They are enantiomers.

e) They are identical.

Questions **21** and **22** refer to the following reagents available to accomplish the transformation given below:

a) $KMnO_4/H^+$

b) $H_2/Pd/C$

c) OsO_4; $NaHSO_3$

d) Li/NH_3(liquid)

e) $Hg(OAc)_2/H_2O$; $NaBH_4$

f) BH_3; H_2O_2/ HO

g) NBS/DMSO/H_2O

h) H_2/Lindlar's catalyst

i) HIO_4

j) H_2SO_4/SO_3

21. What reagent was employed to carry out the third (**III**) step?

22. Availability of which reagent would allow to shorten the synthesis to just two steps?

a) O_3; Zn/AcOH b) $KMnO_4/HO^-$ c) CrO_3/H^+ d) PCC e) None of them

(背面仍有題目,請繼續作答)

23. Considering only monochlorides, what would be the yield of the most abundant product in the radical-chain chlorination of 2,3,4-trimethylpentane?

a) 10% b) 15% c) 20% d) 33% e) 40%

The following reagent list applies to questions **24-25.**

a) $NaNH_2/NH_3$ f) BH_3; H_2O_2/ HO^-

b) H_2/Pd/C g) $POCl_3$/pyr

c) NBS/H_2O/DMSO h) H2/Lindlar's catalyst

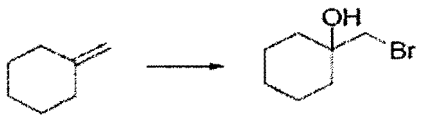
d) CH_3OH/heat i) Li/NH_3(liquid)

e) $Hg(OAc)_2/H_2O$; $NaBH_4$ j) H_2SO_4/SO_3

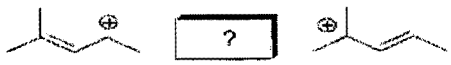
What are the correct reagents necessary to carry out each transformation?

24.

25.



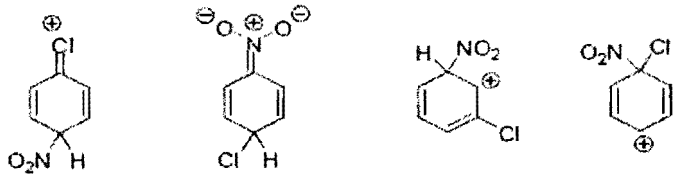
26. Which symbol should be used to correctly represent the relationship between the two structures drawn below?



a) ⟶ b) ⟵ c) ⟷ d) ⇌ e) ⟷

27. Which structure shows a major intermediate formed in the electrophilic nitration of chlorobenzene?

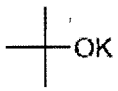
a) b) c) d)



28. When A and B react in t-BuOH, the following rate expression is observed:

A: 

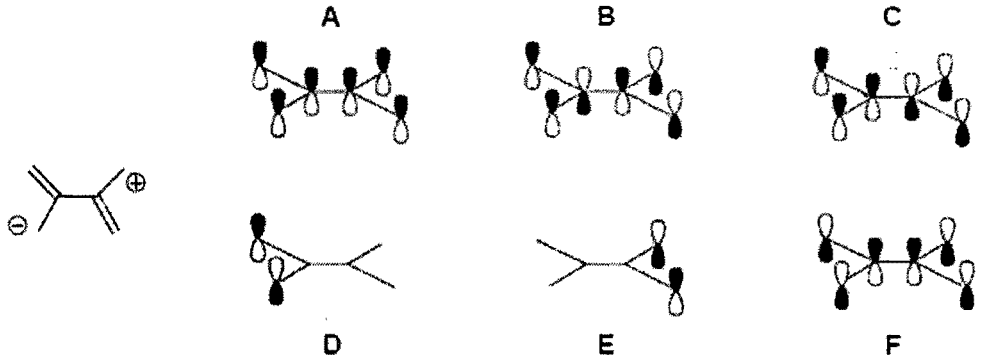
$-d[A]/dt = k[A][B]$

B: 

What is the most likely mechanism of this reaction?

a) E_2 b) SN_2 c) E_1 d) SN_1 e) it cannot be determined

29-30. Consider a 6-carbon π system built of an allyl anion and an allyl cation by connecting their central carbons. The π-type MOs of that system are shown below in a random order. Note that some orbitals may be degenerate.



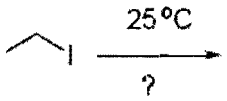
29. Which of the following transitions will have the largest λmax?

a) A F b) D B c) C B d) D F e) E B

30. How many unpaired electrons are there in the molecule according to this MO scheme?

a) 0 b) 1 c) 2 d) 3 e) 4

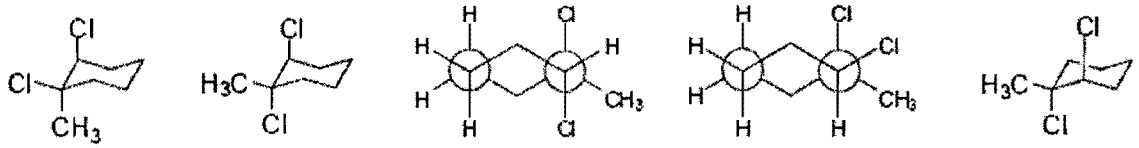
31. Select the reagent and solvent combination which would result in the fastest rate of substitution (R = CH_3 in all cases).



a) ROH, HMPA b) RS^-, H_2O c) RO^-, H_2O d) RS^-, DMSO e) RSH, H_2O

32. What is the best representation of **the lowest energy conformation** of (1R)(2S)-1,2-dichloro-1-methylcyclohexane?

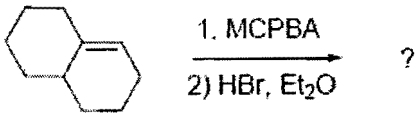
a) b) c) d) e)



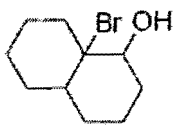
33. The heats of formation, ΔHf (rounded off to simplify the arithmetic), of cyclohexane and cyclooctane are both –30 kcal/mol. What is **the strain energy** (in kcal/mol) of cyclooctane?

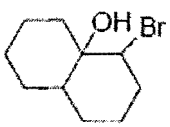
a) 0 kcal/mole b) 5 kcal/mole c) 10 kcal/mole d) 15 kcal/mole e) 20 kcal/mole

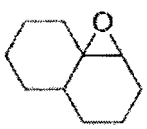
34. What is the major organic product of the reaction shown below?

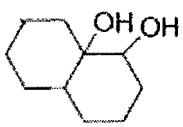


a) 

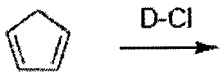
b) 

c) 

d) 

e) 

35-36. In general, different isotopes of the same atom have almost indistinguishable reactivities. Consider the reaction of 1 equivalent of D-Cl with 1,3-cyclopentadiene where D = ^{2}H.



35. Which is true about this reaction?

a) The 1,2-adduct is the kinetic product, and the 1,4-adduct is the thermodynamic product.

b) The 1,4-adduct is the kinetic product, and the 1,2-adduct is the thermodynamic product.

c) The kinetic and thermodynamic products are the same, except for isotopic substitution.

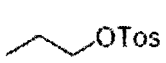
d) There is only 1,2-adduct possible in this reaction.

e) There is only 1,4-adduct possible in this reaction.

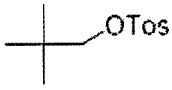
36. How many isomers, including stereoisomers, form in this reaction?

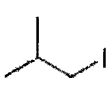
a) 2 b) 4 c) 6 d) 8 e) 16

37. Select the substrate which would react fastest in the substitution reaction under the indicated conditions (at 25 °C)?

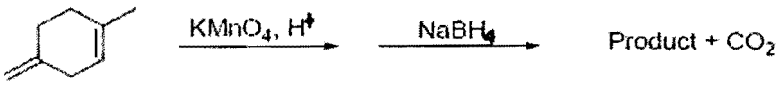
a) 

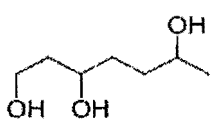
b) 

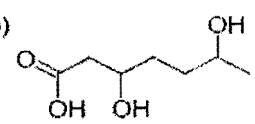
c) 

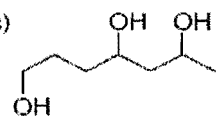
d) 

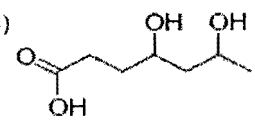
38. What is the product of the following sequence of reactions?



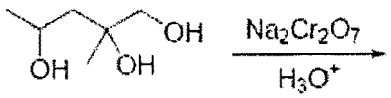
a) 

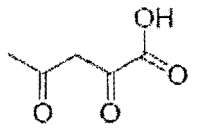
b) 

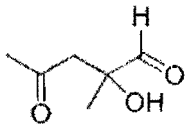
c) 

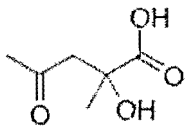
d) 

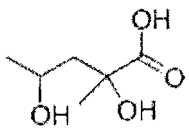
39. What is the product of the following reaction?



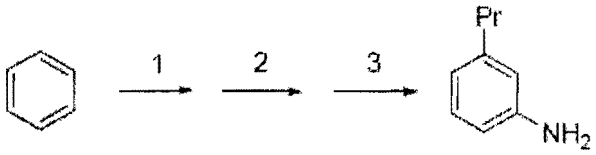
a) 

b) 

c) 

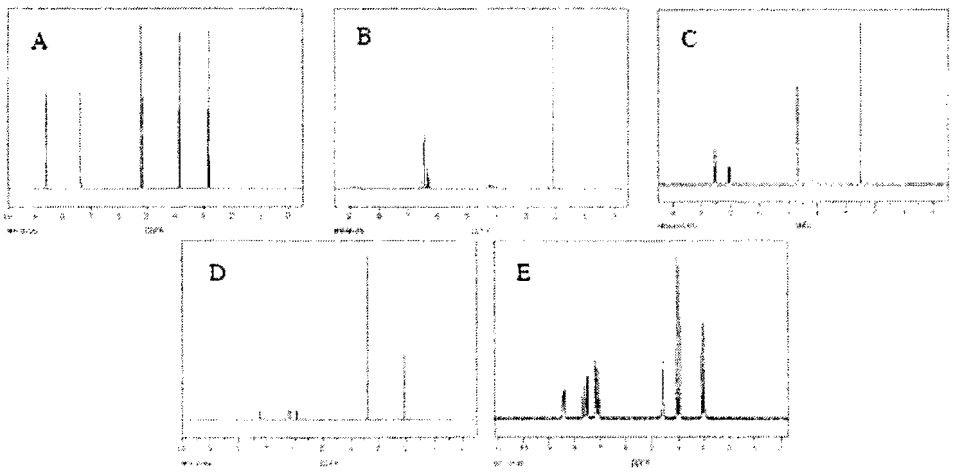
d) 

40. What is the best sequence of reactions to synthesize the desired product?

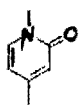


	Step 1	Step 2	Step 3
a)	HNO_3/H_2SO_4	$PrMgBr/H_3O^+$	H_2/Pd
b)	HNO_3/H_2SO_4	$AlCl_3/PrBr$	H_2/Pd
c)	$AlCl_3/PrCl$	HNO_3/H_2SO_4	H_2/Pd
d)	HNO_3/H_2SO_4	H_2/Pd	$PrMgBr/H_3O^+$
e)	$AlCl_3/EtCOCl$	HNO_3/H_2SO_4	H_2/Pd

41-45. Shown below are 5 structural isomers of the anisidines. Match each isomer with its ^1H NMR spectrum by filling in the letters A-E below.

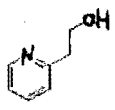


41.



a) A b) B c)C d) D e) E

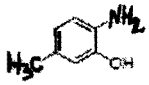
42.



a) A b) B c)C d) D e) E

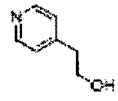
(背面仍有題目,請繼續作答)

43.



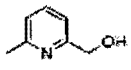
a) A b) B c)C d) D e) E

44.



a) A b) B c)C d) D e) E

45.



a) A b) B c)C d) D e) E

46-50. Match the following compounds with the spectral data by writing its letter on the line.

A $CH_3OCH_2CH_2OCH_3$	**B** $N(CH_2CH_3)_3$	**C** $CH_3\overset{Br}{\underset{|}{C}}HCH_2CH_3$	**D** $ClCH_2\overset{O}{\overset{\|}{C}}OCH_2CH_3$	**E** $CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3$

46.

^{1}H NMR

δ (ppm)	
1.31	triplet(3H)
4.07	singlet(2H)
4.35	quartet(2H)

a) A b) B c)C d) D e) E

47.

^{1}H NMR

δ (ppm)	
3.25	singlet(6H)
3.45	singlet(4H)

a) A b) B c)C d) D e) E

48.

^{1}H NMR

δ (ppm)	
1.05	triplet(3H)
2.13	singlet(3H)
2.47	quartet(2H)

a) A b) B c)C d) D e) E

49.

^{1}H NMR

δ (ppm)	
0.9	triplet(3H)
2.4	quartet(2H)

a) A b) B c)C d) D e) E

50.

^{1}H NMR

δ (ppm)	
1.05	triplet(3H)
1.82	multiplet(2H)
1.7	doublet(3H)
4.1	multiplet(1H)

a) A b) B c)C d) D e) E