CHM 102A End-Sem Exam 2018

Total Marks: 80 Duration: 2 Hours

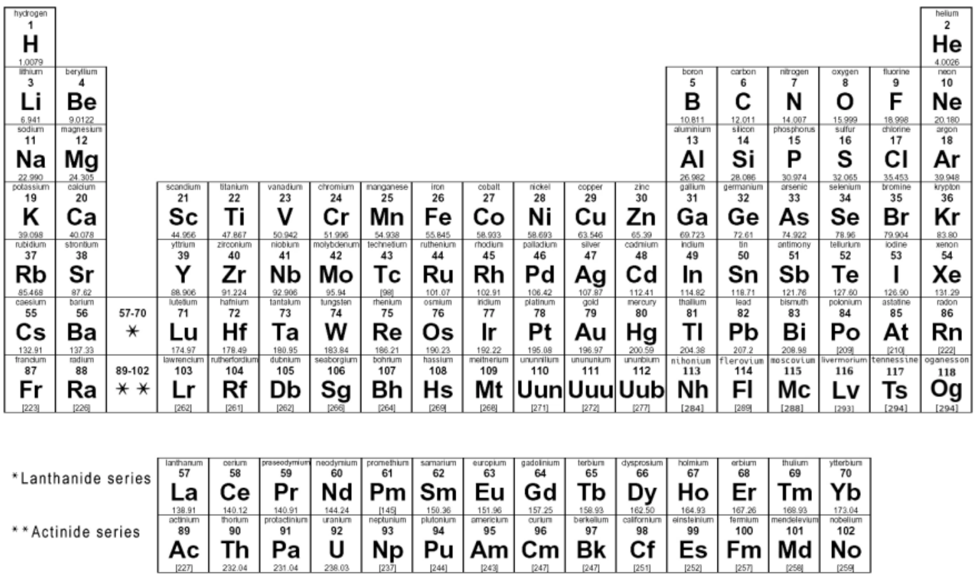
Name:

Roll Number:

Section:

Instructions:

1. **Please write answers in the space (box) provided.**
2. **Please write in ink. (Answers written in pencil will not be re-graded)**
3. **Calculators are allowed. (Sharing calculators in NOT ALLOWED).**



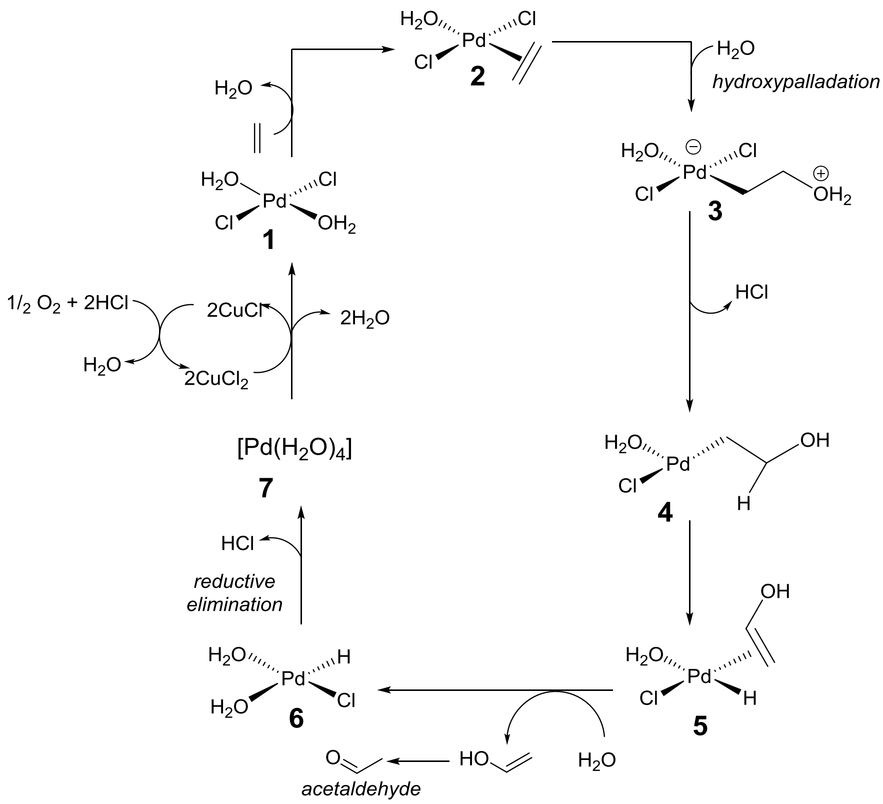
Q. No.	1	2	3	4	5	6	7	8	Total
Marks									

Q1.

(i) Below is a proposed catalytic cycle describing the Wacker oxidation reaction, which is used to produce about 4 million tons of acetaldehyde annually.

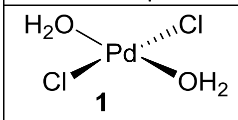
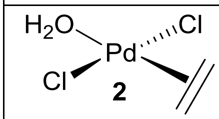
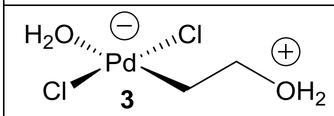
a) In the table below, write the oxidation state and total valence electron count of Pd in each complex (**1** – **7**). (Both values have to be correct to get one mark. No partial marking.) **(1*7 = 7 marks)**

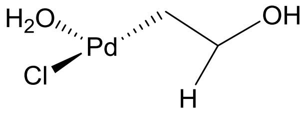
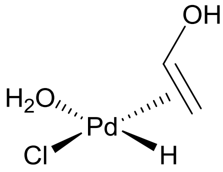
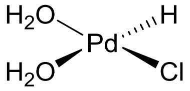
b) What is the correct terminology (name) for the reaction which converts complex **4** to complex **5** ? **(1 mark)**



Answer (i)

a)

Metal complex	Oxidation State of Palladium	Valence Electron Count for Pd
	+2	16 electrons
	+2	16 electrons
	+2	16 electrons

Metal complex	Oxidation State of Palladium	Valence Electron Count for Pd
 **4**	+2	14 electrons
 **5**	+2	16 electrons
 **6**	+2	16 electrons
$[Pd(H_2O)_4]$ **7**	0	18 electrons

b) What is the name of the step that converts **4** to **5** ?.

β-elimination or β-hydride elimination

(marks have been awarded for "elimination" also)

(ii) The following carbonyl complexes give distinct CO stretching peaks when subjected to IR (infrared) spectroscopy. Identify the one with the lowest and highest CO stretching frequency (as measured in cm^{-1}). **(1+1 =2 marks)**

$[Ti(CO)_6]^{2-}$ $Cr(CO)_6$ $[Fe(CO)_6]^{2+}$ $[V(CO)_6]^{-}$ $[Mn(CO)_6]^{+}$

Answer (ii):

Complex with highest stretching frequency: $[Fe(CO)_6]^{2+}$

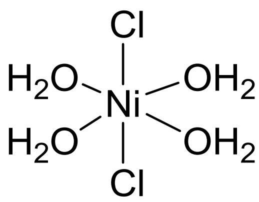
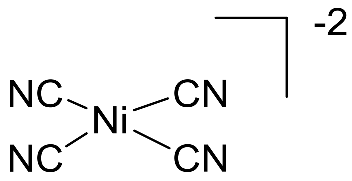
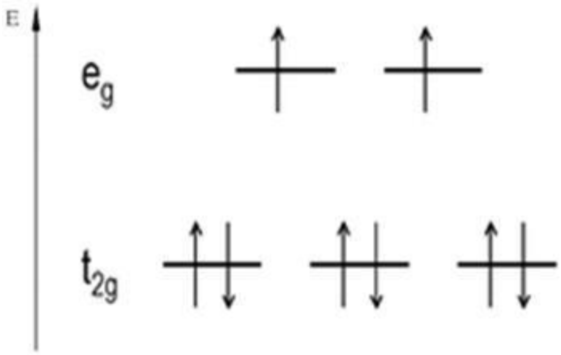
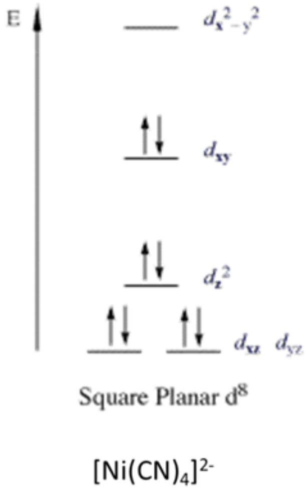
Complex with lowest stretching frequency: $[Ti(CO)_6]^{2-}$

As we progress from Ti(2-) to V(-) to Cr(0) to Mn(1+) to Fe(2+) the positive charge on the metal is increasing which reduces the extent of π-back-donation from the central metal orbital to the $\pi*$ of the ligand. This can be observed via an increase in the ν(CO) stretching frequency in the IR spectrum. This is most obvious, for example, if we compare the least electronegative metal center Ti(2-) where ν(CO) = 1748 cm-1 relative to the most electronegative metal given in Fe(2+) where νCO) = 2204 cm-1 .

Q2.

(i) The complex *trans*-$[NiCl_2(H_2O)_4]$ (**A**) is paramagnetic. Upon treatment with excess NaCN, a diamagnetic complex $[Ni(CN)_4]^{-2}$ (**B**) is obtained. Draw structures for **A** and **B** along with their *d*-orbital splitting diagram showing the electrons. (the entire structure and splitting diagram has to be correct for 1 mark each. No partial marking) **(2 + 2 = 4 marks)**

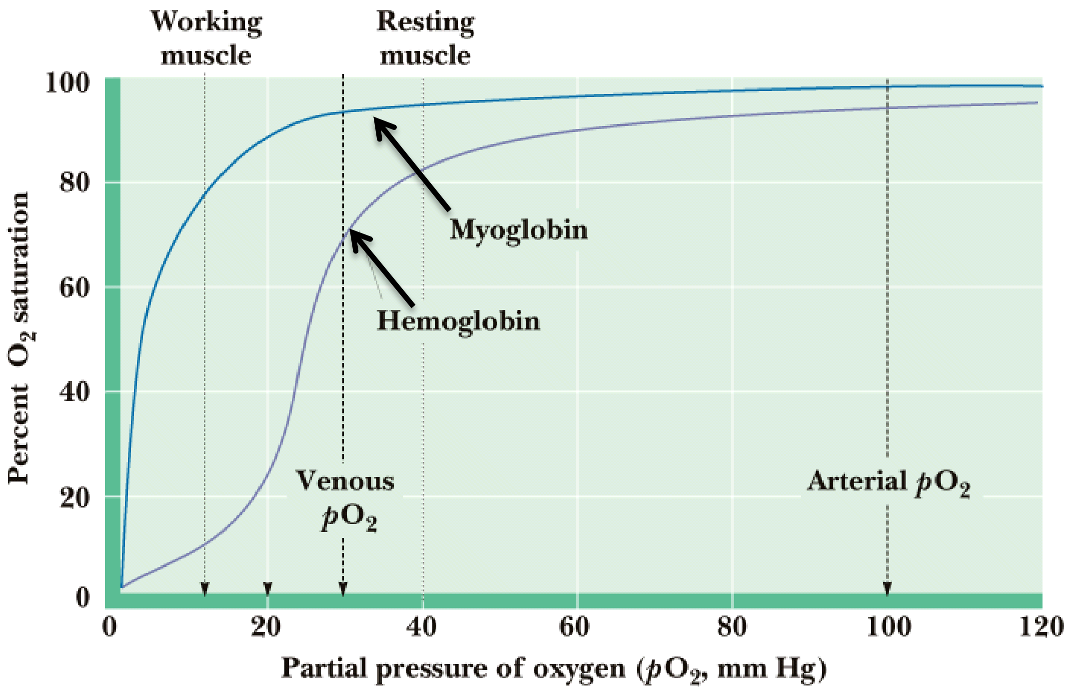
Answer:

	Complex **A**	Complex **B**
Structure		
d-orbital splitting diagram		

Complex **A** is octahedral, d8, $(t_{2g})^6(e_g)^2$ with 2 unpaired electrons, hence paramagnetic.
Complex **B** is square planar with the electron configuration shown, hence diamagnetic.
1 mark for each for the structures of A and B, and 1 mark for each for the orbital splitting diagram including the electrons. (no further partial marking).

(ii) Consider the following oxygen binding curves for Hemoglobin (Hb) and Myoglobin (Mb) and answer the following questions (write **True** or **False** in the box provided).

(1x6 = 6 marks)



a) The sigmoidal curve of Hemoglobin (Hb) indicates that it is more suited for releasing oxygen in the muscles compared to Myoglobin (Mb).

TRUE

b) In the working muscle, Hemoglobin (Hb) is mainly in the "R" state.

FALSE

c) The sigmoidal curve of Hemoglobin (Hb) indicates that the binding of one molecule of oxygen decreases the affinity of other subunits for binding subsequent oxygen molecules.

FALSE

d) When saturated, one molecule of Myoglobin binds to four molecules of oxygen.

FALSE

e) The coordination number of Fe^{+2} in de-oxygenated Hemoglobin and Myoglobin is 4.

FALSE

f) We know that a very small amount of carbon monoxide is produced in the human body. However, it does not result in fatal poisoning because the binding affinity of Mb and Hb towards CO is less than towards O_2.

FALSE

Q3.

(i) An automobile catalytic converter contains solid platinum, palladium, and rhodium compounds and converts NO to N_2 and O_2. This conversion is an example of which of the following: Enzyme Catalysis, Homogeneous Catalysis, Heterogeneous Catalysis. **(1 mark)**

Answer:

Heterogeneous Catalysis

(ii) The rate of a certain enzyme catalyzed reaction is being tracked by determining light absorbance of the product by absorption spectroscopy. The volume of the reaction mixture is 2 cm^3, which contains 5 μg enzyme. The change in light absorbance in 1 minute is $\Delta A = 0.15$ (measured in a 1 cm long sample container).
(It is given that the molar extinction coefficient of the product is $\varepsilon = 3 \cdot 10^4\ M^{-1}cm^{-1}$. The molar mass of the enzyme is 50000 g/mol.) **(1+1 = 2 marks)**

a) What is the change in concentration of the product in 1 minute?

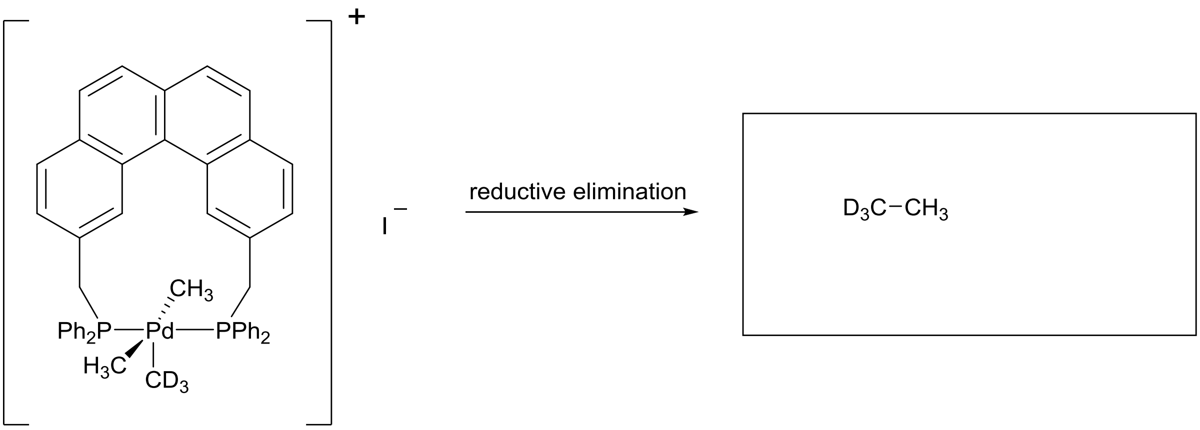
$5x10^{-6}$ M

b) How many moles of substrate are transformed by 1 mole of enzyme in 1 minute?

100

Detailed solution:
According to the Lambert-Beer equation: $A = \varepsilon c l$
$\Delta A = \Delta c \varepsilon l$
$\Delta c_{product} = \Delta E/(\varepsilon \cdot l) = 0.15/(3\cdot10^4\ M^{-1}cm^{-1}\cdot 1\ cm) = 5\cdot10^{-6}$ M
$c_{enzyme} = m_{enzyme}/M_{enzyme}/V = 5\cdot10^{-6}\ g/50000\ gmol^{-1}/0{,}002\ dm^3 = 5\cdot10^{-8}$ M
Turnover number = $\Delta c_{product}/(c_{enzyme}\cdot t) = 100\ min^{-1}$
1 mol enzyme transforms 100 mol substrate in 1 minute.

(iii) Identify the organic product obtained from the reductive elimination of the following complex. **(1 mark)**



(iv) Which of the following complexes undergo oxidative addition to CH_3I faster? **(1 mark)**

$[IrI_2(CO)_2]^-$ or $[RhI_2(CO)_2]^-$

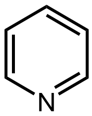
Answer:

$[IrI_2(CO)_2]^-$

Ir is more nucleophilic due to lower electronegativity.

(v) Which two of these octahedral compounds would exhibit chirality? **(1+1 = 2 marks)**

$[Co(NH_3)_3(NO_2)_3]$; $[Cr(NH_3)_3(NO_2)(Cl)(Br)]$; $[Co(NH_3)_2(Br)(Cl)_3]^-$; $[Pt(Py)(NH_3)(NO_2)(Cl)(Br)(I)]$

(Hint: Py = pyridine )

Answer:

$[Cr(NH_3)_3(NO_2)(Cl)(Br)]$

$[Pt(Py)(NH_3)(NO_2)(Cl)(Br)(I)]$

(vi) The energy corresponding to the crystal field splitting of a complex is 2.9×10^{-19} J. **(1+1+1 = 3 marks)**

a) What wavelength of light (in nm) would be absorbed for this d-d electronic transition? (Given that Planck's constant = 6.626×10^{-34} J.s and speed of light = 2.998×10^{8} m/s)

685 nm

Detailed solution:

$$\Delta E_{electron}\Big| = E_{photon} = hc/\lambda$$

$$2.9 \times 10^{-19}\ \text{J} = \frac{(6.626 \times 10^{-34}\ \text{J.s})\ (2.998 \times 10^{8}\ \text{m/s})}{\lambda}$$

$$\lambda = 6.85 \times 10^{-7}\ \text{m} \left(\frac{1\ \text{nm}}{10^{-9}\ \text{m}}\right)$$

$$= 685\ \text{nm}$$

b) To what color of light does this wavelength correspond?

Red

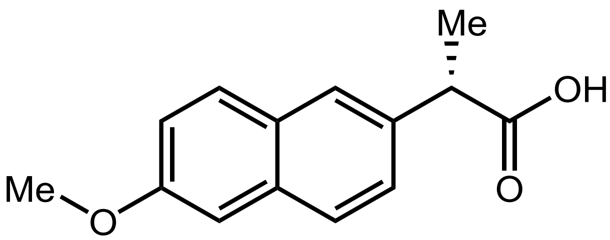
c) What color would a solution of this complex appear?

Green

Q4.

(i) The molecule drawn below is called Naproxen (or "Aleve") and it is a medicine for relieving pain and fever. The "**S**" enantiomer of this molecule is medicinally active while the "**R**" enantiomer is inactive. The specific rotation $[\alpha]_D$ for the "**S**" enantiomer is +50°.

(1*3 = 3 marks)



(a) Is the "S" enantiomer dextrorotatory or levorotatory? Write in the box below.

Dextrorotatory

(b) Determine the enantiomeric excess (ee) of a sample of Naproxen for which the optical rotation $[\alpha]$ is +25°.

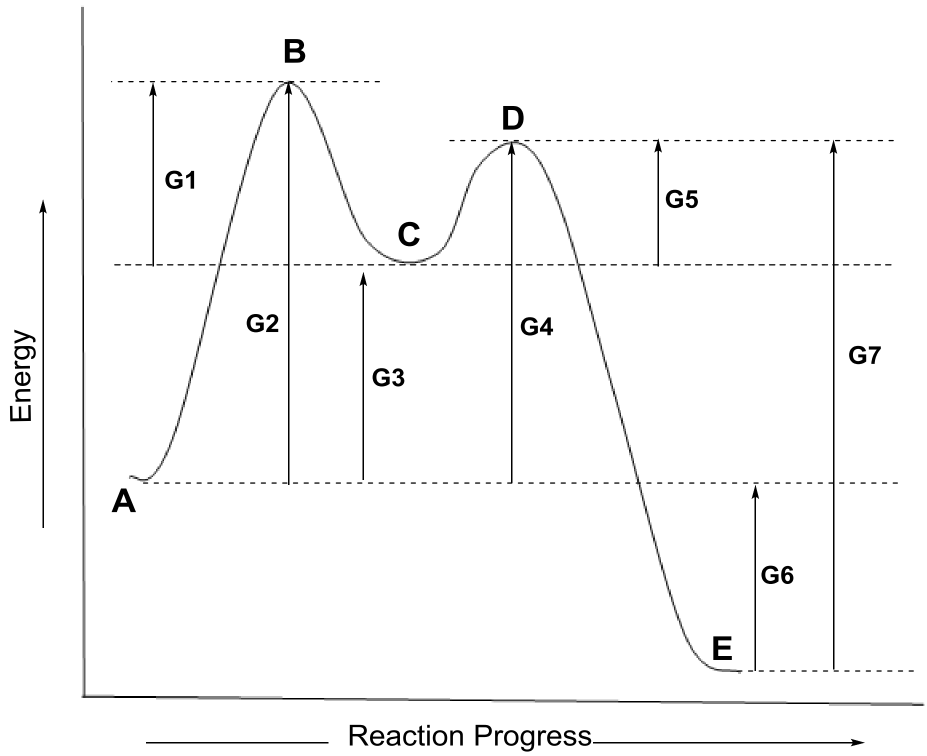
50% ee

(c) In a sample of Naproxen where the ee is 64% and the optical rotation has a (+) sign, what percentage of the sample is the "**S**" enantiomer.

82%

(ii) An energy profile diagram for the reaction **A→E** is given below. The various energy differences for the steps involved are marked as numbered arrows G_1-G_7. For the following questions, write the number of the arrow that corresponds to the correct energy.

(1*5 = 5 marks)



For the following questions, write the number of the arrow that corresponds to the correct energy.

(a) For the reaction **A→E,** the activation energy for the rate determining step is:

G2

(b) For the reaction **A**→**E**, ΔG is:

G6

(c) For the step **E**→**C**, the activation energy is:

G7

(d) For the step **C**→**E**, the activation energy is:

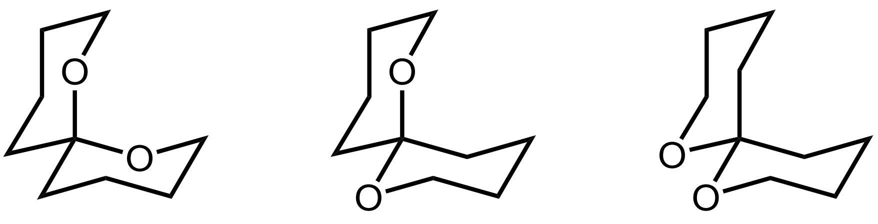
G5

(e) Is the reaction **A**→**E** is endothermic or exothermic?

Exothermic

(iii) Among the following conformers, identify the least stable and most stable conformer.

(1+1=2 marks)



A **B** **C**

Answer:

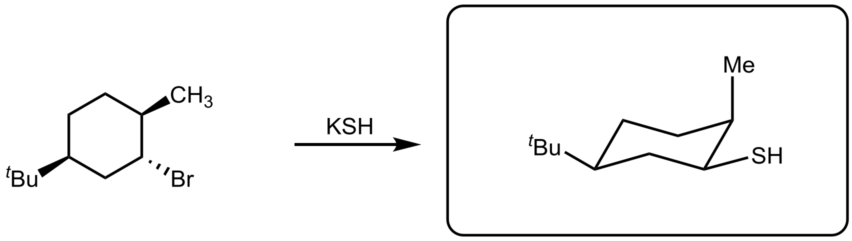
Least stable conformer: C

Most stable conformer: A

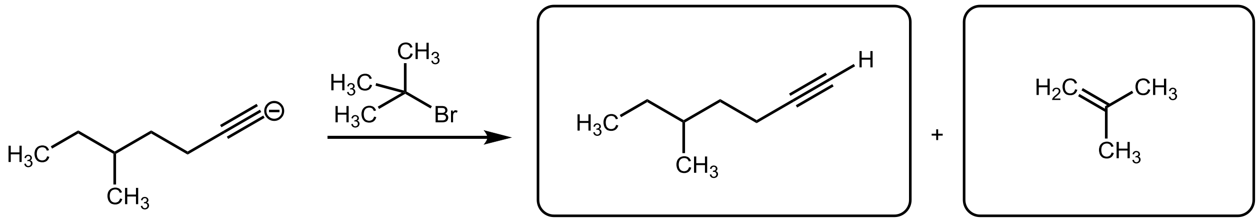
Q5.

(i) Write the structure of the major organic product(s) in the following reactions. Partial structure of the product is provided in some cases; add the required functionality to make it the right answer. (The entire structure has to be correct; no partial marking unless otherwise indicated) **(1+2+2 = 5 marks)**

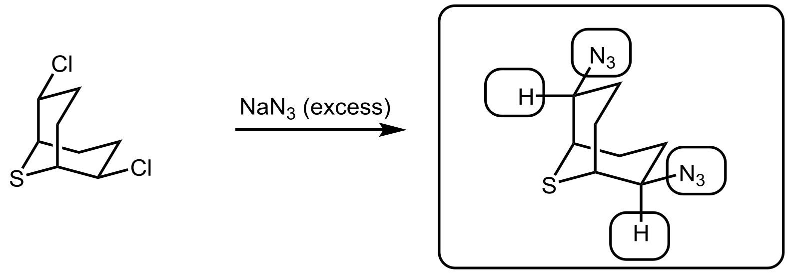
(a)



(b)

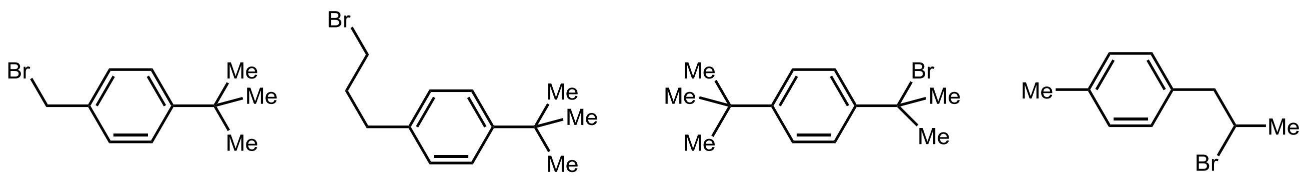


(c)



(one mark for each carbon atom)

(ii) Arrange the following molecules in ***increasing*** order of S_N1 reactivity. **(1 mark)**

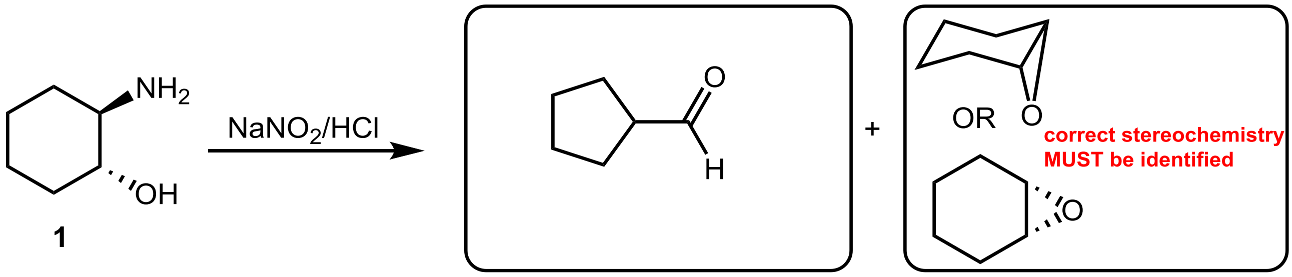


A **B** **C** **D**

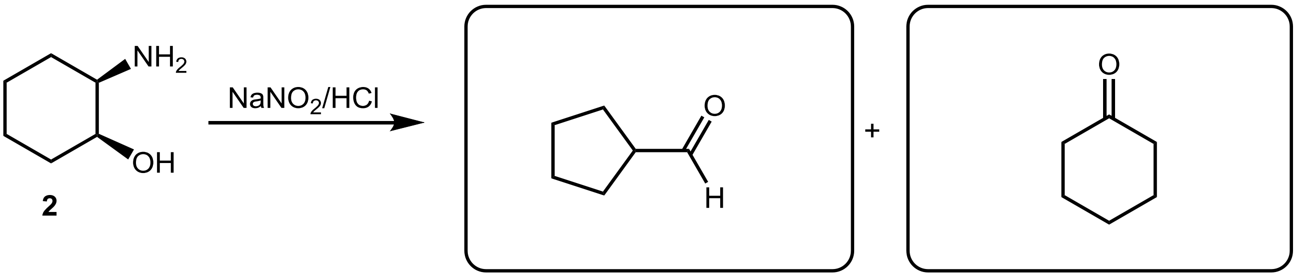
Answer:

B<D<A<C

(ii) For the two amino alcohols shown below (**1** and **2**), write the organic products that can be obtained upon treatment with $NaNO_2$/HCl. **(1*4 = 4 marks)**



1



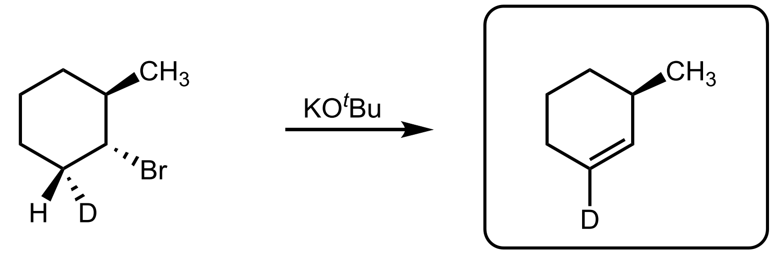
2

Q6.

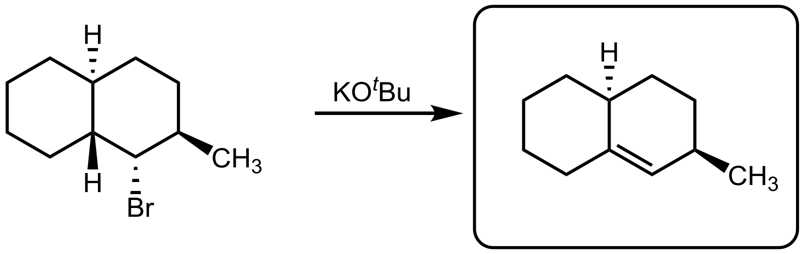
(i) Write the structure of the major organic product for the following reactions.

(1 * 6 = 6 marks)

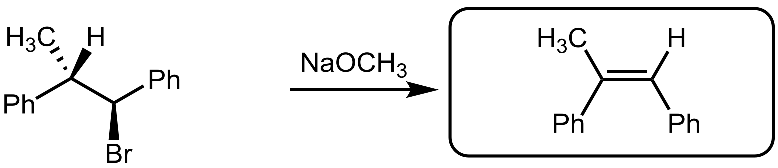
(a)

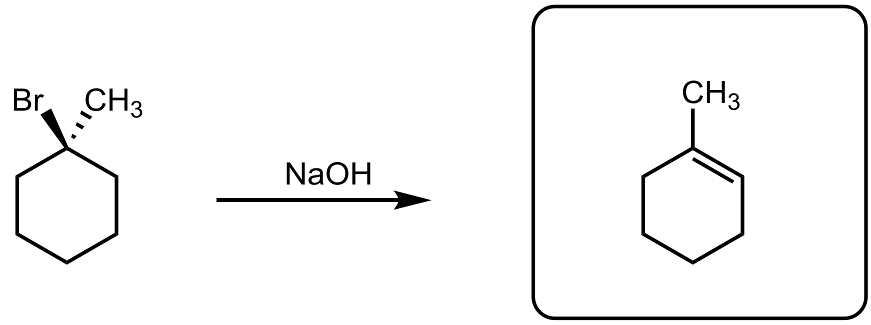


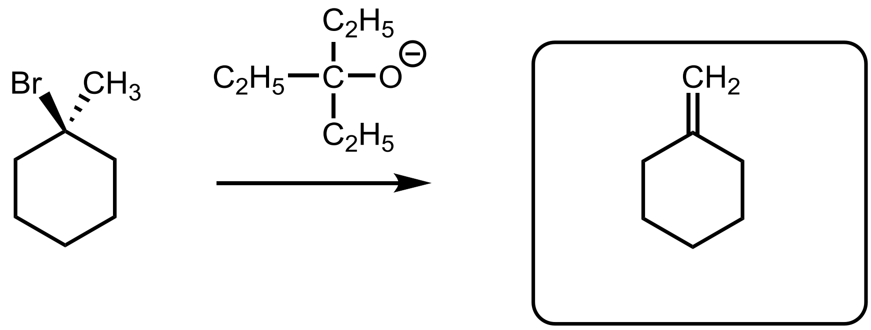
(b)



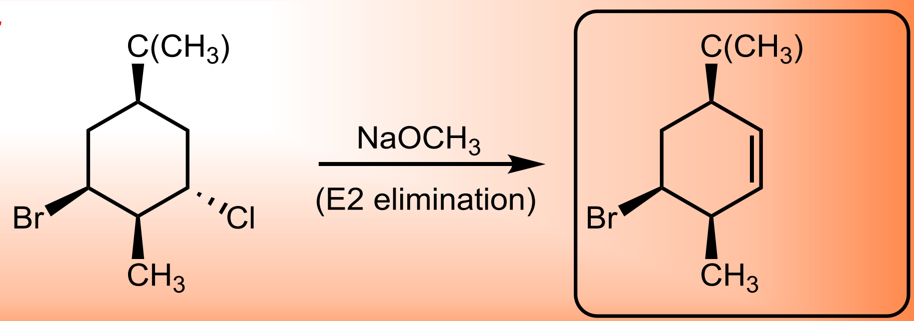
(c)



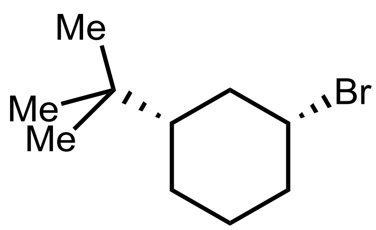
(d) 

(e) 

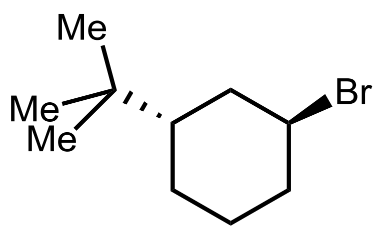
For this part (f), 1 mark has been given to EVERYONE (beacuse of a typo in the question).

(f) 

(ii) Which of the following two molecules will undergo an E2 elimination faster. Write the answer in the box provided (indicate **A** or **B**). **(1 mark)**



A

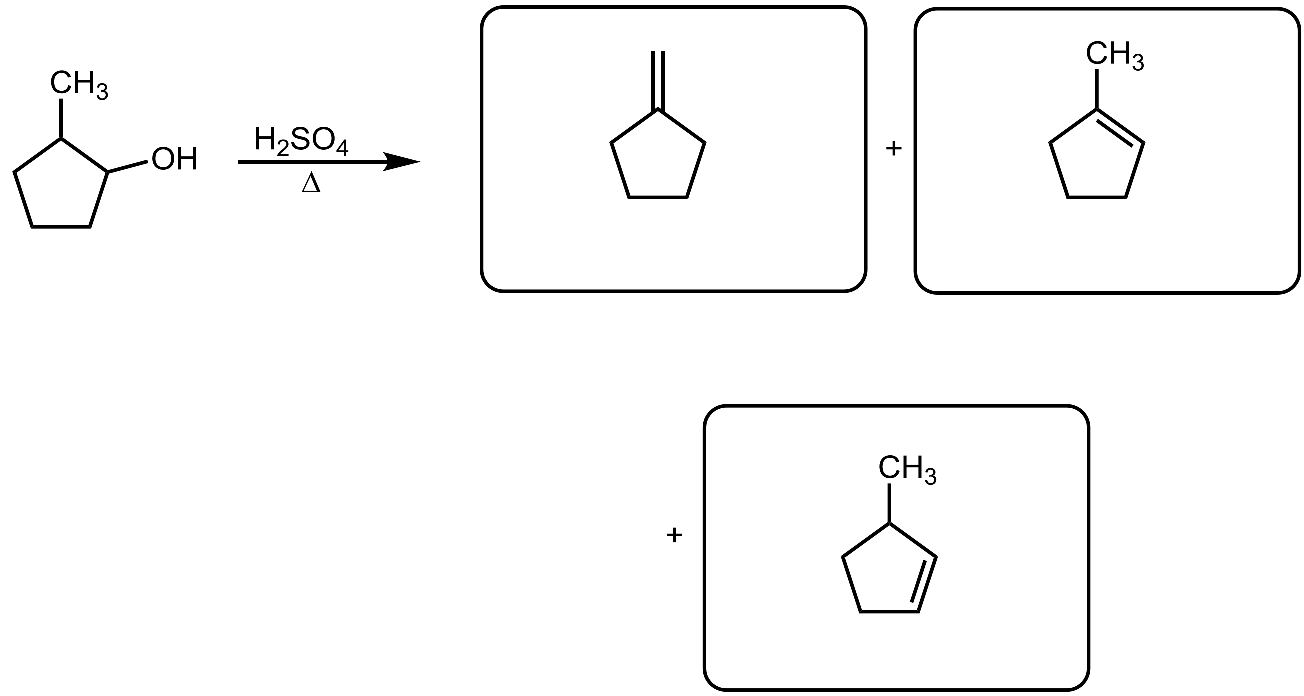


B

Answer:

B

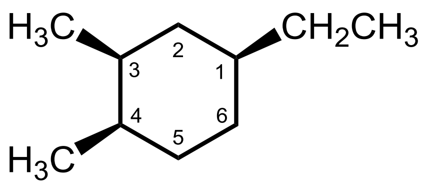
(iii) Draw all likely products of the following reaction. **(1*3 = 3 marks)**



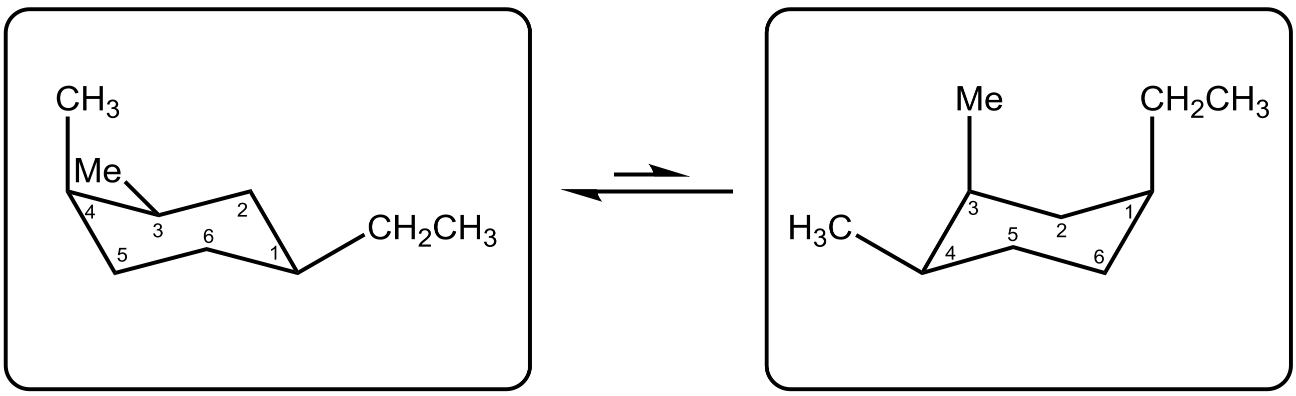
Q7.

(i) The cyclohexane derivative shown below can exist in two conformations, one of which is favoured over the other. Complete the chair conformations by adding the appropriate substituents. (All substituents have to be correct in order to get one mark. No partial marking)

(1*2 = 2 marks)

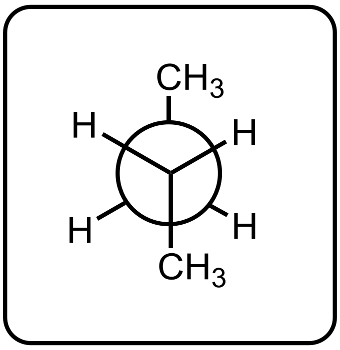


Answer:

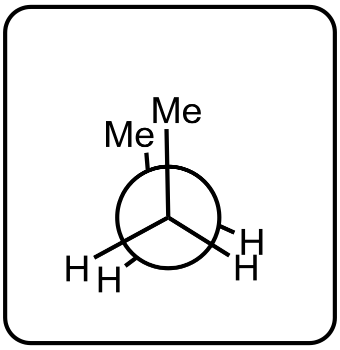


(ii) Viewing along the C2-C3 bond of the *n*-butane molecule, draw the Newman projections for the most stable and least stable conformers. **(1+1 = 2 marks)**

Answer:



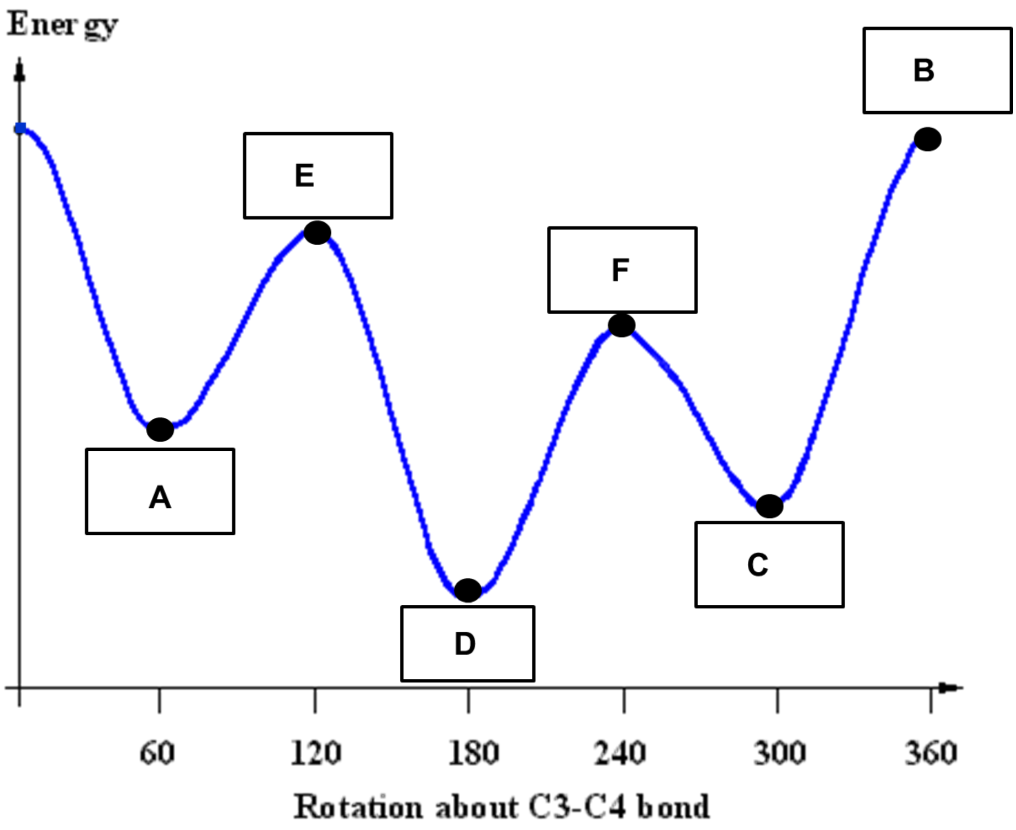
most stable conformation

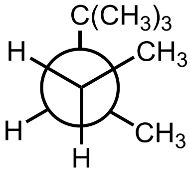


least stable conformation

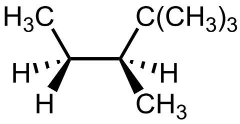
(iii) The following is the energy profile diagram for the conformational analysis of 2,2,3-trimethylpentane, considering rotation of the C3-C4 bond. Match the given conformations (**A**-**F**) with the points (darkened circles) on the energy profile diagram. Simply write the letters in the boxes provided.

(1*6 marks)

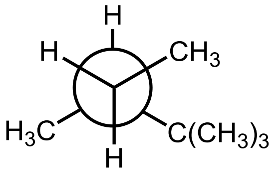




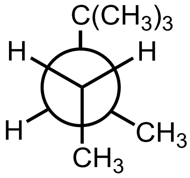
A



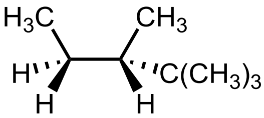
B



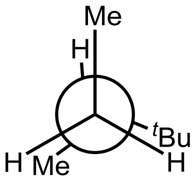
C



D



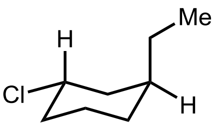
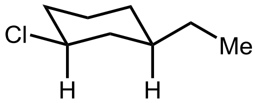
E



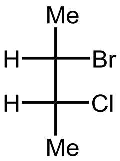
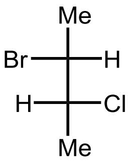
F

Q8.

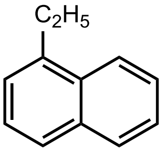
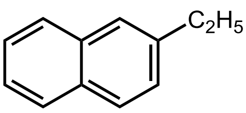
(i) For the following pairs of molecules, identify the relationship between the structures in each pair (whether they are enantiomers, diastereomers, constitutional isomers, identical). Write your answer in the boxes provided. **(1*5 = 5 marks)**

(a)  

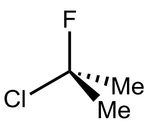
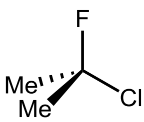
diastereomers

(b)  

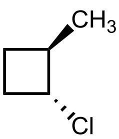
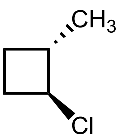
diastereomers

(c)  

constitutional/
structural isomers

(d)  

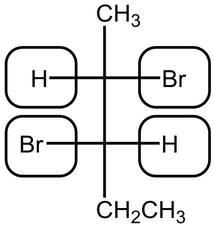
identical

(e)  

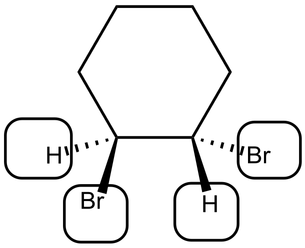
enantiomers

(ii) The name and partial structures of two compounds are provided. Complete the structures by adding the appropriate substituents. **(1*2 = 2 marks)**.
(Entire structure has to be correct to get 1 mark. No partial marking.)

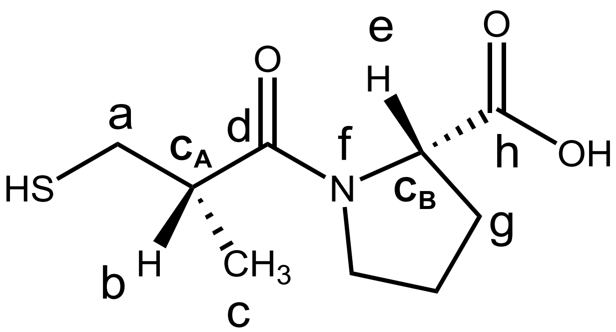
a) 2(*S*), 3(*S*)-dibromopentane



b) 1(*S*), 2(*S*)-dibromocyclohexane



(iii) The following molecule is Captopril, a medicine used for combating hypertension. The two stereogenic carbons are labelled **C_A** (with substituents coded as "a-d") and **C_B** (with substituents coded as "e-h").

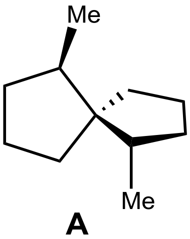


In the table below, for both the stereogenic carbon atoms, write the substituent with <u>*second highest priority*</u> and assign **R** and **S** configuration. **(1*2 = 2 marks)**.

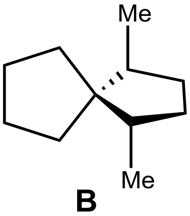
(Both answers for each carbon atom have to be correct to get 1 mark. No partial marking.)

Carbon Atom (number indicated in structure)	Substituent with second-highest priority (just write the letter code)	Configuration (**R** or **S**)
C_A	d	S
C_B	h	S

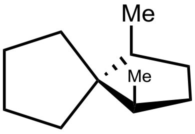
(iv) Which of the following molecules are chiral? (All correct molecules must be identified; no partial marking). **(1 mark)**



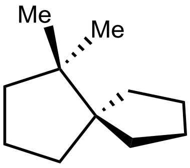
A



B



C



D

Answer: Among the four molecules shown, the following are chiral:

A, B