1.

(a) Arrange the following gases in order of increasing density at STP.
HCl, CO, CO_2, H_2S, Cl_2 (5 points)
36.5 28 44 34 71

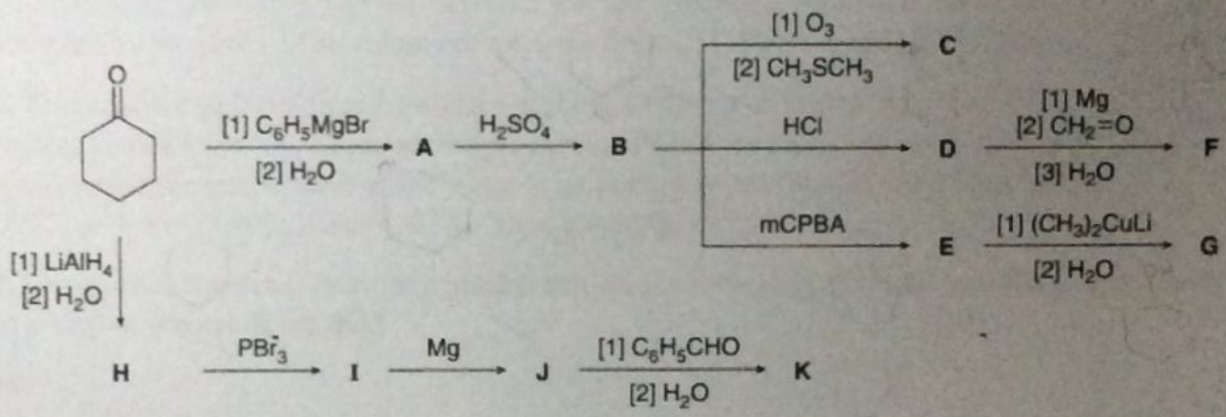
(b) Associate one van der Waals constant a (17.58, 1.378, 3.392, 2.253, 0.2107 L^2 atm mol^{-2}) with each of the following gases: O_2, CH_3CN, Ne, CH_4, CO_2. (5 points)
32 41 20 16 44

(c) Give a brief explanation for the very high value in part (b) (2 points)

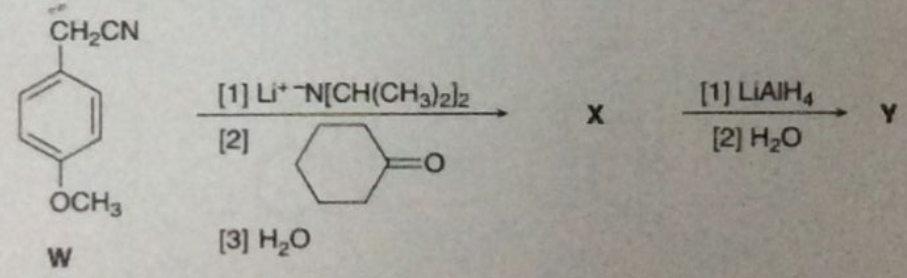
2. A sample of an oxide of osmium (1.509 g) is gaseous at 200.0 °C /0.980 atm pressure and occupies 235 mL under these conditions. Assuming ideal gas behavior, determine the molecular formula of the oxide. [Molar masses (g mol^{-1}): Os = 190.2; O = 16.00. R = 0.08206 L atm $K^{-1}mol^{-1}$. Take 0 °C to be 273 K]. Show working. (10 points)

3. [Carbonyl Chemistry]

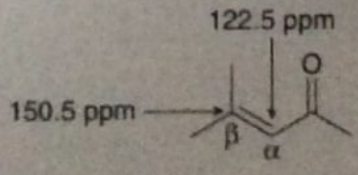
(a) Identify the lettered compounds in the following reaction scheme.



(b) Identify **X** and **Y**, two of the intermediates in a synthesis of the antidepressant venlafaxine (trade name Effexor), in the following reaction scheme. Write a mechanism for the formation of **X** from **W**.



(c) Explain why the β carbon of an α,β-unsaturated carbonyl compound absorbs farther downfield in the ^{13}C NMR spectrum than the α carbon, even though the α carbon is closer to the electron-withdrawing carbonyl group. For example, the β carbon of mesityl oxide absorbs at 150.5 ppm, while the α carbon absorbs at 122.5 ppm.



mesityl oxide

1.

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HCl, CO, CO_2, H_2S, Cl_2 (5 points)
36.5 28 44 34 71

(b) Associate one van der Waals constant a (17.58, 1.378, 3.392, 2.253, 0.2107 L^2 atm mol^{-2}) with each of the following gases: O_2, CH_3CN, Ne, CH_4, CO_2. (5 points)
3.2 4.1 2.3 1.6 4.4

(c) Give a brief explanation for the very high value in part (b) (2 points)

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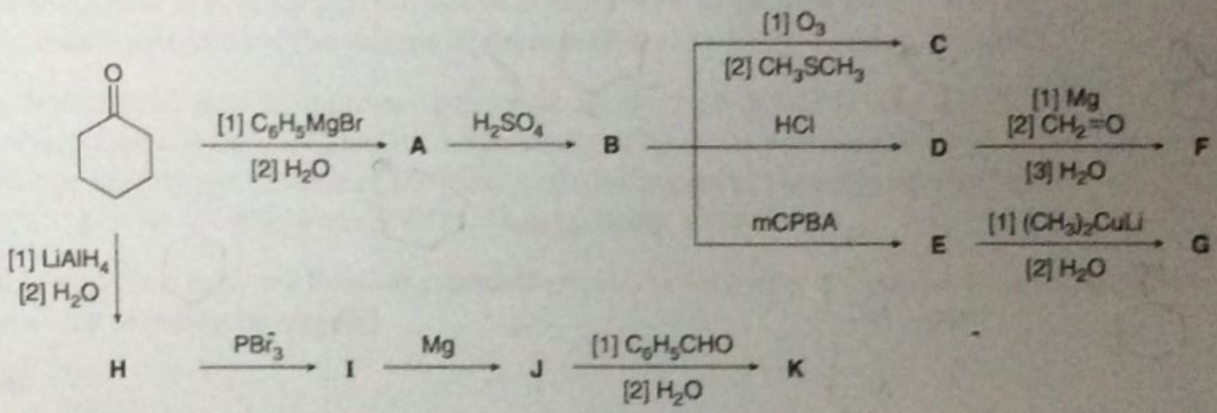

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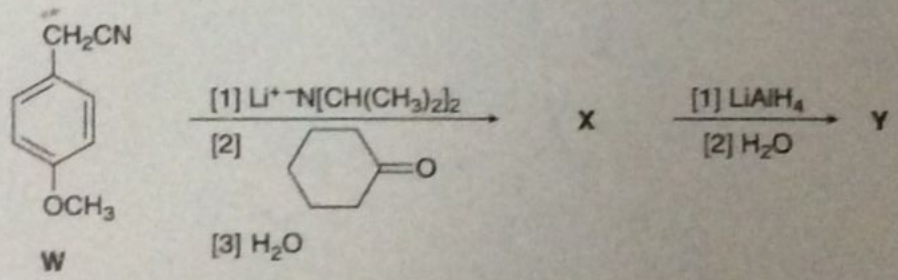

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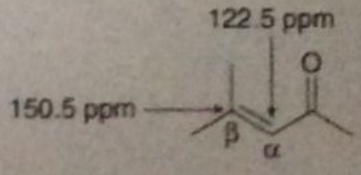


mesityl oxide

4.

(a) Identify the substance that has the higher boiling point in the following pairs.

(i) BF_3 and BCl_3 (ii) pentane and 2,2-dimethylpropane (iii) *cis*-ClHC=CHCl and *trans*-ClHC=CHCl (iv) hexane (C_6H_{14}) and benzene (C_6H_6) (v) SO_2 and CO_2 (vi) CH_3COOH and HOOC-COOH (6 x 1 points)

(b) An oxide of manganese (Mn) has a unit crystal in which Mn ions are situated at the corners and oxide ions are found half way along the edges of the cube. Determine the formula unit of the oxide. Show working. (4 points)

5.

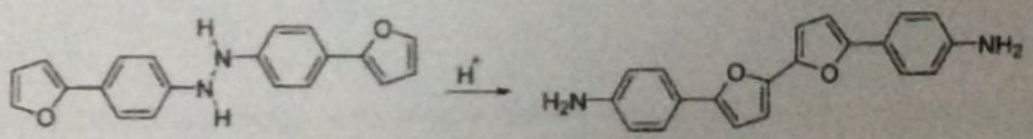
(a) Calculate the atomic radius of aluminum (Al) atoms (in picometers) in a face-centered cubic (fcc) crystal lattice, whose density is 2.718 g cm^{-3}. [Avogadro number = 6.022×10^{23} mol^{-1}; molar mass of Al = 26.98 g mol^{-1}]. Show working. (7 points)

(b) From your answer for part (a), calculate the fraction of the volume of aluminum occupied by its atoms. [The volume of a sphere is $4\pi r^2/3$]. Show working. (3 points)

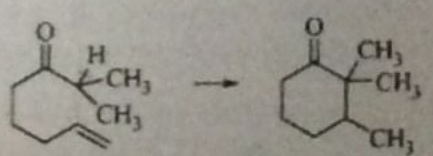
6. Water (400.0 g) in an aluminum pan weighing 151.5 g was heated from 22.0 °C to boiling point (100.0 °C). Calculate the percentage (%) of the total heat supplied that is used to raise the temperature of the water to its boiling point. [Specific heat capacities (J $°C^{-1}$ g^{-1}): Al = 0.900; Water = 4.18]. Show working. (10 points)

7. [Pericyclic Reactions] Propose a mechanism for the following reactions and characterize each as a kind of pericyclic reaction.

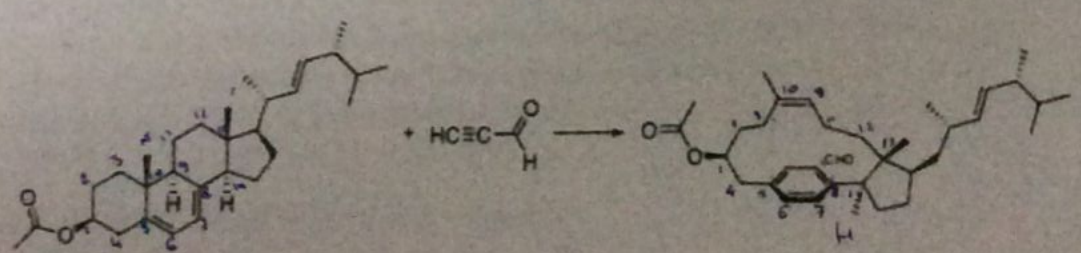
(a)



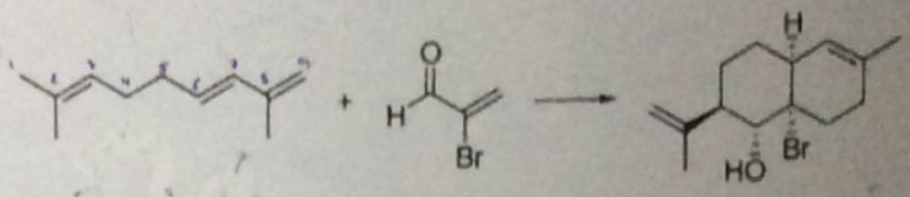
(b)



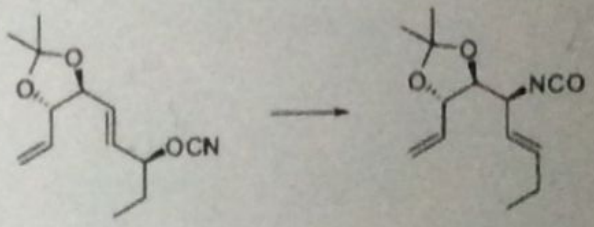
(c)



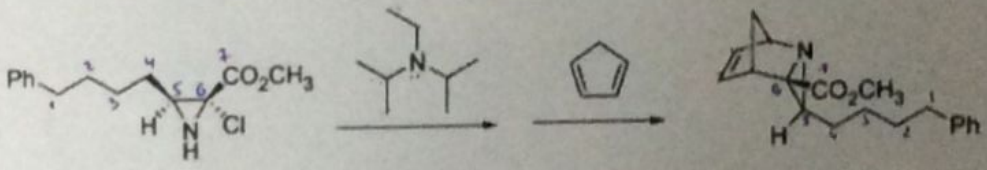
(d)



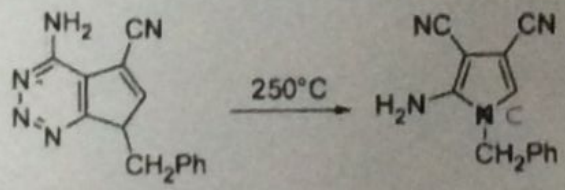
(e)



(f)



(g)



8.

(a) Calculate the lattice energy of the sodium oxide lattice, given the following data (in kJ mol^{-1}). Show working.
ΔH°(sublimation or atomization) of Na(s) = 107.32; ΔH°(dissociation) of O_2(g) = 498; ΔH°(ionization) (ionization energy, IE_1) of Na(g) = 494; Electron affinities of O(g) EA_1 = -141 and EA_2 = +844; ΔH°(formation) of Na_2O(s) = -409. (10 points)

(b) State whether (i) calcium oxide (CaO) and (ii) potassium oxide (K_2O) will have higher or lower lattice energies than sodium oxide. (2 points)

9. The Boltzmann equation $S = k_B \ln W$, allows us to calculate the residual entropy of a crystal at (or very close to) 0 K. W is the number of microstates, which for a molecular crystal is the number of possible degenerate (same energy) orientations of molecules. Write the possible orientations of the following molecules and calculate their molar residual entropies according to the Boltzmann expression. [Avogadro's number is 6.02 x 10^{23} and kB is 1.38 x 10^{-23} J K^{-1}]. Show working.

(i) $FClO_3$ (ii) HBF_2 (iii) BF_3 (4 + 3 + 1 = 8 points)

10. Thermodynamic data for the reaction between BF3 and water,
$2BF_3(g) + 3H_2O(l) \rightarrow B2O3(_s) + 6HF(g)$, is given below.
Standard enthalpies of formation (ΔH_f° in kJ mol^{-1}): BF_3(g) = -1137.0; H_2O(l) –285.83 = ;

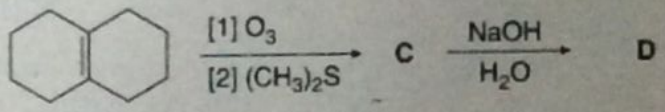
$B_2O_3(s)$ = -1272.8; HF(g) =-271.1.
Standard entropies (S° in $J\,K^{-1}\,mol^{-1}$): $BF_3(g)$ = 254.12; $H_2O(l)$ = 69.91; $B_2O_3(s)$ = 53.97; HF(g) = 173.78.

(a) Calculate the Gibbs free energy of reaction at 700 K and state whether the reaction is spontaneous at this temperature, assuming variation of ΔH° and ΔS° with temperature is negligible. Show working. (9 points)

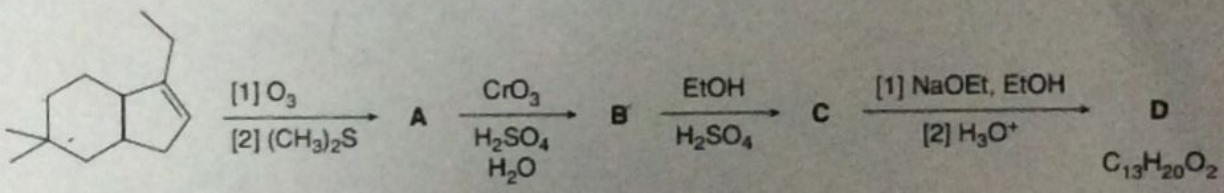
(b) Determine the temperature at which the reaction is reversible. Show working. (3 points)

11. [Carbonyl Chemistry]

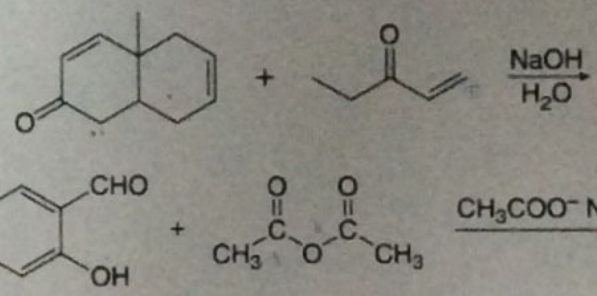
(a) Identify the structures of **C** and **D** in the following reaction sequence.



(b) Identify lettered intermediates A–D in the following reaction sequence.



(c) Identify products and draw stepwise mechanisms for the following reactions:



(d) Propose stepwise mechanisms for the following reactions: