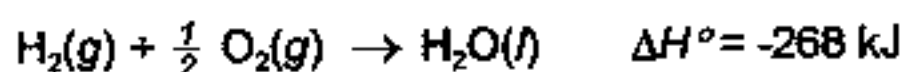


(6%) 1. (a) Give  $\Delta H^\circ$  for the reaction



along with the information that the heat of combustion of ethane is 1560 kJ/mol and that of ethylene is 1410 kJ/mol, calculate  $\Delta H^\circ$  for the hydrogenation of ethylene:



(b) If the heat of combustion of acetylene is 1300 kJ/mol, what is the value of  $\Delta H^\circ$  for its hydrogenation to ethylene? To ethane?

(c) What is the value of  $\Delta H^\circ$  for the hypothetical reaction.



(8%) 2. Write structural formulas for the most stable conformation of each of the following compounds:

(a) *trans*-1-*tert*-Butyl-3-methylcyclohexane

(b) *cis*-1-*tert*-Butyl-3-methylcyclohexane

(c) *trans*-1-*tert*-Butyl-4-methylcyclohexane

(d) *cis*-1-*tert*-Butyl-4-methylcyclohexane

(3%) 3. Hydrogen cyanide (HCN) has a  $\text{p}K_a$  of 9.1. What is its  $K_a$ ? Is HCN a strong or a weak acid?

(3%) 4. Arrange the following alkenes in order of decreasing stability: 1-pentene; (*E*)-2-pentene; (*Z*)-2-pentene; 2-methyl-2-butene.

(5%) 5. Use curved arrows to show electron movement in the dehydrohalogenation of *tert*-butyl chloride by sodium methoxide by E2 mechanism.

(5%) 6. Addition of hydrogen chloride to 3,3-dimethyl-1-butene gives a mixture of two isomeric chlorides in approximately equal amounts. Suggest reasonable structures for these two compounds, and offer a mechanistic explanation for their formation.

(12%) 7. Write the structure of the major organic product obtained by hydroboration-oxidation of each of the following alkenes:

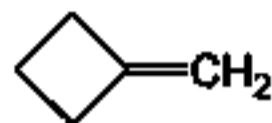
(a) 2-methylpropene

(d) cyclopentene

(b) cis-2-butene

(e) 3-ethyl-2-pentene

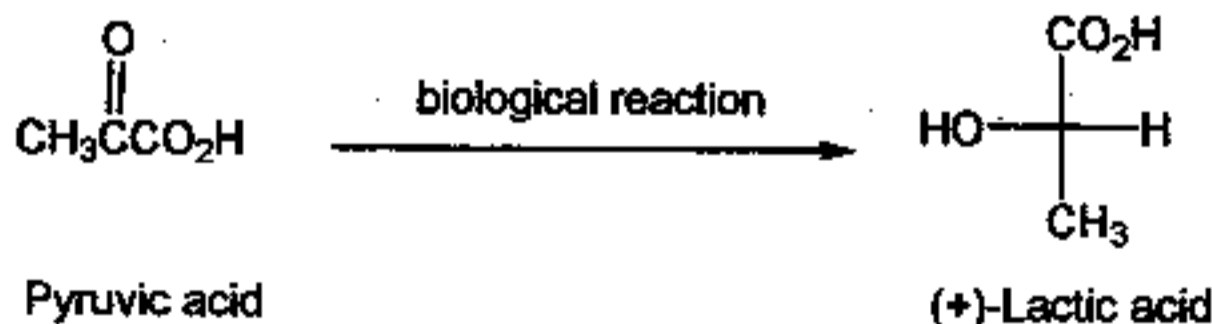
(c)



(f) 3-ethyl-1-pentene

(5%) 8. A certain compound of molecular formula  $C_{19}H_{38}$  was isolated from fish oil and from plankton. On hydrogenation it gave 2,6,10,14-tetramethyl-pentadecane. Ozonation followed by hydrolysis in the presence of zinc gave  $(CH_3)_2C=O$  and a 16-carbon aldehyde. What is the structure of the natural product? What is the structure of the aldehyde?

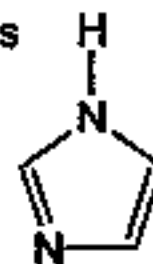
(5%) 9. Biological reaction of pyruvic acid, catalyzed by enzyme lactate dehydrogenase, gives (+)-lactic acid, represented by the Fischer projection shown. What is the configuration of (+)-lactic acid according to the Cahn-Ingold-Prelog R-S notational system?



(6%) 10. In the resolution of 1-phenylethylamine using (-)-malic acid, the compound obtained by recrystallization of the mixture of diastereomeric salts is (R)-1-phenylethylammonium (S)-malate. The other component of the mixture is more soluble and remains in solution. What is the configuration of the more soluble salt?

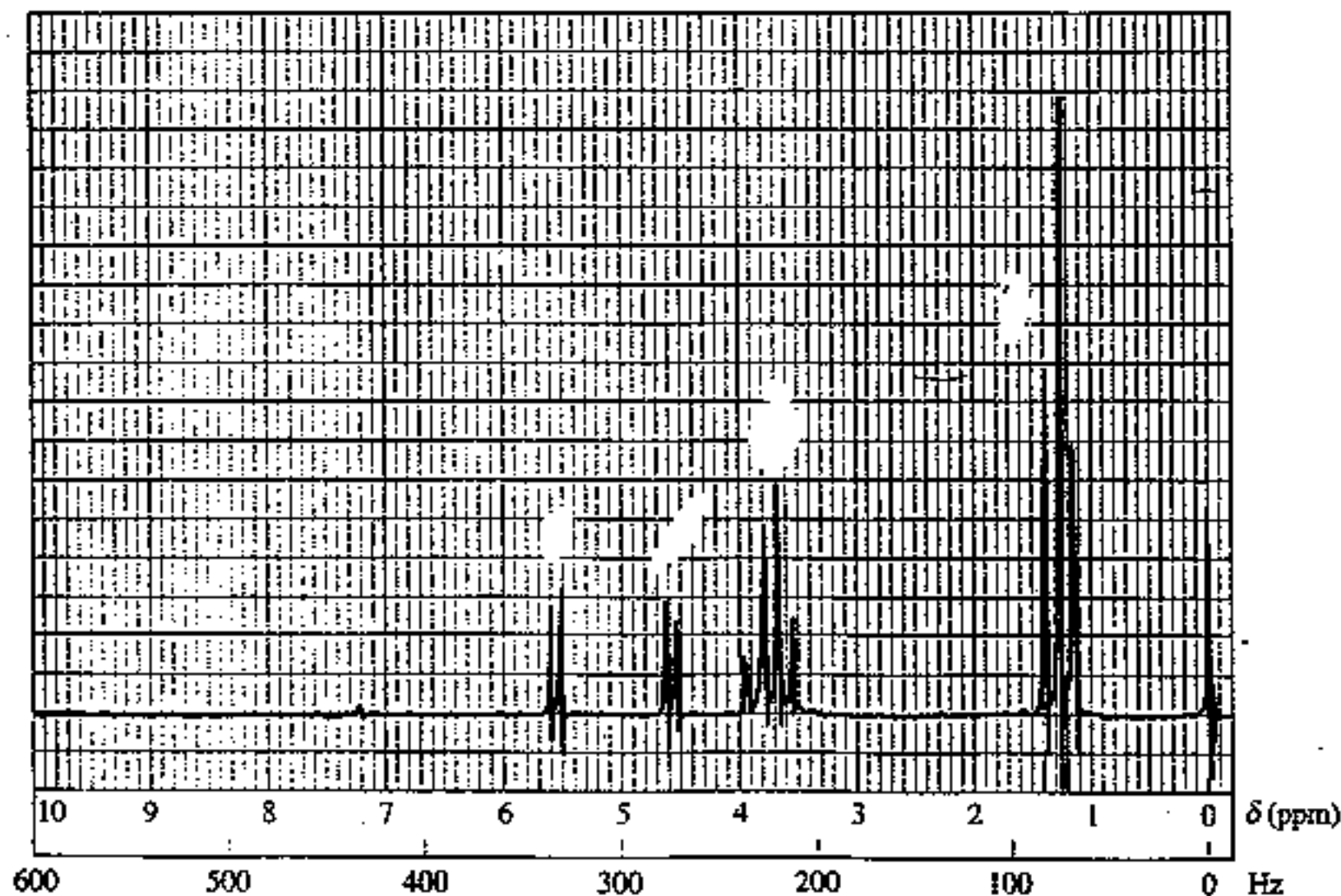
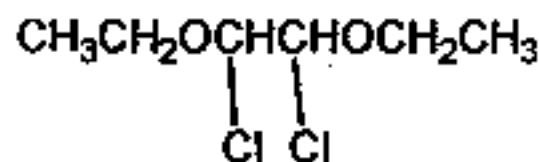
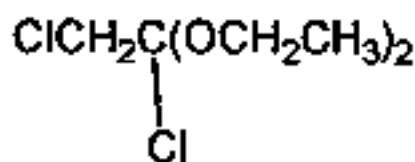
(6%) 11. Suggest a structure for the product of nucleophilic substitution obtained on solvolysis of *tert*-butyl bromide in methanol, and outline a reasonable mechanism for its formation.

(4%) 12. Imidazole is a much stronger base than pyrrole. Predict which nitrogen is protonated when imidazole reacts with an acid, and write a structural formula for the species formed.

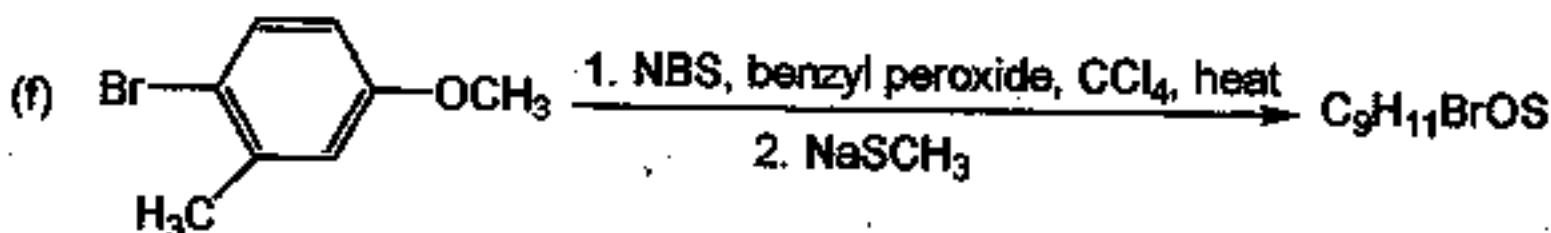
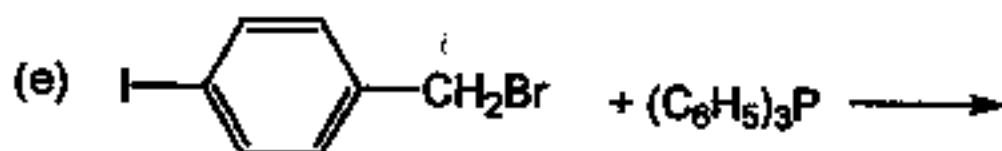
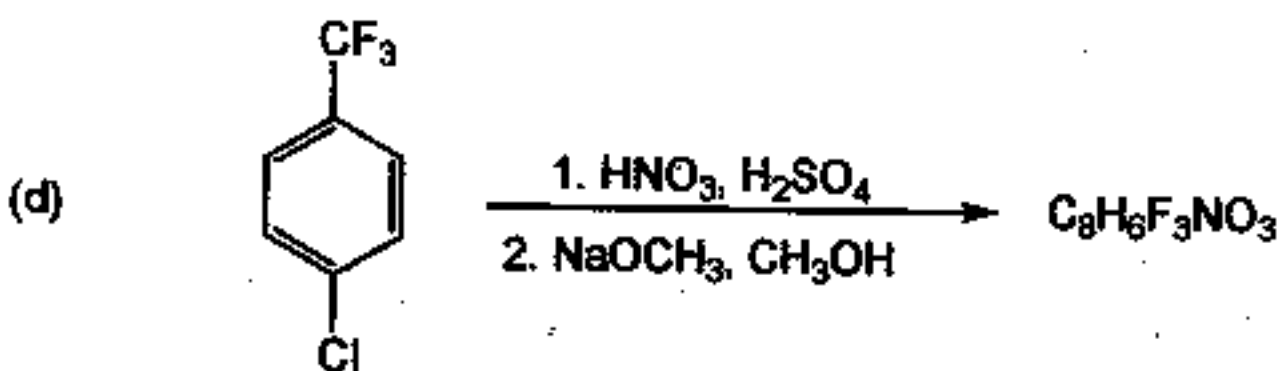
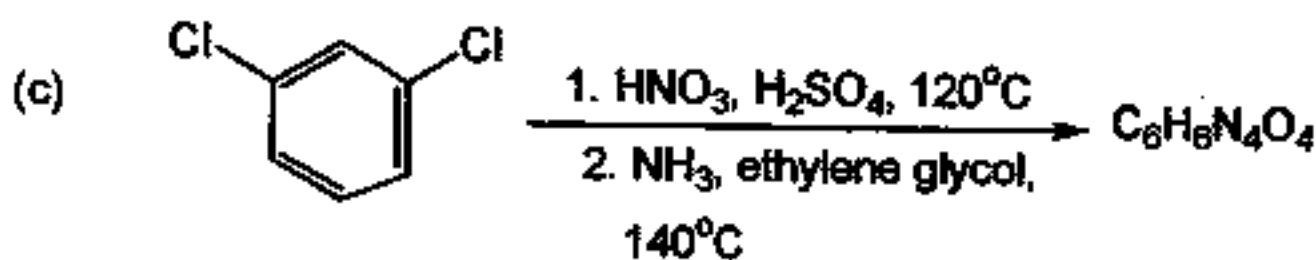
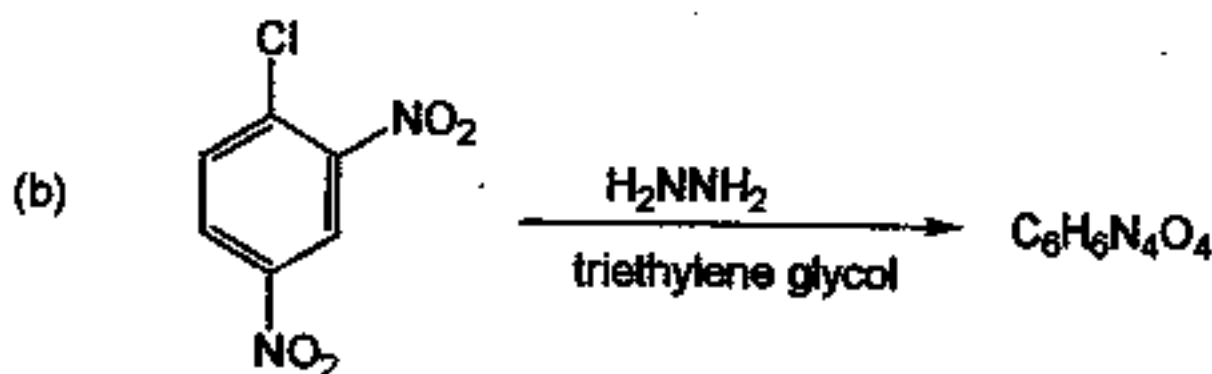
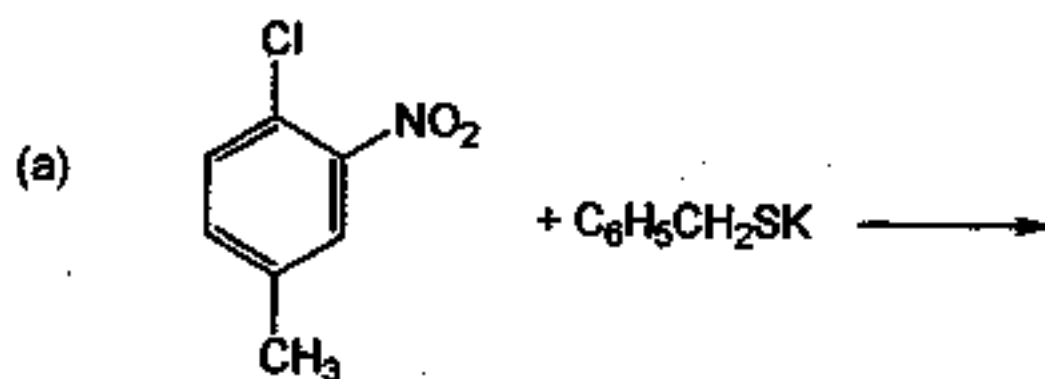


imidazol

(6%) 13. To which one of the following compounds does the NMR spectrum correspond?



(12%) 14. Predict the principal organic product in each of the following reactions:

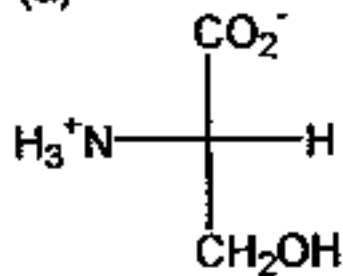


(8%) 15. Clearly represent the most stable conformation of the  $\beta$ -pyranose form of each of the following sugars:

- (a) D-galactose (b) D-Mannose (c) L-Mannose (d) L-Ribose

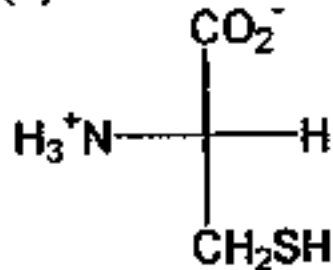
(6%) 16. What is the absolute configuration (R or S) at the  $\alpha$  carbon atom in each of the following L amino acids?

(a)



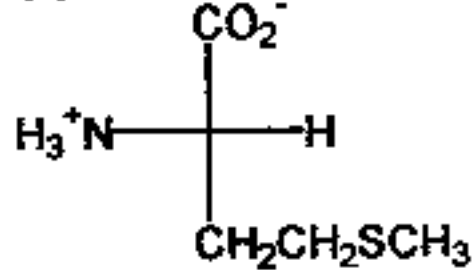
L-Serine

(b)



L-Cysteine

(c)



L-Methionine