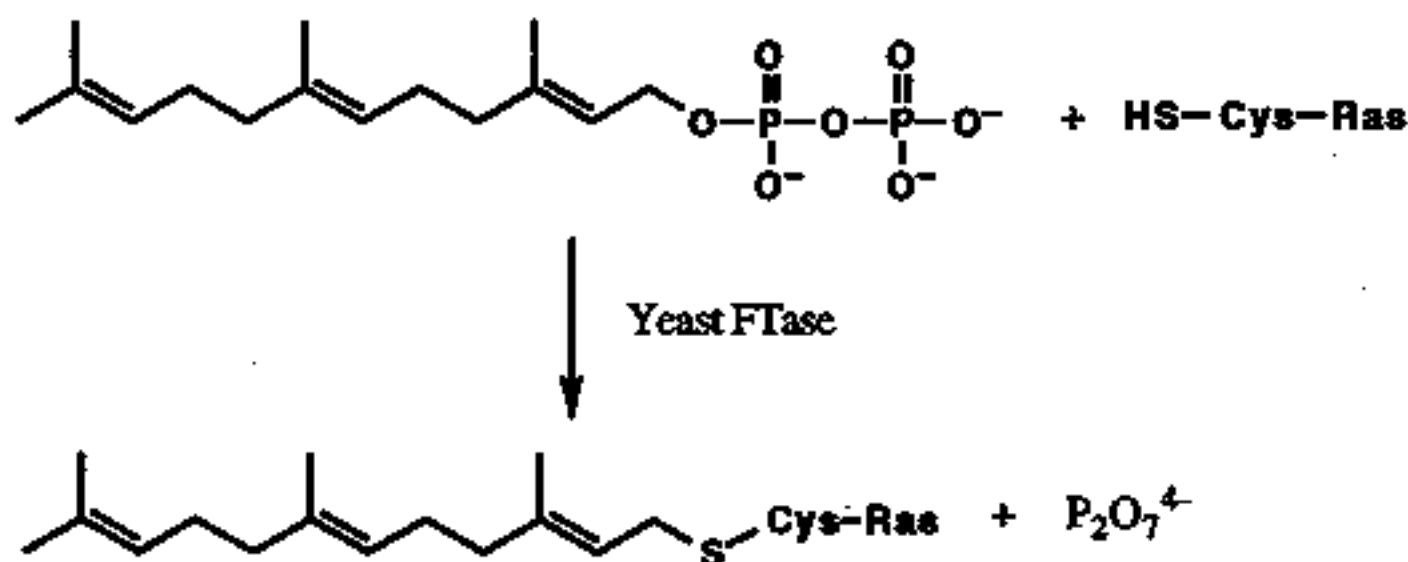


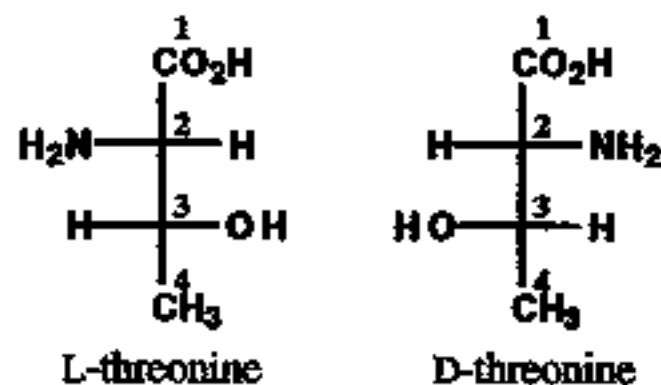
I. Please provide proper answers for each of the following questions. (20%)

(A). It has been proposed that yeast protein farnesyltransferase (FTase) catalyzes the farnesylation of Ras protein through the S_N1 reaction (see below).

Write down the chemical mechanism of this reaction and indicate the intermediate or transition state if any. (2%)

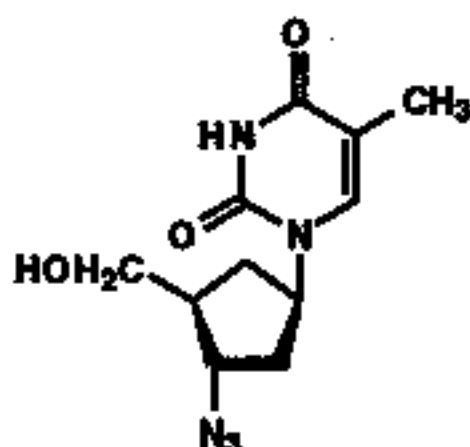


(B).

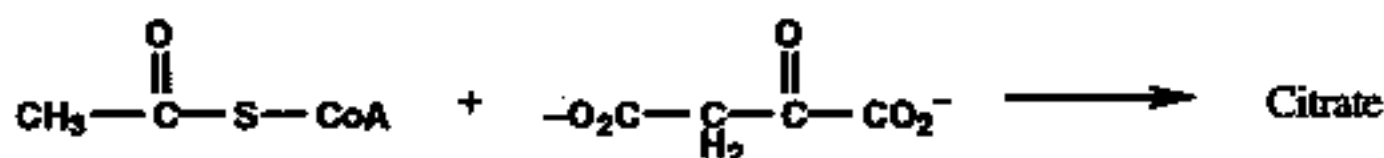


- L-threonine and D-threonine are (1) diastereomers (2) enantiomers (3) structural isomers (4) identical. (1%)
- How many asymmetric carbons are there in L-threonine? What are their configuration? (2%)
- Draw the zwitterionic structure of L-threonine. (1%)
- Calculate the formal charges on the carbons 1, 2, 3, 4 of D-threonine. (2%)

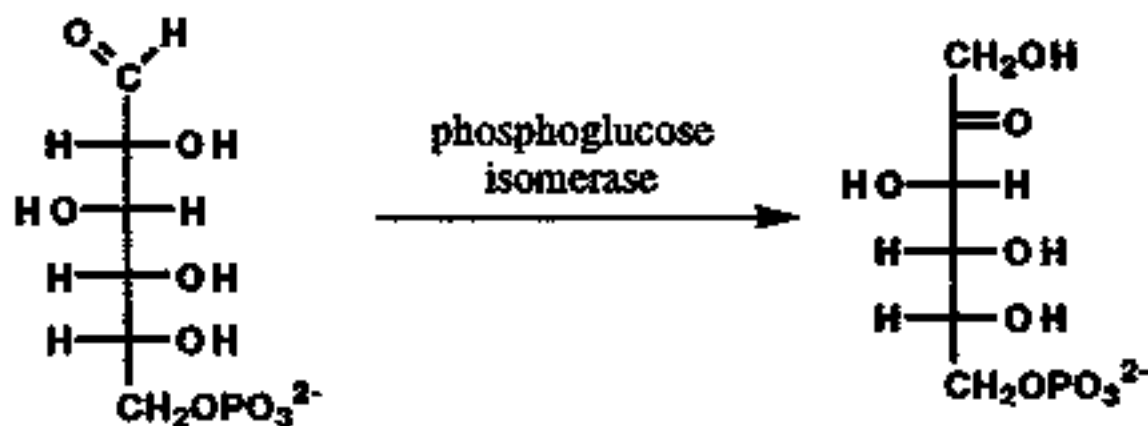
- (C). Azidothymidine (AZT) is a commonly used nucleotide medication against AIDS. Propose a mechanism for AZT inhibition on HIV reverse transcriptase? (4%)



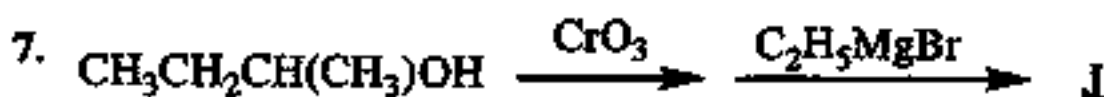
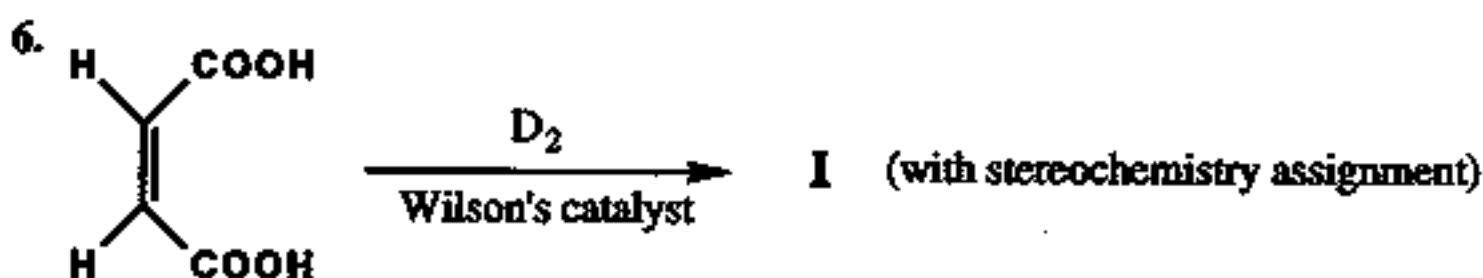
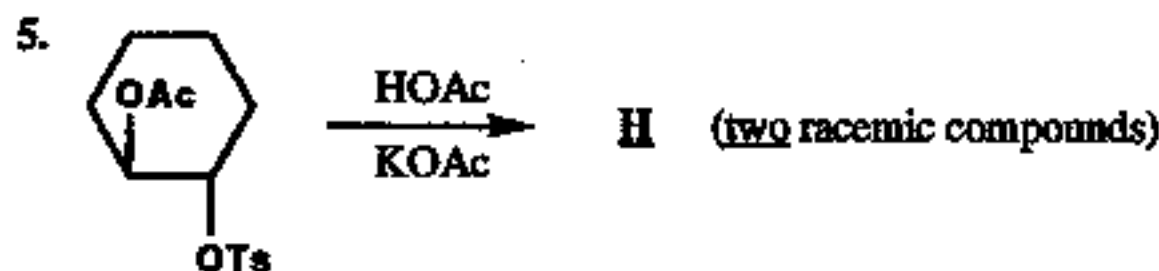
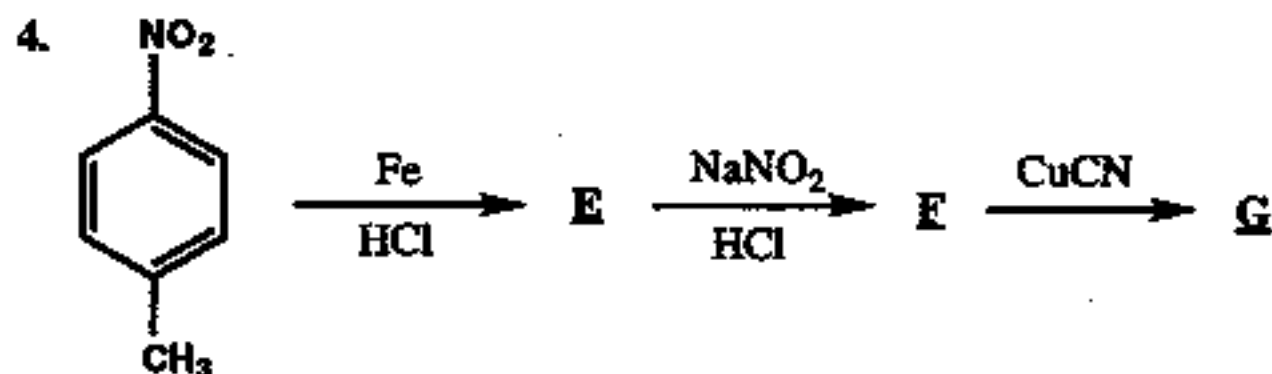
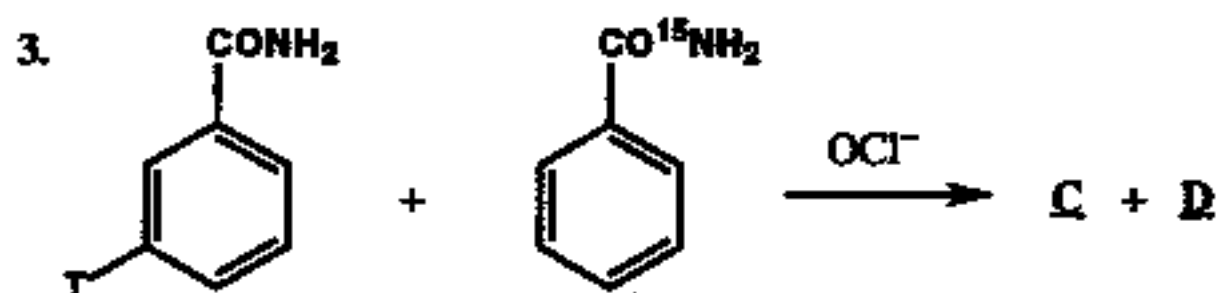
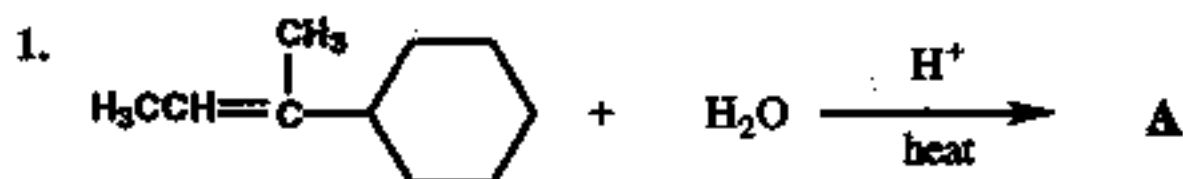
- (D). Citrate synthase manages a Claisen-like condensation of acetyl CoA with oxaloacetate in TCA cycle. Draw the reaction mechanisms and the structure of citrate. (4%)



- (E). Propose a mechanism for the interconversion between glucose-6-phosphate and fructose-6-phosphate catalyzed by phosphoglucose isomerase in glycolysis. (4%)



II. Predict the major product of each of the following reactions (20%, 2% each)



III. Determine the structures of A, B, C, D, E based on their spectroscopic data. (20%)

A) $C_3H_5F_2Cl$: H^1NMR : δ 1.75 (3H, t, $J=17.5$ Hz); δ 3.63 (2H, t, $J=13$ Hz)B) $C_8H_{10}O$: H^1NMR : δ 1.2 (3H, t, $J=6$ Hz); δ 2.6 (2H, q, $J=5.5$ Hz); δ 6.0 (1H, broad s); δ 6.95 (4H, apparent pair of doublets)IR: $3150-3600\text{ cm}^{-1}$ (broad)C) $C_4H_{11}N$: H^1NMR : δ 0.9 (1H, s); δ 1.0 (6H, t); δ 2.6 (4H, q)IR: 3200 cm^{-1} ; 3400 cm^{-1} D) C_3H_8O : H^1NMR : δ 1.15 (6H, d); δ 2.25 (1H, multiple); δ 9.58 (1H, s)IR: 1720 cm^{-1} ; 2710 cm^{-1} E) $C_{10}H_{12}O_2$: H^1NMR : δ 1.4 (3H, t, $J=5.5$ Hz); δ 2.5 (3H, s); δ 4.1 (2H, q, $J=6$ Hz); δ 6.9 (2H, d, $J=10$ Hz); δ 7.9 (2H, d, $J=10$ Hz).IR: 1690 cm^{-1} ; 1612 cm^{-1}

IV. Choose a correct answer from each of the following questions. (40%)

1. Which one of the following statements is wrong?

- (1) Constitutional isomers differ in molecular frameworks.
- (2) Stereoisomers differ only in geometry.
- (3) *Cis*-2-butene and *trans*-2-butene are constitutional isomers.
- (4) Mirror images of diastereoisomers are superimposable.

2. The natural vitamin B₃ (panthothenic acid) is *dextrorotatory* with a specific rotation $[\alpha]_D$ of $+37.5^\circ$.

What is the observed optical rotation of its *levorotatory* enantiomer at a concentration of 1.00 g/100 mL in a tube of 10 cm length?

- (1) -375 (2) -37.5 (3) -3.75 (4) -0.375

3. What color does not match the positive results of the following chemical reactions?

- (1) Benedict's test, brick red (2) Tollen's test, gold
(3) Hinsberg test, clear (4) iodoform test, yellow

4. Which of the following agents can denature proteins by disruption of hydrogen bonds?

I. heat II. organic solvent III. salts of heavy metals IV. strong acids and bases

- (1) I, II, IV (2) I, III, IV (3) II, III, IV (4) I, II, III, IV

5. What is (are) the product(s) when *cis*-2-butene reacts with bromine?

- (1) (*S,S*)-2,3-dibromobutane (2) (*R,R*)-2,3-dibromobutane
(3) *rac*-2,3-dibromobutane (4) *meso*-2,3-dibromobutane

6. Which of the followings belong to polar aprotic solvent?

I. water II. dimethylsulfoxide III. methanol IV. dimethylformamide

- (1) I, III (2) II, IV (3) II, III, IV (4) III, IV

7. Determine the hybrid orbital between the C-H bond of the following compounds:

benzene, alkyne, alkene, alkane

- (1) sp , sp , sp^2 , sp^3
(2) sp , sp^3 , sp^2 , sp
(3) sp^2 , sp^3 , sp^2 , sp
(4) sp^2 , sp , sp^2 , sp^3

8. What is the order of stability of the following radicals (in decreasing order):

I. $\cdot\text{CH}_3$ II. $\cdot\text{CH}_2(\text{CH}_3)$ III. $\cdot\text{CH}(\text{CH}_3)_2$ IV. $\cdot\text{C}(\text{CH}_3)_3$

- (1) I, II, III, IV
(2) IV, III, II, I
(3) II, III, IV, I
(4) I, IV, III, II

9. Which two of the following compounds cannot contain a benzene ring?

I. $\text{C}_{10}\text{H}_{16}$ II. $\text{C}_8\text{H}_6\text{Cl}_2$ III. C_5H_4 IV. $\text{C}_{10}\text{H}_{15}\text{N}$

- (1) I, IV (2) II, III (3) I, II (4) I, III

10. Choose the one true statement.

- (1) An achiral compound can have chiral centers.
- (2) An optically inactive substance must be achiral.
- (3) In chemical reactions the change from an *S* reactant to an *R* product always signals an inversion of configuration.
- (4) When an achiral molecule reacts to give a chiral molecule the product is always racemic.

11. Compare the net dipole moments of the following compounds:

I. 1,1-dichloroethene II. *trans*-1,2-dichloroethene III. *cis*-1,2-dichloroethene

- (1) I > II > III
- (2) III > II > I
- (3) II > I > III
- (4) I > III > II

12. The following alcohols reacts with H_2SO_4 at $\sim 170^\circ\text{C}$. Compare the relative reaction rates of these alcohols. I. $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ II. $\text{CH}_3\text{CHOHCH}_3$ III. $(\text{CH}_3)_3\text{COH}$.

- (1) I > II > III
- (2) II > III > I
- (3) III > II > I
- (4) II > I > III

13. Predict the order of relative reactivity of the following compounds towards $\text{S}_{\text{N}}1$ reactions.

I. benzyl chloride II. *p*-methoxybenzyl chloride III. *p*-nitrobenzyl chloride

- (1) I > II > III
- (2) III > II > I
- (3) II > I > III
- (4) I > III > II

14. Determine the sequence of successively higher oxidation states of the compounds listed below:

- (1) $\text{RSH} > \text{RSOH} > \text{RSO}_2\text{H} > \text{RSSR}$
- (2) $\text{RSH} > \text{RSSR} > \text{RSOH} > \text{RSO}_2\text{H}$
- (3) $\text{RSO}_2\text{H} > \text{RSOH} > \text{RSH} > \text{RSSR}$
- (4) $\text{RSSR} > \text{RSH} > \text{RSOH} > \text{RSO}_2\text{H}$

15. How many ESR signals are there in an allyl radical?

- (1) 2 (2) 3 (3) 4 (4) 5

16. Compare the acidities of the following compounds:

I. CH_3NO_2 II. $\text{CH}_3\text{CO}_2\text{R}$ III. CH_3COH .

- (1) $\text{I} > \text{II} > \text{III}$
- (2) $\text{III} > \text{II} > \text{I}$
- (3) $\text{II} > \text{I} > \text{III}$
- (4) $\text{I} > \text{III} > \text{II}$

17. Which one of the following factors does not determine the wavenumber of an infrared absorption band?

- (1) strength of the bonds involved
- (2) masses of the atoms involved
- (3) the type of vibration
- (4) the number of absorbing groups in a molecule

18. Choose the one true statement for NMR.

- (1) Chemical shift in Hz is proportional to operating frequency.
- (2) Coupling constant J is dependent of operating frequency.
- (3) Chemical shift in ppm is proportional to operating frequency.
- (4) The differences in chemical shift between all signals, in Hz, is smaller than their coupling constants.

19. A water-insoluble phenol is most likely to dissolve in an aqueous solution with a pH that is:

- (1) well below the pK_a of the phenol.
- (2) equal to the pK_a of the phenol.
- (3) well above the pK_a of the phenol.
- (4) independent of the pK_a of the phenol.

20. Which one of the following alkenes has E configuration?

