

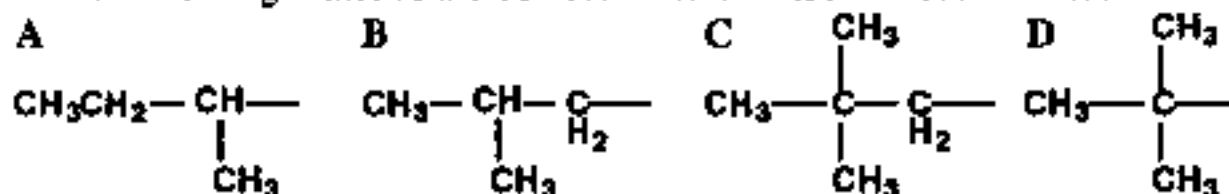
I. Please choose a correct answer for each of the following questions. (60%)

1. Which of the following species are isoelectronic? I Be^{2+} II Ne III S^{2-} IV Mg^{2+} V N^{3-}
(A) I, IV, V (B) II, III, IV (C) I, II, V (D) II, IV, V

2. Which of the following belong in the group of constitutional isomers for $\text{C}_3\text{H}_6\text{O}_2$?
I $\text{CH}_3\text{CO}_2\text{CH}_3$ II $\text{CH}_2=\text{CHCH}_2\text{OH}$ III $\text{CH}_2=\text{CHCO}_2\text{H}$ IV $\text{HOCH}_2\text{CH}_2\text{OH}$
V $\text{CH}_3\text{OCH}_2\text{OH}$ (A) II, III (B) II, IV, V (C) I, II, V (D) I

3. In which of the following molecules does carbon have both sigma and pi bonds? I CH_4
II C_2H_2 III H_2CO IV CH_3NH_2 V CO_2 (A) II, V (B) I, IV (C) II, III, V (D) II, III

4. Which of the following matches are correct? I *tert* II *iso* III *sec* IV *neo*



(A) III and A, II and B (B) III and B, I and D (C) I and C, IV and D (D) II and A, IV and C

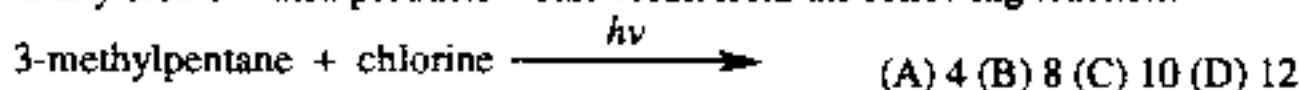
5. How many isomers (constitutional and geometric) are there for dimethylcyclopentane?
(A) 3 (B) 5 (C) 7 (D) 9

6. Which of the following are more stable isomers?

I. *cis* or *trans* 1,4-dibromocyclohexane II. *cis* or *trans* 1,3-dibromocyclohexane

(A) I *cis* and II *cis* (B) I *cis* and II *trans* (C) I *trans* and II *cis* (D) I *trans* and II *trans*

7. How many dichlorinated products would result from the following reaction?



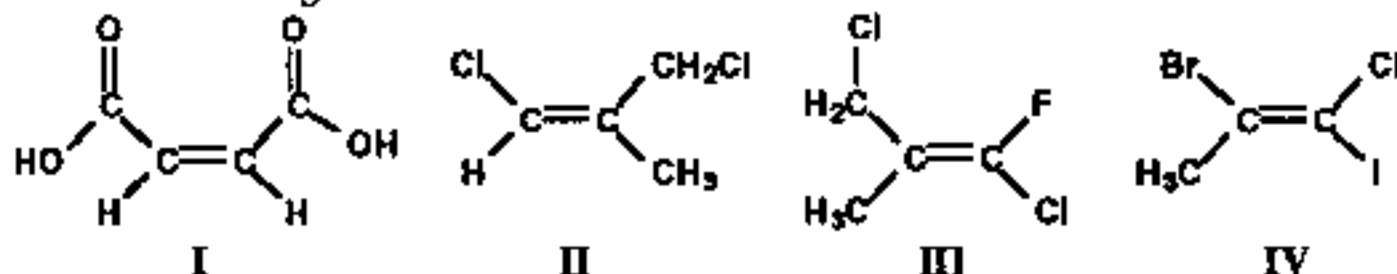
8. What is the pH of a 10% ionized solution of vitamin C ($\text{pK}_{\text{a}1} = 4.17$)?
(A) 3.17 (B) 5.17 (C) 4.17 (D) 2.17

9. Arrange the following compounds in the order of increasing acid strength (weakest first).

I phenol ($\text{K}_{\text{a}} = 1.12 \times 10^{-10}$) II pyruvic acid ($\text{pK}_{\text{a}} = 2.49$) III aspirin ($\text{K}_{\text{a}} = 3.3 \times 10^{-4}$)
IV carbonic acid ($\text{pK}_{\text{a}} = 6.38$)

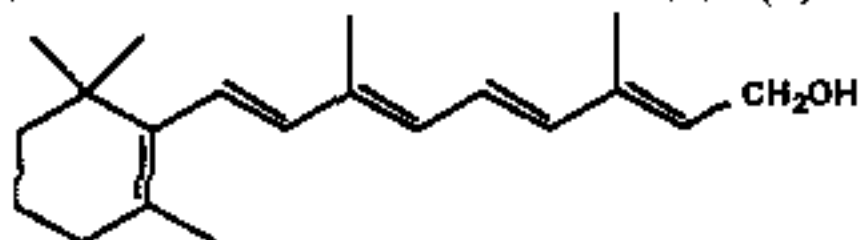
(A) I, III, IV, II (B) I, IV, III, II (C) II, IV, III, I (D) IV, II, I, III

10. Which of the following alkenes are *E*-forms?



(A) I, II (B) II, III (C) III, IV (D) II, IV

11. How many isoprene units are there in vitamin A? (A) 2 (B) 3 (C) 4 (D) 8



12. Which of the following reagents will add to an alkene in a Markovnikov orientation?

I H_2 II HBr /peroxides III HCl IV $\text{Hg}(\text{OAc})_2/\text{H}_2\text{O}$

(A) I, II, III (B) III, IV (C) II, IV (D) II, III, IV

13. Which of the following react with alkenes by a free radical mechanism? I HBr /peroxide

II BH_3 III $\text{Hg}(\text{OAc})_2$ IV NBS /heat (A) I, II (B) II, IV (C) I, IV (D) II, III

14. Which of the following are examples of *syn* addition to alkenes?

I hydrogenation II hydration III hydrobromination IV hydroboration

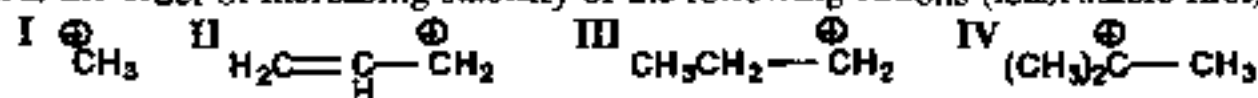
(A) I, II (B) III, IV (C) II, III (D) I, IV

15. What is the order of increasing acidity for the following compounds (weakest first)?

I $\text{HC}\equiv\text{CH}$ II NH_3 III CH_3OH IV H_2O

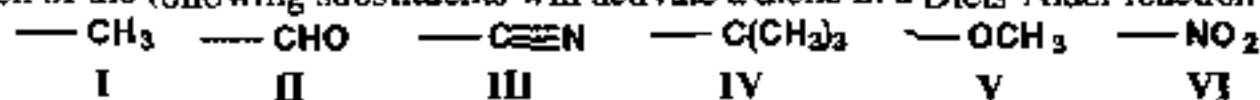
(A) IV, III, II, I (B) II, IV, III, I (C) I, II, III, IV (D) II, I, III, IV

16. What is the order of increasing stability of the following cations (least stable first)?



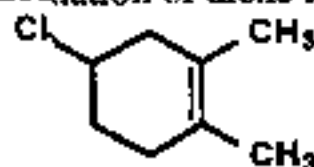
(A) I, III, IV, II (B) IV, II, III, I (C) II, I, III, IV (D) I, II, III, IV

17. Which of the following substituents will activate a diene in a Diels-Alder reaction?



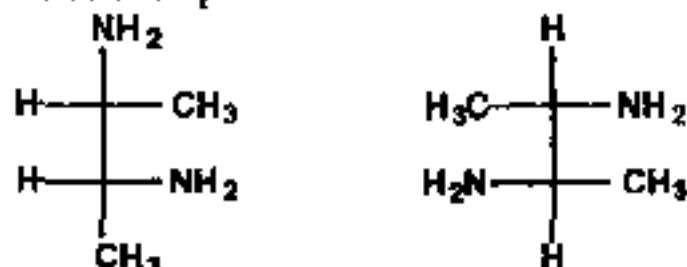
(A) II, III (B) I, IV, V (C) II, III, VI (D) I, IV

18. Which combination of diene and dienophile will form the following Diels-Alder product?

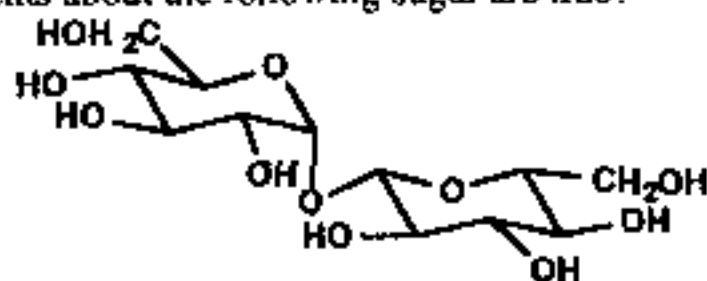


- (A) 2-methyl-1,3-butadiene and 1-chloropropene (B) 2-chloro-1,3-butadiene and *cis*-2-butene
(C) 1,3-pentadiene and *cis*-2-chloropropene (D) 2,3-dimethyl-1,3-butadiene and vinyl chloride
19. The specific rotation of levorotatory tartaric acid is +15.9 degrees. A mixture of dextrotatory and levorotatory tartaric acid has a specific rotation of +7.45 degrees. What is the optical purity of the mixture? (A) 75% (B) 50% (C) 33.33% (D) 25%
20. Which peak in the mass spectra could distinguish between 1-butanol and 2-butanol? (A) 74 (B) 28 (C) $M - 18$ (D) $M + 2$

21. What is the relationship between these two structures?

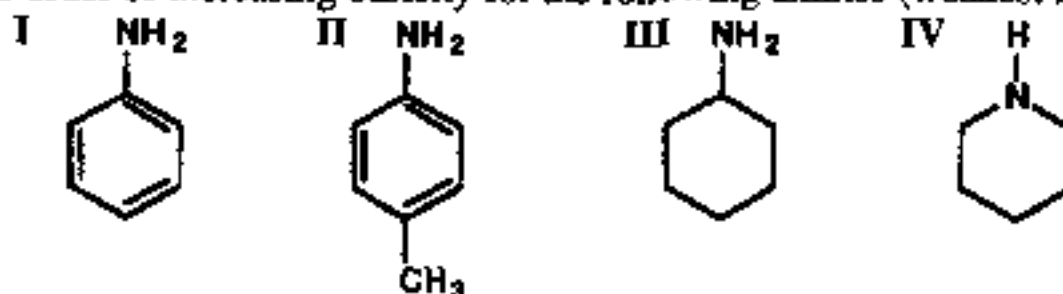


- (A) identical structures (B) enantiomers (C) diastereomers (D) constitutional isomers
22. A chiral compound, C_5H_8 , on catalytic hydrogenation yields an achiral compound, C_5H_{10} . What is the original chiral compound? (A) 1-methylcyclobutene (B) 3-methylcyclobutene (C) 1,2-dimethylcyclopropene (D) cyclopentene
23. Which of the following statements apply to an S_N2 reaction?
- I. The reaction is first order in alkyl halide and first order in the nucleophile.
 - II. The order of reactivity is methyl $>$ $1^\circ > 2^\circ > 3^\circ$.
 - III. The reaction is first order in alkyl halide and zero order in the nucleophile.
 - IV. Rearrangements are common.
- (A) I, II (B) III, IV (C) I, IV (D) II, IV
24. Compound A gives two signals in the ^{13}C NMR spectrum and a single signal in the 1H -NMR spectrum. Which of the following is most likely compound A?
- (A) dimethyl ether (B) diethyl ether (C) neopentane (D) methyl acetate
25. What is the wavelength (μm) of an infrared absorption band at a wavenumber of 500 cm^{-1} ?
- (A) 0.2 (B) 2.0 (C) 20 (D) 25
26. How can phenol be distinguished from cyclohexanol?
- (A) solubility in water (B) solubility in hydrochloric acid (C) solubility in sodium bicarbonate (D) solubility in sodium hydroxide
27. Which of the following reactions does not create a C-H bond?
- (A) Cannizzaro (B) Wolff-Kishner (C) Grignard (D) Wittig
28. Which of the statements about the following sugar are true?



- I. It is a reducing sugar
 - II. It will undergo mutarotation
 - III. The linkage is 1,1
 - IV. It is composed of 2 units of D-glucose
- (A) I, II (B) II, III (C) III, IV (D) I, IV

29. What is the order of increasing basicity for the following amines (weakest first)?



(A) IV, II, III, I (B) II, I, III, IV (C) I, II, III, IV (D) II, I, IV, III

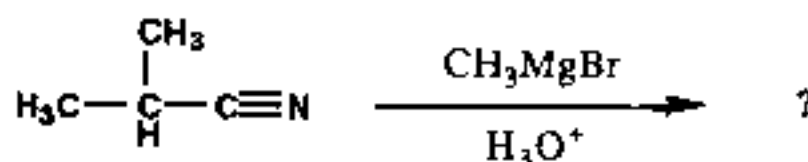
30. What is the structure of the pentapeptide that gave Lys-Leu-Phe on reaction with cyanogen bromide, and gave the fragments Met-Lys, Leu-Phe and Arg on reaction with trypsin?

(A) Arg-Met-Phe-Leu-Lys (B) Lys-Leu-Phe-Arg-Met (C) Arg-Met-Lys-Leu-Phe (D) Met-Arg-Lys-Leu-Phe

II. Propose a structure for each based on its spectroscopic data.

(16%)

1.



MS: $M^+ = 86$

IR: 1715 cm^{-1}

$^1\text{H NMR}$: 1.05 ppm (6H, doublet, $J = 7\text{ Hz}$); 2.12 ppm (1H, septet, $J = 7\text{ Hz}$)

$^{13}\text{C NMR}$: 18.2, 27.2, 41.6, 211.2 ppm

2. $\text{C}_4\text{H}_7\text{BrO}$:

$^1\text{H NMR}$: 2.11 ppm (3H, singlet); 3.52 ppm (2H, triplet, $J = 6\text{ Hz}$);
4.4 ppm (2H, triplet, $J = 6\text{ Hz}$)

3. $\text{C}_9\text{H}_{11}\text{Br}$:

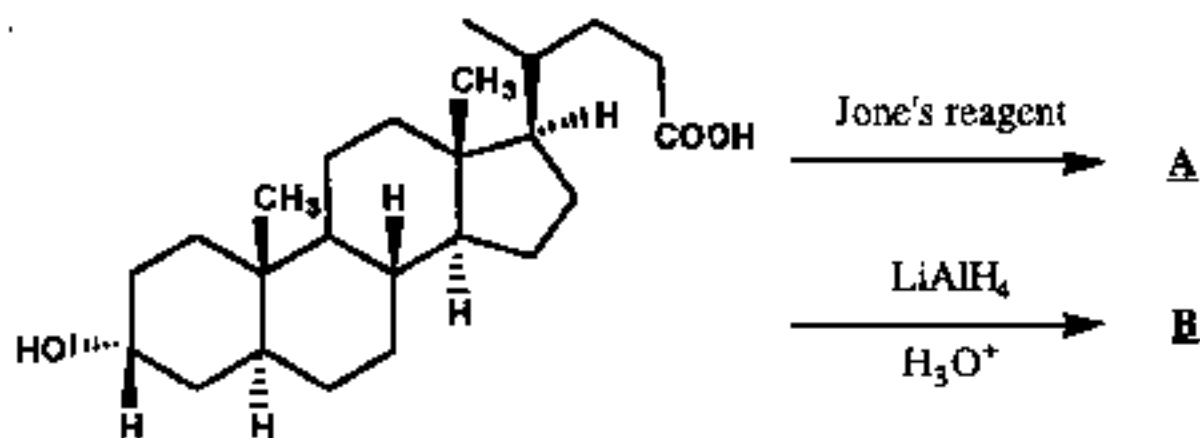
$^1\text{H NMR}$: 2.15 ppm (2H, quintet, $J = 7\text{ Hz}$); 2.75 ppm (2H, triplet, $J = 7\text{ Hz}$);
3.38 ppm (2H, triplet, $J = 7\text{ Hz}$); 7.22 ppm (5H singlet)

4. An optically active compound $\text{C}_5\text{H}_{10}\text{O}$ with an IR absorption at 1730 cm^{-1} .

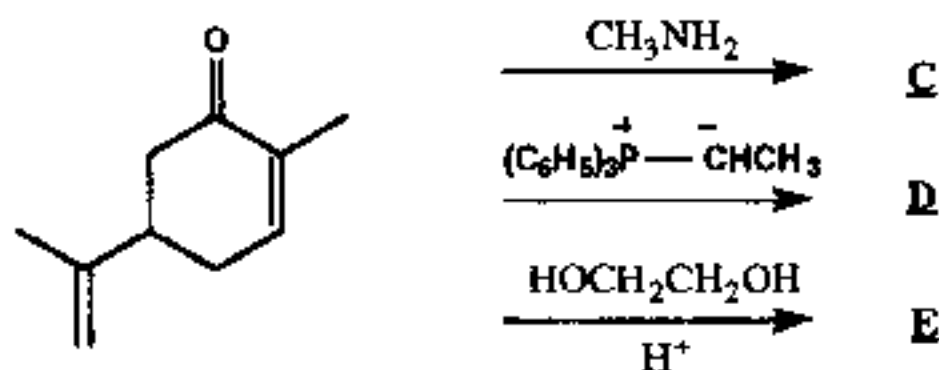
III. Predict the major product for each of the following reactions.

(24%)

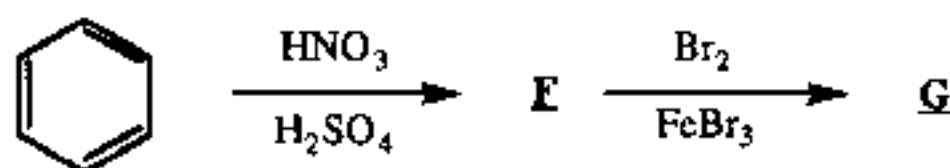
1.



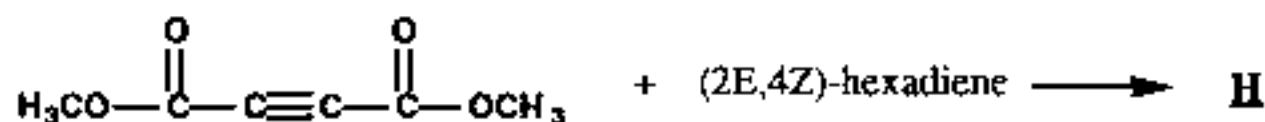
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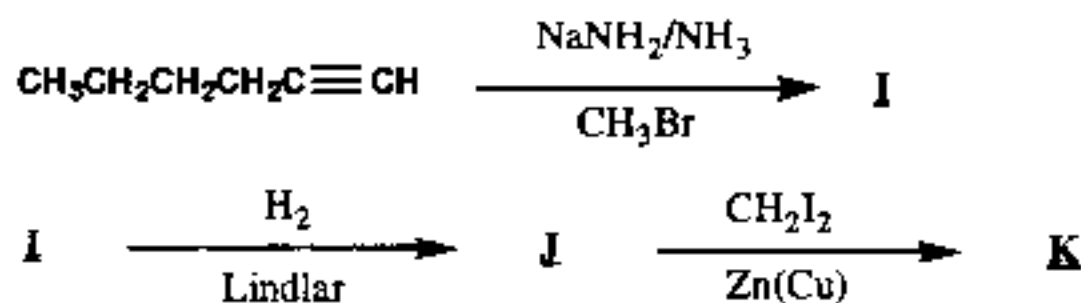
3.



4.



5.



6.

