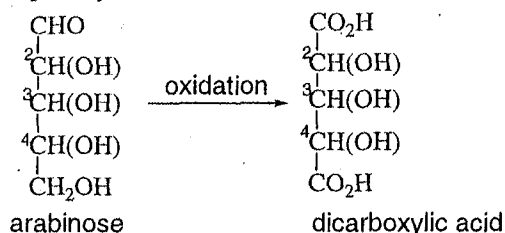
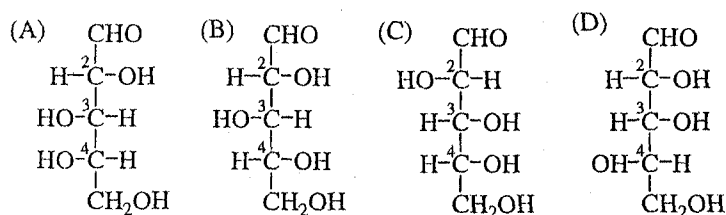


## I. 選擇題 (請依序作答, 不需抄題, 皆為單選題, 每題三分, 答錯倒扣一分) (45%)

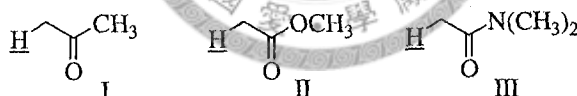
- 1) In the structure determination of sugars, Emil Fisher oxidized the following sugar, D-arabinose, to a dicarboxylic acid that was optically active.



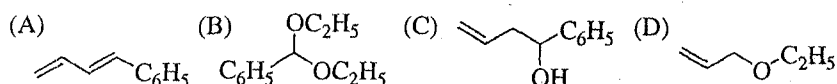
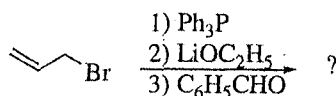
One of the possible structures in Fisher projection formula for D-arabinose is



- 2) Which of the following statement is **incorrect**?
- (A) In formaldehyde ( $\text{H}_2\text{C}=\text{O}$ ), the nonbonding orbital is the HOMO
- (B) A Lewis acid uses its LUMO to interact with the HOMO of a Lewis base.
- (C) The longer the absorption wavelength, the narrower gap between HOMO and LUMO
- (D) In formaldehyde ( $\text{H}_2\text{C}=\text{O}$ ), the  $\pi$  orbital, like that in ethylene, normally serves as a nucleophile to react with an electrophile.
- 3) Of the following acids (the underlined hydrogen atoms), the  $pK_a$  values decrease according to the following order



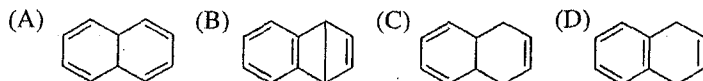
- (A) I > II > III. (B) I > III > II. (C) III > II > I. (D) II > I > III
- 4) Which of the following reactions may **NOT** occur via a six-membered-ring transition state?
- (A) Diels-Alder cycloaddition of butadiene with ethene
- (B) Grignard reaction of  $\text{MeMgI}$  with acetone.
- (C) Acid-catalyzed decarboxylation of a  $\beta$ -ketocarboxylic acid.
- (D) Base-catalyzed condensation of ethyl acetate
- 5) What is the product of the following reaction sequence?



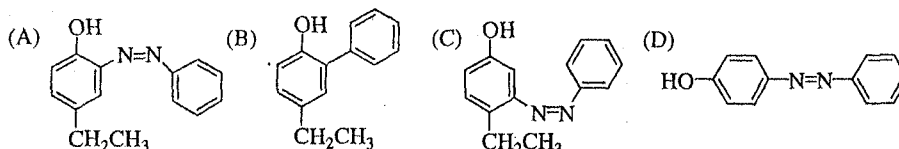
- 6) The two coupled protons exhibit absorptions at 45, 55, 75, and 85 Hz when a 100 MHz NMR instrument is used. When a 200 MHz NMR instrument is employed, the four signals appear at
- (A) 95, 105, 125, and 135 Hz; (B) 145, 155, 175, and 185 Hz;
- (C) 90, 110, 150, and 170 Hz; (D) 22.5, 27.5, 37.5, and 42.5 Hz.

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- 7) What product should be obtained if benzyne is generated in the presence of 1,3-butadiene?



- 8) What is the principal product (regardless of N=N configuration) when aniline is treated with sodium nitrite and hydrochloric acid at 0-5°C and this mixture is added to *p*-ethylphenol?

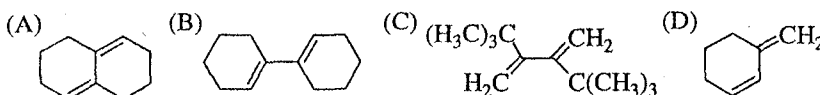


- 9) Which of the following would provide the best synthesis of 3,5-dimethyl-2-hexanone?

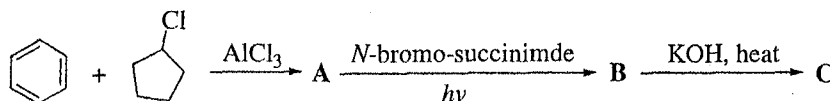
- (A) Ethyl acetoacetate/NaOC<sub>2</sub>H<sub>5</sub>/CH<sub>3</sub>I; then KO<sup>t</sup>Bu/(CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>Br; then NaOH; then H<sub>3</sub>O<sup>+</sup>; then heat  
 (B) Ethyl acetoacetate/NaOC<sub>2</sub>H<sub>5</sub>/(CH<sub>3</sub>)<sub>3</sub>CBr; then KO<sup>t</sup>Bu/CH<sub>3</sub>I; then NaOH; then H<sub>3</sub>O<sup>+</sup>; then heat  
 (C) Ethyl acetoacetate/NaOC<sub>2</sub>H<sub>5</sub>/(CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>Br; then KO<sup>t</sup>Bu/CH<sub>3</sub>I; then NaOH; then H<sub>3</sub>O<sup>+</sup>; then heat  
 (D) Ethyl acetoacetate/NaOC<sub>2</sub>H<sub>5</sub>/(CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>CHBrCH<sub>3</sub>; then NaOH; then H<sub>3</sub>O<sup>+</sup>; then heat
- 10) What is the correct description of this disaccharide?  
 (A) The α-anomer of two D-galactose units joined by an α (1→4) linkage  
 (B) The β-anomer of two D-galactose units joined by a β (1→4) linkage  
 (C) The α-anomer of two D-glucose units joined by an α (1→4) linkage  
 (D) The β-anomer of two D-glucose units joined by a β (1→4) linkage
- 11) Which is a correct name for the following compound?

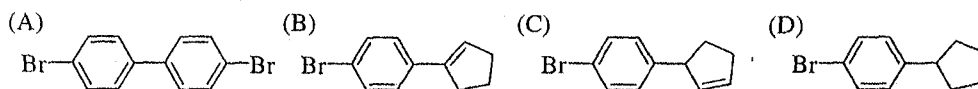


- (A) (*E*)-1-Bromo-1-chloro-2-methyl-1-hexene; (B) (*Z*)-2-Bromochloromethylhexane  
 (C) 2-(*E,Z*)-Bromochloromethyl-1-hexene; (D) (*Z*)-1-Bromo-1-chloro-2-methyl-1-hexene
- 12) Cyclohexene reacts with bromine to yield 1,2-dibromocyclohexane. Molecules of the product would:  
 (A) be a racemic form and, in their most stable conformation, they would have one bromine atom equatorial and one axial.  
 (B) be a racemic form and, in their most stable conformation, they would have both bromine atoms equatorial.  
 (C) be a meso compound and, in its most stable conformation, it would have both bromine atoms equatorial.  
 (D) be a pair of diastereomers and, in their most stable conformation, one would have the bromines equatorial and axial, and the other would have the bromines equatorial and equatorial.
- 13) Which of these conjugated dienes can undergo a Diels-Alder reaction?

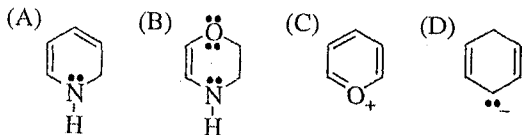


- 14) The product, C, that would result from the following series of reactions





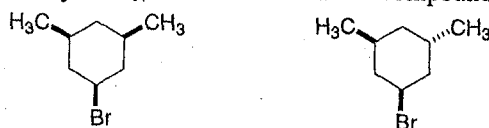
15) Which of the following would you expect to be aromatic?



II. What is called a stereospecific reaction? Give one representative example to illustrate your point. (5%)

III. Suggest an explanation for each of the following observations. (10%)

(a) Compound A reacts faster by the  $S_N2$  mechanism than the compound B.



A

B

(b) Compound C reacts faster by the  $S_N1$  mechanism than compound D.

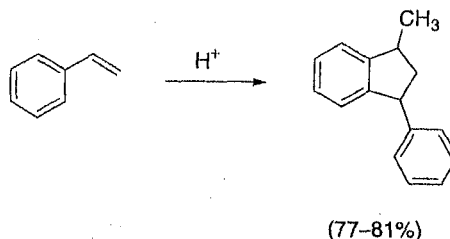


C

D

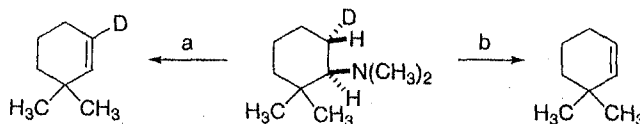
IV. A neutral compound,  $C_7H_{13}O_2Br$ , does not give an oxime or phenylhydrazone derivative. The infrared spectrum shows bands at  $2850-2950\text{ cm}^{-1}$  but none above  $3000\text{ cm}^{-1}$ . Another strong band is at  $1740\text{ cm}^{-1}$ . The NMR shows the following pattern:  $\delta = 1.0$  (t, 3 H),  $1.3$  (d, 6 H),  $2.1$  (m, 2 H),  $4.2$  (t, 1 H),  $4.6$  (m, 1 H). Deduce the structure and assign their bands. (10%)

V. On heating with aqueous sulfuric acid styrene reacts to form a dimer in good yield.



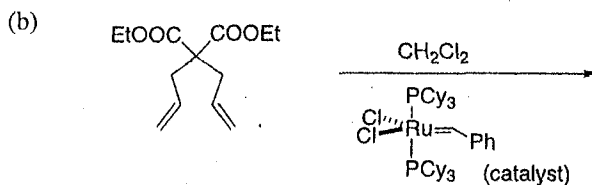
Write a reasonable mechanism, showing all intermediates involved. (10%)

VI. Show how to accomplish each of the following conversions. (6%)



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(6%)



(8%)

