

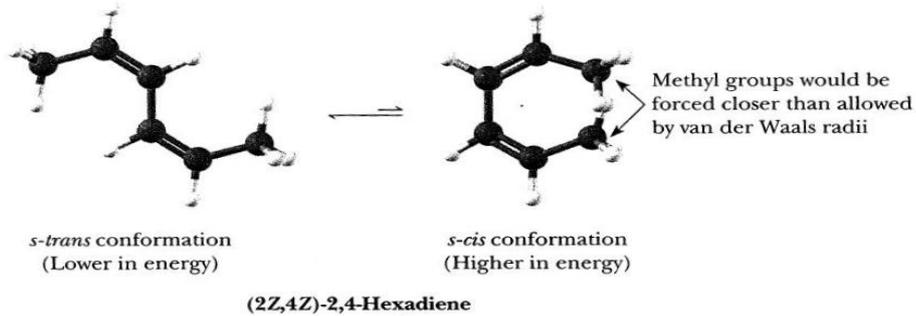
## 《有機化學》 試題解析

## 爭議試題

## 一、第 17 題：

此答案應為(A)

詳見 Organic Chemistry by Brown, Foote, Iverson, Anslyn. 5e (Fifth Edition) p.945

(2Z,4Z)-2,4-Hexadiene is unreactive in Diels-Alder reactions because it is prevented by steric hindrance from assuming the required *s-cis* conformation.

## 二、第 38 題：

此答案應為(C)

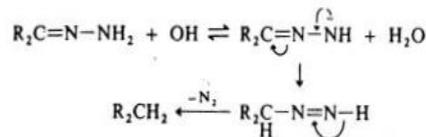
詳見 Advanced Organic Chemistry by Francis A. Carey p.150

Advanced Org. Chem. Francis A. Carey

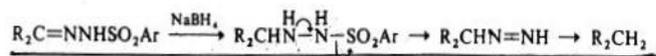
150

CHAPTER 4  
REDUCTION  
OF CARBONYL  
GROUPS

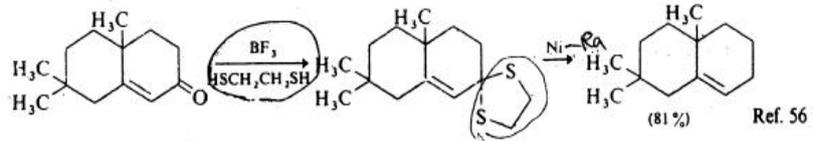
Although they are not dissolving-metal processes, several other important means for effecting reduction of a carbonyl group to methylene can be conveniently discussed at this point. The Wolff-Kishner reaction involves the base-catalyzed decomposition of hydrazones.<sup>53</sup> Alkyl diimides are believed to be formed and then to collapse with loss of nitrogen:



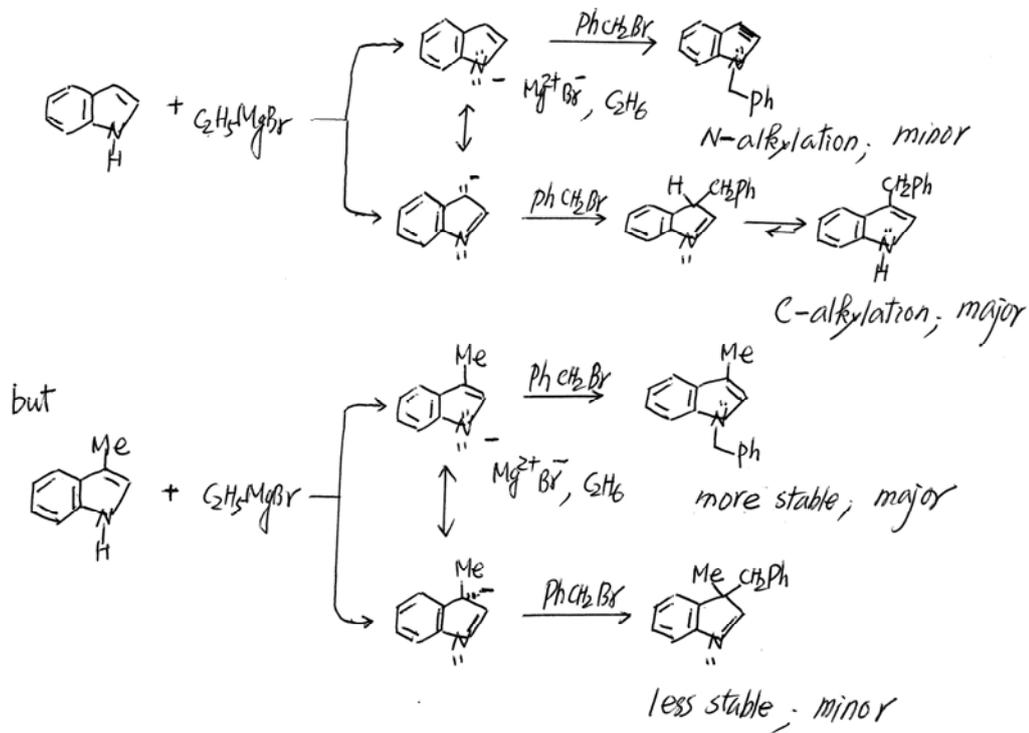
The reduction of tosylhydrazones by  $\text{LiAlH}_4$  or  $\text{NaBH}_4$  also converts carbonyl groups to methylene.<sup>54</sup> It is believed that a diimide intermediate is involved, as in the



Wolff-Kishner reaction. Excellent yields of carbonyl-to-methylene reduction products have been reported using the mild reducing agent sodium cyanoborohydride.<sup>55</sup> This reagent is added to a mixture of the carbonyl compound to be reduced and *p*-toluenesulfonylhydrazide. Hydrazone formation is faster than reduction of the carbonyl group by cyanoborohydride. As the hydrazone is formed, it is reduced to the hydrocarbon by NaBH<sub>3</sub>CN. Carbonyl groups can also be reduced to methylene via thioketal intermediates. The preparation of the cyclic thioketals derived from ethanedithiol is common. Heating the thioketal with excess Raney nickel causes hydrogenolysis of the C-S bonds.



三、第 76 題：  
此答案應為(A)



解題師資

張亮

# 《有機化學》

## I. Choose one correct answer for the following questions

【單選題】每題 1 分，共計 60 分，答錯 1 題倒扣 0.25 分，倒扣至本大題零分為止，未作答，不給分亦不扣分。

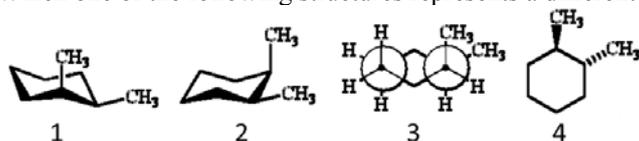
(E) 1. According to atomic theory:

- (A) The nucleus is positively charged  
 (B) The nucleus contains both charged and uncharged particles  
 (C) The electrons contribute very little to the total mass of the atom  
 (D) The electrons are located in the atomic space outside the nucleus  
 (E) All of the above.

(B) 2. A coenzyme frequently encountered in transamination reactions is

- (A) Tetrahydrofolate (B) Pyridoxal phosphate  
 (C) Thiamine pyrophosphate (D) Biotin (E) NADH

(D) 3. Which one of the following structures represents a different compound from the other three?

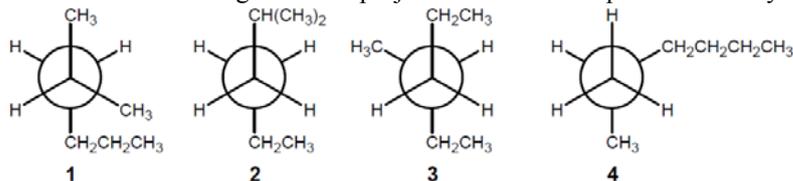


- (A) 1 (B) 2 (C) 3 (D) 4 (E) All of the above are the same.

(E) 4. Which of the standard amino acids is achiral?

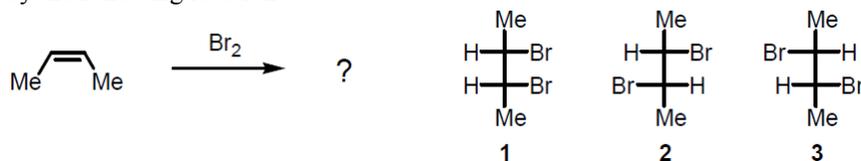
- (A) Lysine (B) Proline (C) Valine (D) Alanine (E) Glycine

(C) 5. Which of the following Newman projections does **not** represent 2-methylhexane?



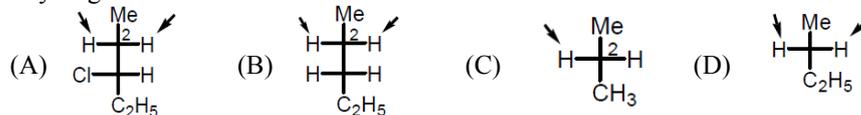
- (A) 1 (B) 2 (C) 3 (D) 4 (E) both 2 and 3

(E) 6. 2,3-Dibromobutane can exist three stereoisomers as shown below. What stereoisomers would be formed by the following reaction?



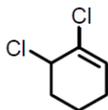
- (A) 1 only (B) 2 only (C) 3 only (D) 1 and 2 (E) 2 and 3

(A) 7. In the following structures, the protons pointed by arrow (on C2) which belong to diastereotopic hydrogens.

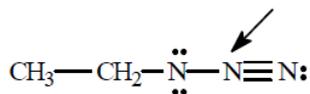


- (E) None of the above.

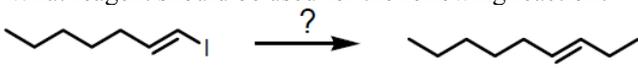
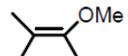
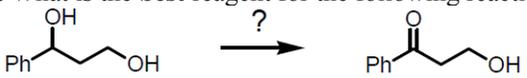
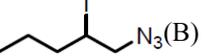
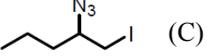
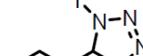
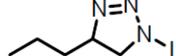
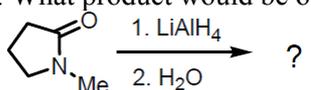
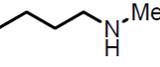
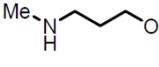
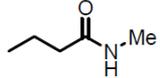
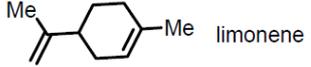
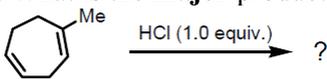
(C) 8. What is the **correct** IUPAC systematic name for the following compound?

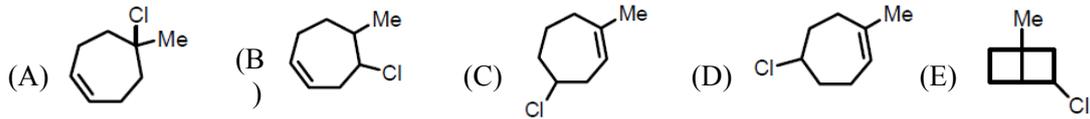


- (A) 1,2-Dichlorocyclohexene (B) 2,3-Dichlorocyclohexene (C) 1,6-Dichlorocyclohexene  
 (D) 1,2-Dichloro-2-cyclohexene (E) None of the above.
- (C) 9. What is the formal charge on the nitrogen atom indicated with the arrow in the following compound?

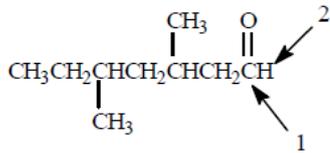


- (A) 0 (B) -1 (C) +1 (D) -2 (E) +2
- (E) 10. Which of the following nucleophiles reacts with MeI in greatest rate in an aqueous solution?  
 (A) MeO<sup>⊖</sup> (B) MeOH (C) HO<sup>⊖</sup> (D) CH<sub>3</sub>CO<sub>2</sub><sup>⊖</sup> (E) MeS<sup>⊖</sup>
- (C) 11. Which of the following compounds would have a greater dipole moment than you expect?  
 (A) (B) (C) (D) (E) None of the above.
- (C) 12. Compound A: M<sup>+</sup> = 86, IR absorption: 3400 cm<sup>-1</sup>,  
<sup>13</sup>C NMR spectral data: Broadband-decoupled <sup>13</sup>C NMR: δ 30.2, 31.9, 61.8, 114.7, 138.4,  
 DEPT-90: δ 138.4; DEPT-135: δ 138.4, negative peaks at δ 30.2, 31.9, 61.8, 114.7.  
 What is the structure of compound A?  
 (A) (B) (C) (D) (E)
- (A) 13. In the following, which one is the **most** acidic compound?  
 1 2 3 4   
 (A) 1 (B) 2 (C) 3 (D) 4 (E) 2 = 3
- (E) 14. Compound I has a molecular formula C<sub>5</sub>H<sub>10</sub>O, and <sup>1</sup>H-NMR data shown below: δ 0.95 (d, J = 7 Hz, 6H),  
 2.10 (s, 3H), 2.43 (m, 1H). What structure fits compound I?  
 (A) (B) (C) (D) (E)
- (E) 15. What is the coupling constant for the H<sub>a</sub> and H<sub>b</sub> protons in the <sup>1</sup>H NMR spectra of the following compound?  
  
 (A) 0 Hz (B) 3 Hz (C) 7 Hz (D) 10 Hz (E) 15 Hz
- (D) 16. Which of the following orbital represents the HOMO of 1,3-butadiene in ground state?  
 (A) (B) (C) (D) (E)
- (E) 17. Which of the following dienes would **not** react with a dienophile in a Diels-Alder reaction?  
 (A) (B) (C) (D) (E) None of the above.
- (D) 18. Arrange the following compounds in order of increasing reactivity to electrophilic aromatic substitution reaction.  
 1 2 3 4 5   
 (A) 2<3<4<1<5 (B) 1<2<4<3<5 (C) 2<4<1<3<5 (D) 2<1<4<3<5 (E) 2<4<1<5<3
- (D) 19. Which of the following reactions could **not** produce the desired product?

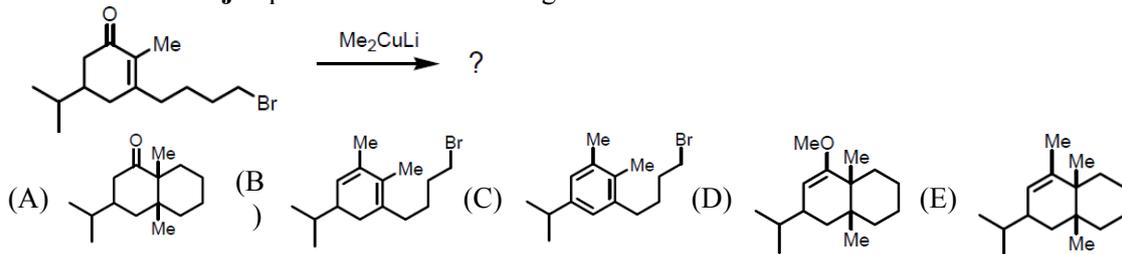
- (A)  $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{HBr} \longrightarrow \text{CH}_3\text{CH}_2\overset{\text{Br}}{\text{C}}\text{HCH}_3$  (B)  $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{HBr} \xrightarrow{\text{ROOR}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$
- (C)  $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{HCl} \longrightarrow \text{CH}_3\text{CH}_2\overset{\text{Cl}}{\text{C}}\text{HCH}_3$  (D)  $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{HCl} \xrightarrow{\text{ROOR}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$
- (E) None of the above.
- (C) 20. Select the **most** reasonable formula for the compounds with the following mass spectral data:  $M^+$  at  $m/z$  101 with a minor  $M+1$  peak.  
 (A)  $\text{C}_5\text{H}_9\text{Cl}$  (B)  $\text{C}_5\text{H}_{12}\text{N}_2$  (C)  $\text{C}_6\text{H}_{15}\text{N}$  (D)  $\text{C}_9\text{H}_{12}\text{O}$  (E)  $\text{C}_6\text{H}_9\text{S}$
- (E) 21. What reagent should be used for the following reaction?  
  
 (A)  $\text{CH}_3\text{CH}_2\text{MgBr}$  (B)  $\text{CH}_3\text{CH}_2\text{Li}$  (C)  $(\text{CH}_3\text{CH}_2)_2\text{Zn}$   
 (D)  $\text{CH}_3\text{CH}_2\text{B}(\text{OH})_2$  (E)  $(\text{CH}_3\text{CH}_2)_2\text{CuLi}$
- (D) 22. Which of the following alkenes is **most** reactive toward ozonolysis?  
 (A)  (B)  (C)  (D)  (E) 
- (A) 23. Which of the following ketones show **strong** characteristic band at  $1815\text{ cm}^{-1}$ ?  
 (A)  (B)  (C)  (D)  (E) 
- (C) 24. In aromatic nitration reactions, nitric acid ( $\text{HNO}_3$ ) is used in conjunction with the stronger acid, sulfuric acid,  $\text{H}_2\text{SO}_4$ , to form an intermediate. Which of the following could be the formula for this intermediate?  
 (A)  $\text{NO}_3^-$  (B)  $\text{H}_3\text{SO}_4^+$  (C)  $\text{H}_2\text{NO}_3^+$  (D)  $\text{HNO}_2$  (E)  $\text{NO}$
- (D) 25. What is the **best** reagent for the following reaction?  
  
 (A) PCC (B)  $\text{Na}_2\text{Cr}_2\text{O}_7, \text{H}_2\text{SO}_4$   
 (C)  $\text{DMSO}, (\text{COCl})_2$  then  $\text{Et}_3\text{N}$  (D)  $\text{MnO}_2$  (E)  $\text{H}_2\text{CrO}_4$
- (B) 26. What is the **major** product of the following reaction?  
  
 (A)  (B)  (C)  (D)   
 (E) None of the above.
- (A) 27. What product would be obtained by the following reaction?  
  
 (A)  (B)  (C)  (D)   
 (E) None of the above.
- (D) 28. Which fragment would you expect to be the base peak in the mass spectrum of limonene?  
 limonene  
 (A)  $m/z = 136$  (B)  $m/z = 121$  (C)  $m/z = 93$  (D)  $m/z = 68$  (E)  $m/z = 49$
- (A) 29. What is the **major** product of the following reaction?  




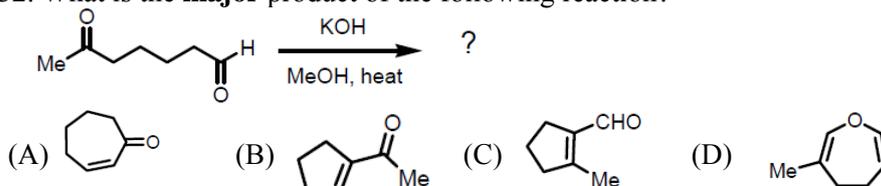
(C) 30. Which of the following would correctly describe the respective  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR spectra for the indicated atoms for the compound shown below?



- (A) Atom 1 would produce a peak at 205 ppm and atom 2 would appear as doublet  
 (B) Atom 1 would produce a peak at 175 ppm and atom 2 would appear as a singlet  
 (C) Atom 1 would produce a peak at 205 ppm and atom 2 would appear as a triplet  
 (D) Atom 1 would produce a peak at 175 ppm and atom 2 would appear as a triplet  
 (E) Atom 1 would produce a peak at 175 ppm and atom 2 would appear as a doublet
- (A) 31. What is the **major** product of the following reaction?

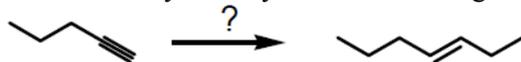


(B) 32. What is the **major** product of the following reaction?

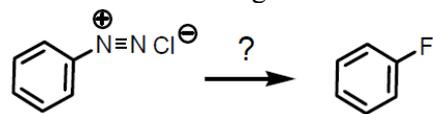


(E) None of the above.

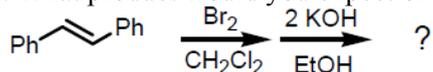
(D) 33. How would you carry out the following transformation?

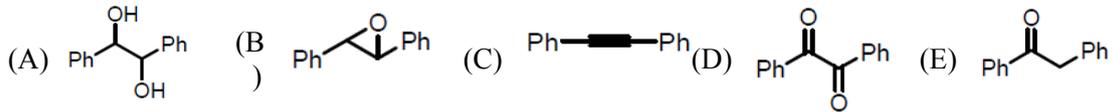


- (A) 1. (a) NaOH, (b)  $\text{CH}_3\text{CH}_2\text{Br}$ ; 2. Na,  $\text{NH}_3(l)$   
 (B) 1. Na,  $\text{NH}_3(l)$ ; 2. (a)  $\text{CH}_3\text{MgBr}$ , (b)  $\text{CH}_3\text{CH}_2\text{Br}$   
 (C) 1. (a)  $\text{NaNH}_2$ , (b)  $\text{CH}_3\text{CH}_2\text{Br}$ ; 2.  $\text{H}_2$ , Lindlar's catalyst  
 (D) 1. (a)  $\text{NaNH}_2$ , (b)  $\text{CH}_3\text{CH}_2\text{Br}$ ; 2. Na,  $\text{NH}_3(l)$   
 (E) 1. (a) BuLi, (b)  $\text{CH}_3\text{CH}_2\text{Br}$ ; 2.  $\text{H}_2$ , Lindlar's catalyst
- (C) 34. What is the **best** reagent for the following transformation?

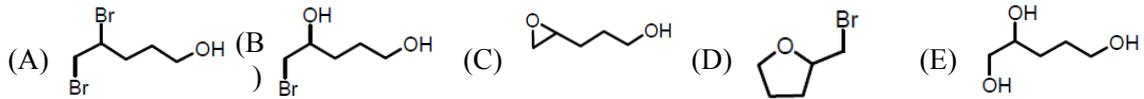
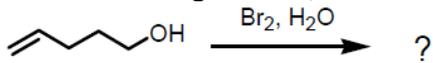


- (A) HF (B) CuF (C)  $\text{HBF}_4$  (D)  $\text{Bu}_4\text{NF}$  (E)  $\text{F}_2$
- (C) 35. What product would you expect of the following transformation?

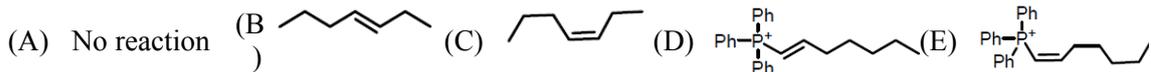
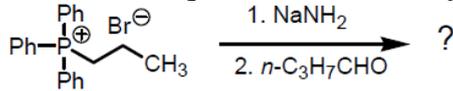




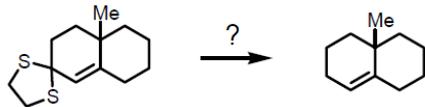
(D) 36. In the following reaction, what is the **major** product?



(C) 37. In the following reaction, which compound is the **major** product?

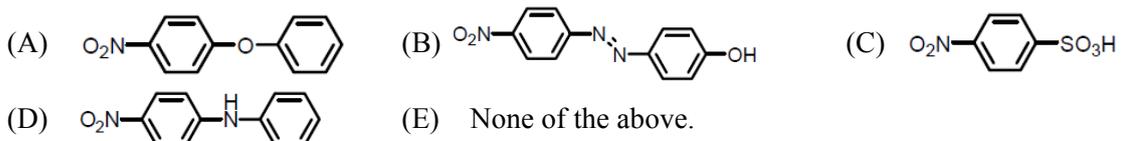
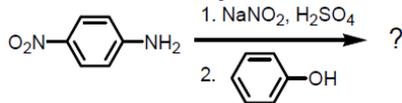


(A) 38. Which of the following reagents could not be applied to the following transformation?

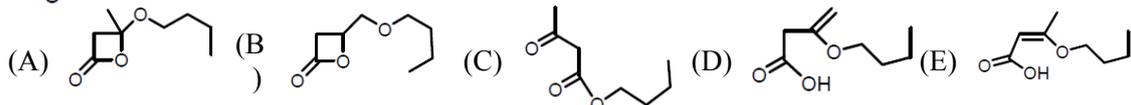
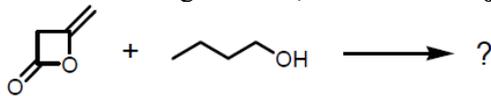


- (A) HgCl<sub>2</sub>, CaCO<sub>3</sub>, acetone (B) NiCl<sub>2</sub>, NaBH<sub>4</sub>, DMF (C) Raney-Ni, EtOH  
(D) *n*-Bu<sub>3</sub>SnH, AIBN, benzene (E) All of the above work well.

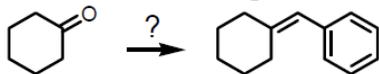
(B) 39. What is the **final** product of the following reaction?



(C) 40. In the following reaction, what is the **major** product?

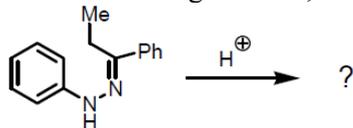


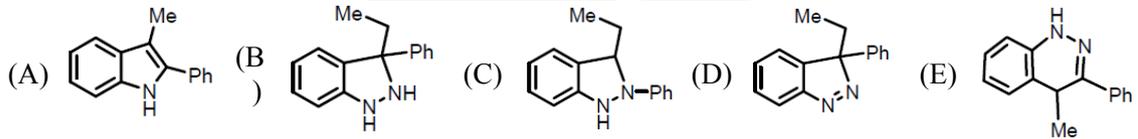
(C) 41. What is the **best** reagent for the following transformation?



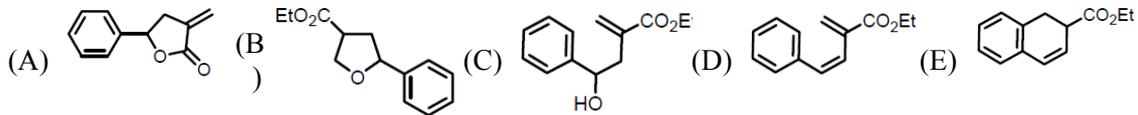
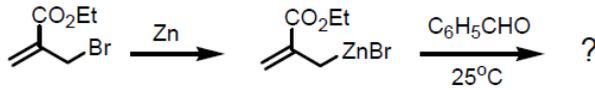
- (A) 1. PhMgBr, ether 2. H<sub>3</sub>O<sup>+</sup> (B) PhCH<sub>2</sub>MgBr, ether 2. H<sub>3</sub>O<sup>+</sup> (C) Ph<sub>3</sub>P=CHPh, THF  
(D) (PhCH<sub>2</sub>)<sub>2</sub>CuLi (E) All of the above work well.

(A) 42. In the following reaction, which compound is the **major** product?

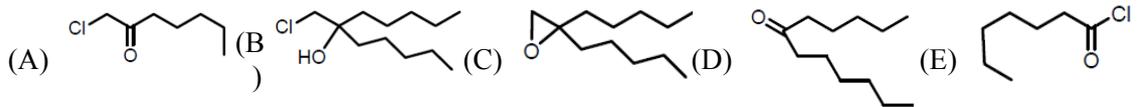
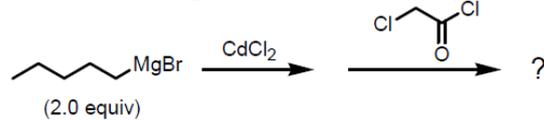




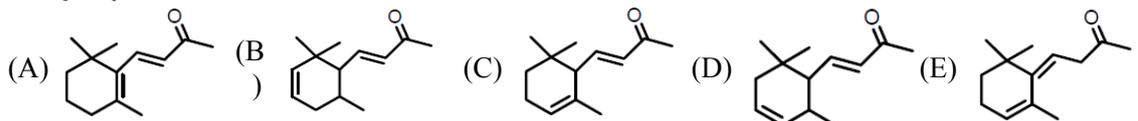
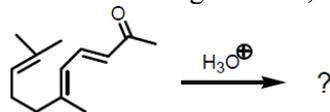
(A) 43. What is the **final** product of the following sequential reactions?



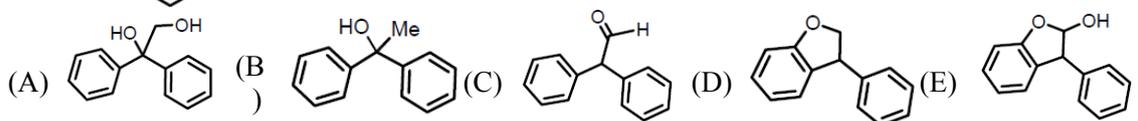
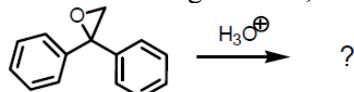
(A) 44. In the following reaction, which compound is the **major** product?



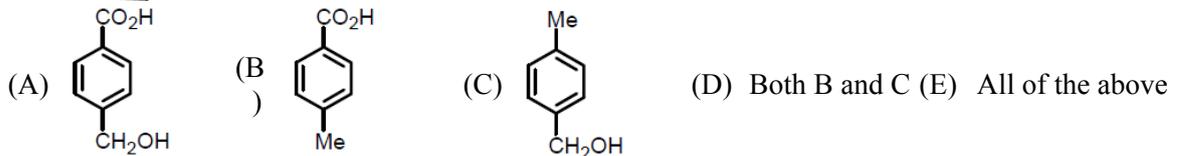
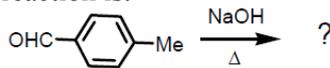
(A) 45. In the following reaction, what is the **major** product?



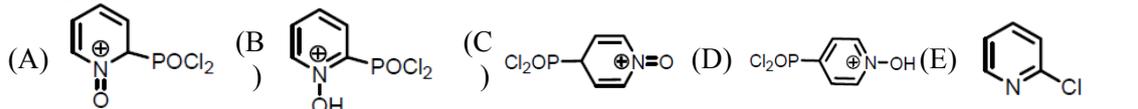
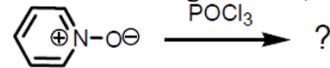
(C) 46. In the following reaction, which compound is the **major** product?



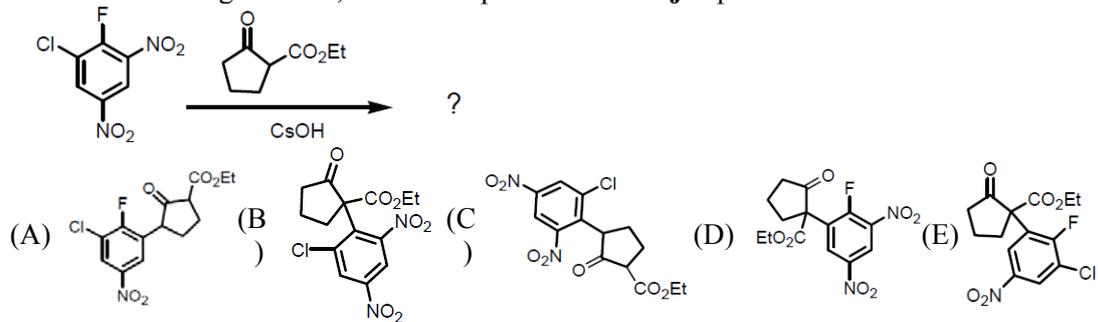
(D) 47. The following substance is heated in the presence of aqueous NaOH. The product of the reaction is:



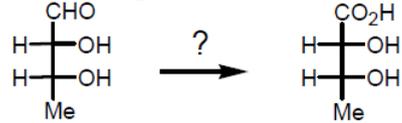
(E) 48. In the following reaction, which compound is the **major** product?



(B) 49. In the following reaction, which compound is the **major** product?

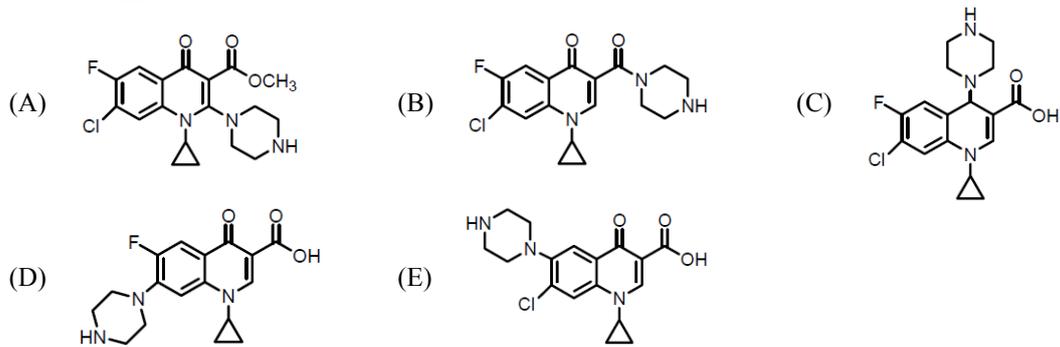
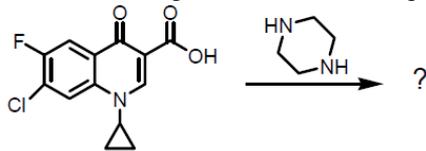


(B) 50. Which reagent would be **best** suited for the transformation shown?

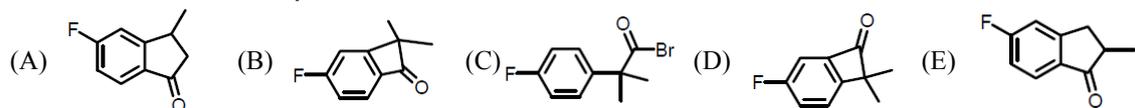
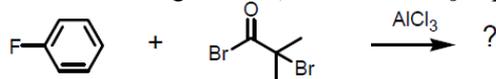


- (A) alkaline  $\text{Cu}^{2\oplus}$  in  $\text{H}_2\text{O}$     (B)  $\text{Ag}^{\oplus}$  in  $\text{H}_2\text{O}/\text{NH}_3$     (C)  $\text{H}_2$ , with Ni catalyst  
 (D)  $\text{NaNO}_3$  at  $0^\circ\text{C}$     (E)  $\text{NaBH}_4$  in  $\text{H}_2\text{O}$

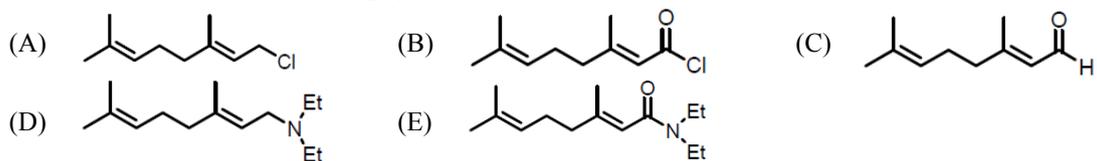
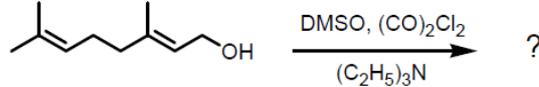
(D) 51. In the following reaction, which compound is the **major** product?



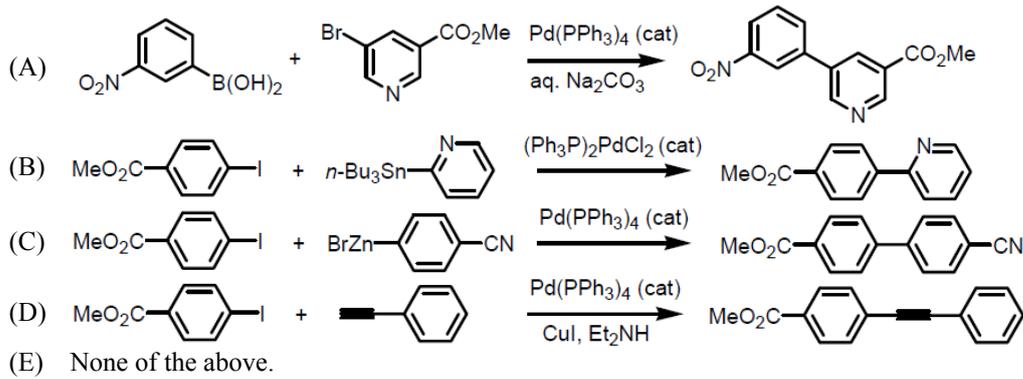
(E) 52. In the following reaction, what is the **major** product?



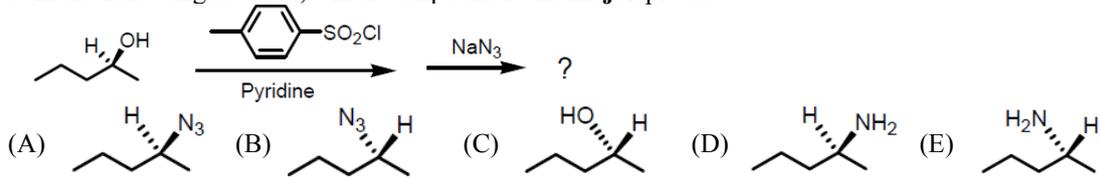
(C) 53. In the following reaction, which compound is the **major** product?



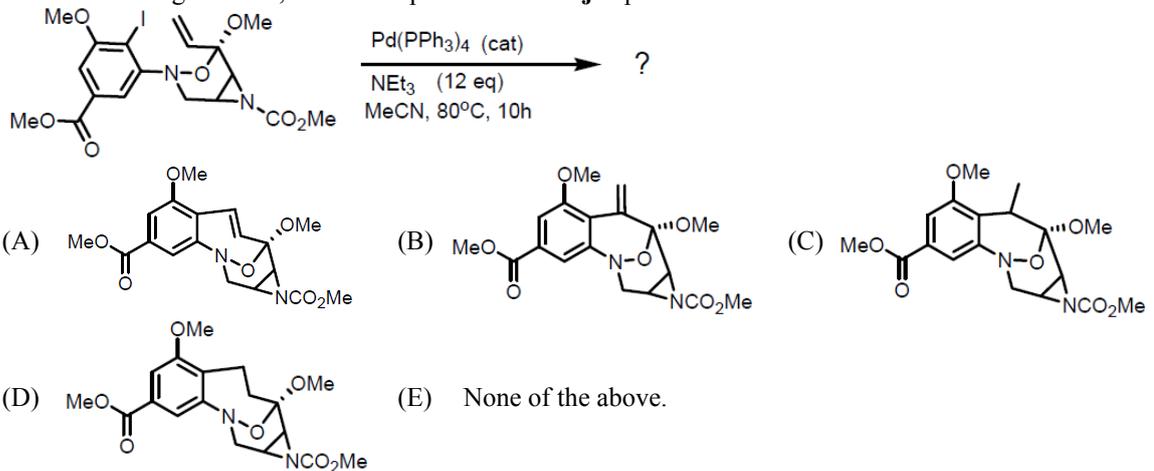
(A) 54. Which of the following reaction is called Suzuki-Miyaura coupling reaction?



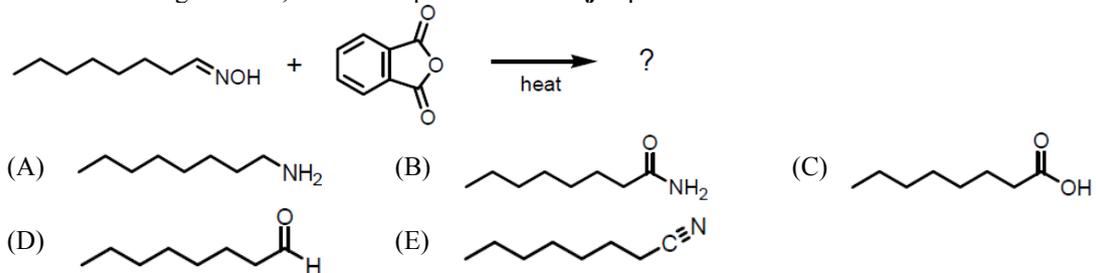
(B) 55. In the following reaction, which compound is the **major** product?



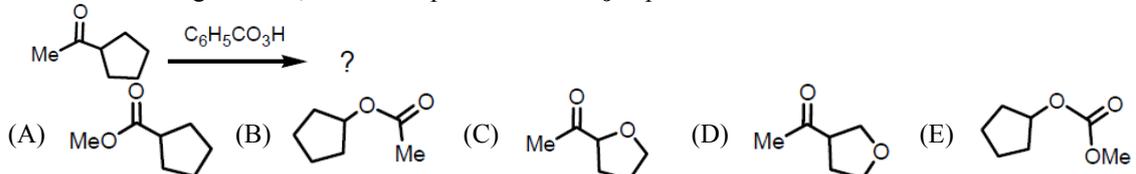
(B) 56. In the following reaction, which compound is the **major** product?



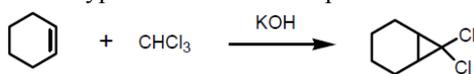
(E) 57. In the following reaction, which compound is the **major** product?



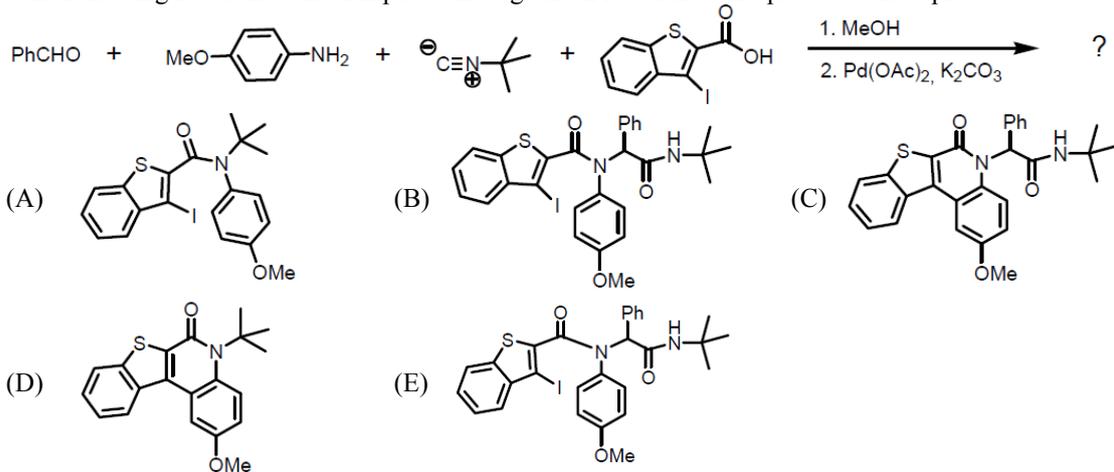
(B) 58. In the following reaction, which compound is the **major** product?



(D) 59. What type of intermediate is present in the following reaction?

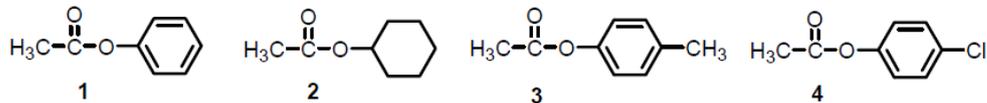


- (A) Carbocation (B) Carbanion (C) Free radical  
 (D) Carbene (E) This reaction has no intermediate.
- (C) 60. The following reaction is an example of the Ugi-Heck reaction. What product can be produced?

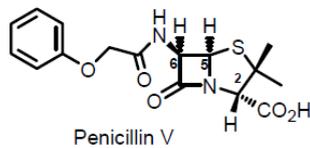


【單選題】每題 2 分，共計 40 分，答錯 1 題倒扣 0.5 分，倒扣至本大題零分為止，未作答，不給分亦不扣分。

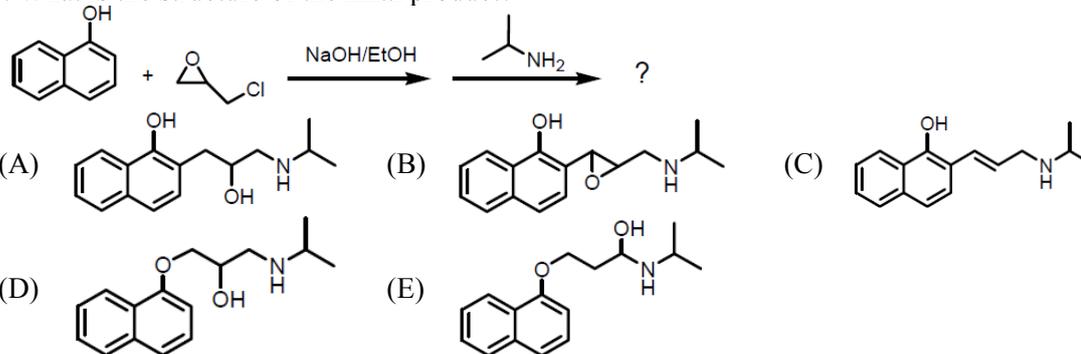
- (B) 61. List the following esters in order of **decreasing** reactivity in the first step of a nucleophilic acyl substitution reaction:



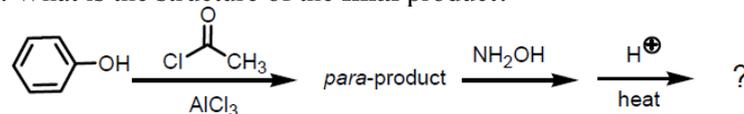
- (A) 2>3>1>4 (B) 4>1>3>2 (C) 2>4>1>3 (D) 3>1>4>2 (E) 4>2>1>3
- (D) 62. The chiral centers in the structure of penicillin V are indicated ( C-2, C-5, and C-6). In the following assignments which one is **wrong**?

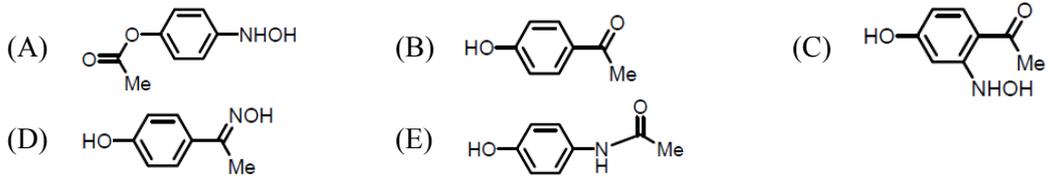


- (A) 2S (B) 5R (C) 6R (D) 6S (E) None of the above.
- (D) 63. What is the structure of the **final** product?

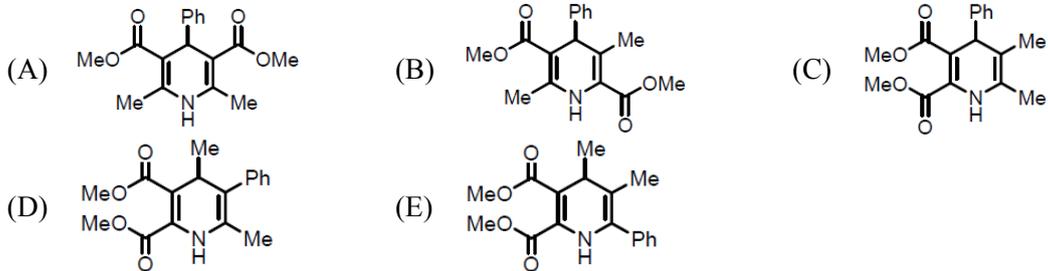
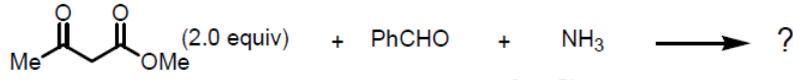


- (E) 64. What is the structure of the **final** product?

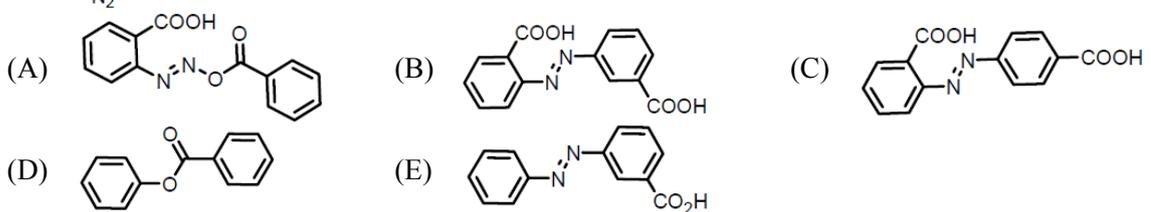
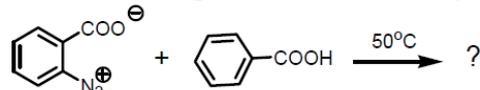




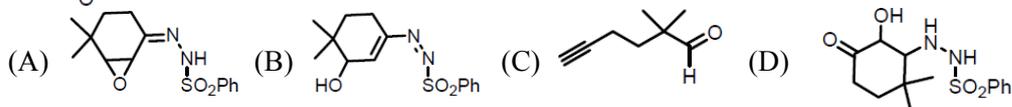
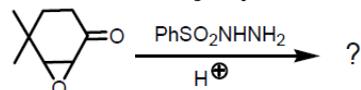
(A) 65. What is the **major** product of the following four components' reaction?



(D) 66. In the following reaction, which compound is the **major** product?

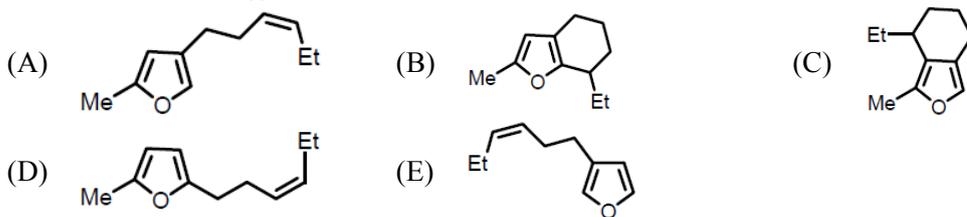
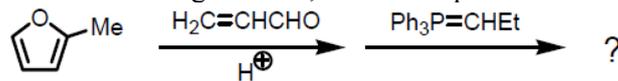


(C) 67. What is the **major** product of the following reaction?

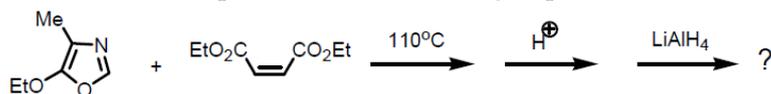


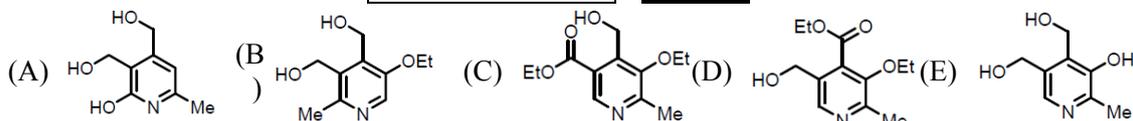
(E) None of the above.

(D) 68. In the following reaction, which compound is the **major** product?

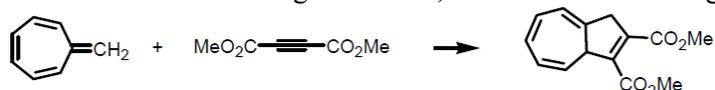


(E) 69. What is the **final** product of the following sequential reactions?



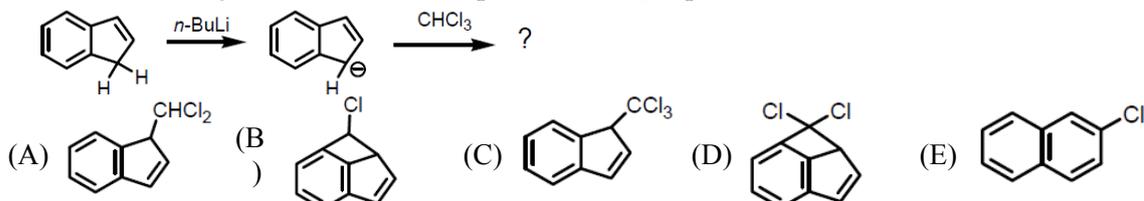


(C) 70. Consider the reaction given below, which of the following is **not** applicable to this reaction?

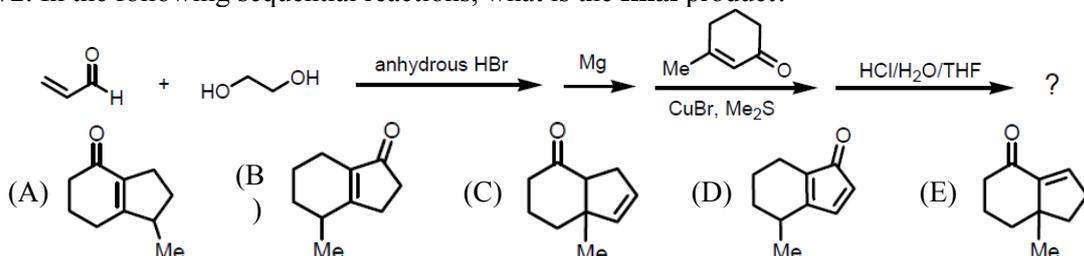


- (A) An example of cycloaddition reaction (B) Bond formation is suprafacial  
 (C) Bond formation is antarafacial (D) Prefer under thermal conditions  
 (E) All of these apply to this reaction.

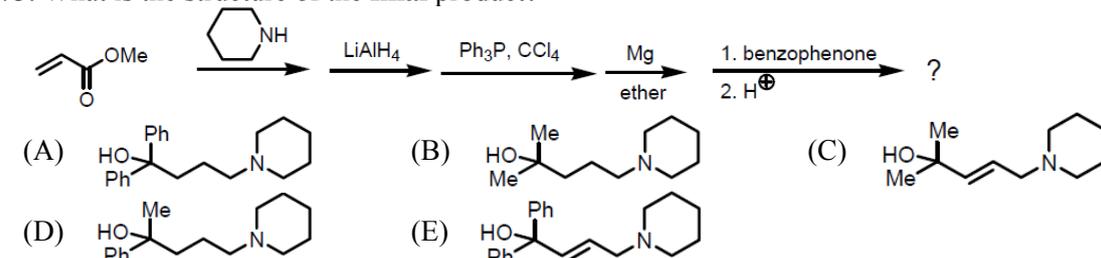
(E) 71. In the following reaction, which compound the **major** product?



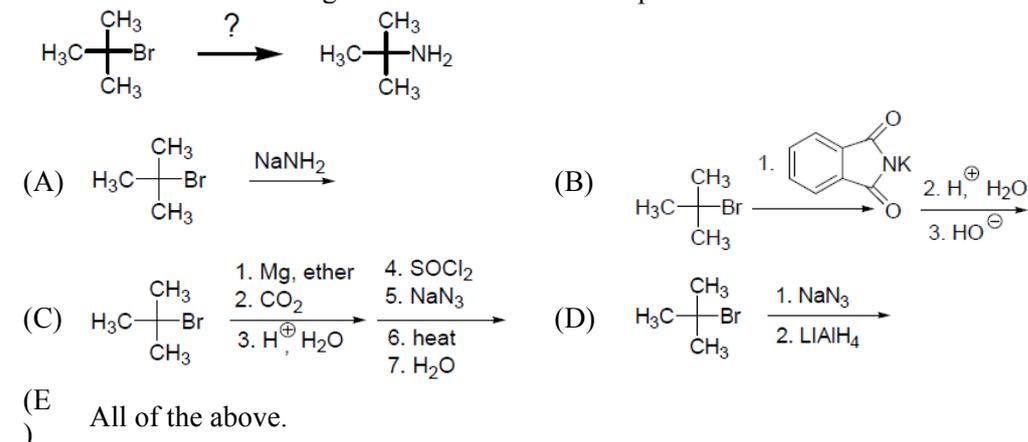
(E) 72. In the following sequential reactions, what is the **final** product?



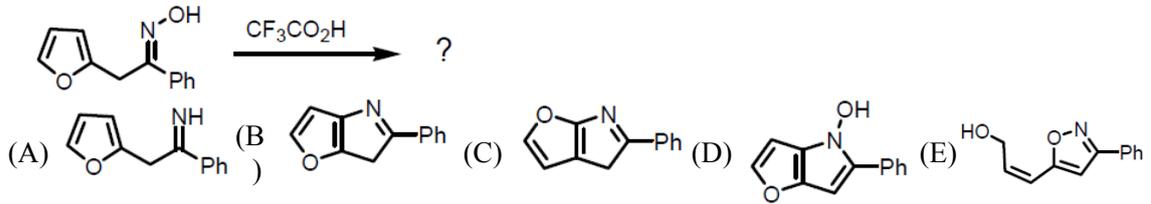
(A) 73. What is the structure of the **final** product?



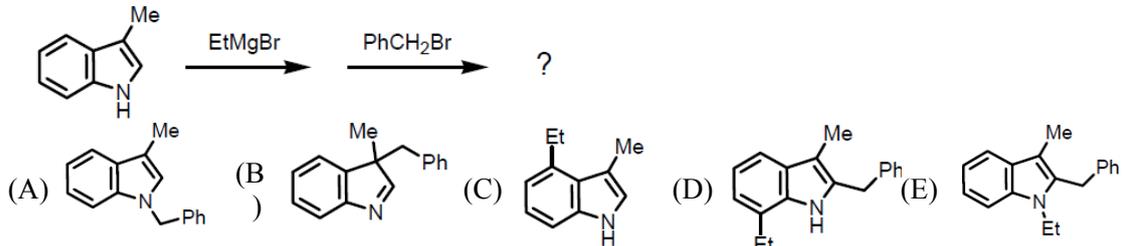
(C) 74. How could the following transformation be accomplished?



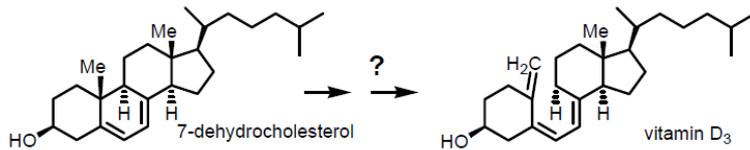
(E) 75. In the following reaction, which compound is the **major** product?



(B) 76. In the following reaction, which compound is the **major** product?

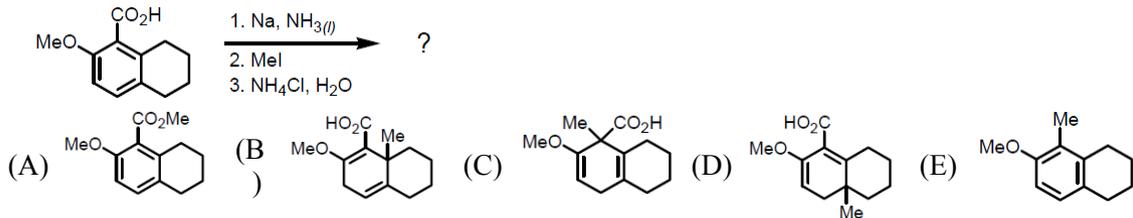


(A) 77. Photochemical reaction of 7-dehydrocholesterol to vitamin D<sub>3</sub> involves two types of pericyclic reactions. What are those?

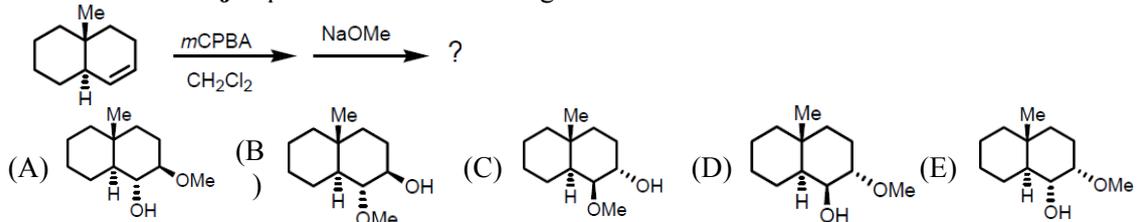


- (A) Electrocyclic reaction and sigmatropic rearrangement  
 (B) Electrocyclic reaction and ene reaction  
 (C) Cycloaddition and electrocyclic reactions  
 (D) Cycloaddition reaction and sigmatropic rearrangement  
 (E) Ene reaction and sigmatropic rearrangement.

(C) 78. What is the **final** product of the following reaction?



(C) 79. What is the **major** product of the following transformation?



(D) 80. What is the **final** product?

