Chemistry 2542
Fall 2012; Midterm 1 Exam

This exam has 6 problems on 8 pages. Make sure your copy is complete and correct.

Printed Name (Last, First) _____ *Key* _____

Scores:

Problem 1: _____ *15* _____

Problem 2: _____ *16* _____

Problem 3: _____ *26* _____

Problem 4: _____ *21* _____

Problem 5: _____ *10* _____

Problem 6: _____ *12* _____

Total: _____ *100* _____

3

1. (15 pts) Answer the questions on mechanisms of the following reactions.

(a) (5 pts) Which one of the following four schemes (**A-D**) gives the best representation of a step in the mechanism of the reaction in the box (circle the correct answer):
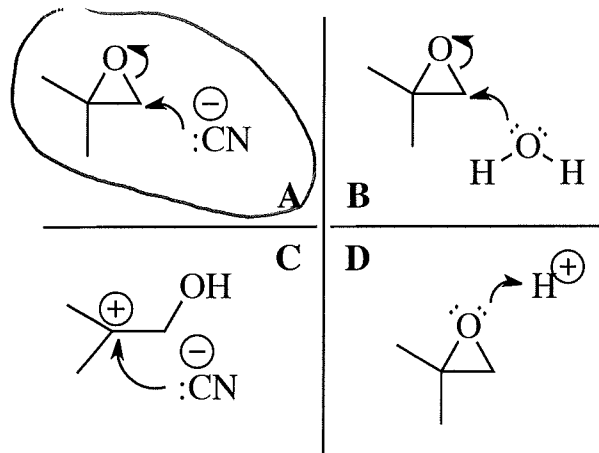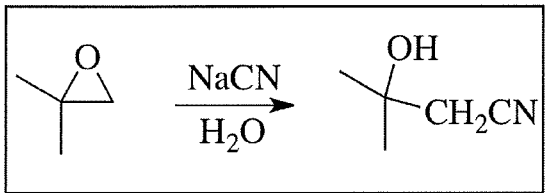
(b) (5 pts) Which one of the following four schemes (**A-D**) gives the best representation of a step in the mechanism of the reaction in the box (circle the correct answer):
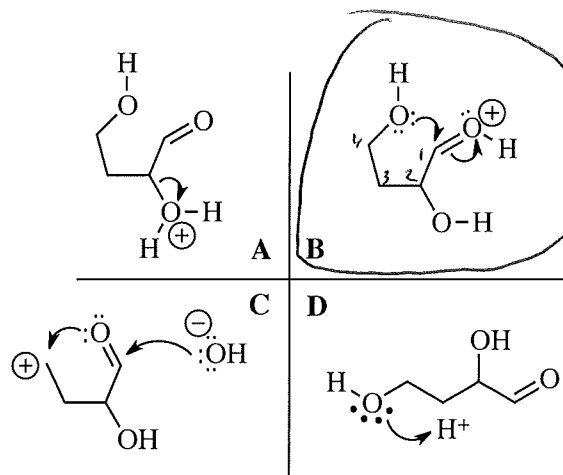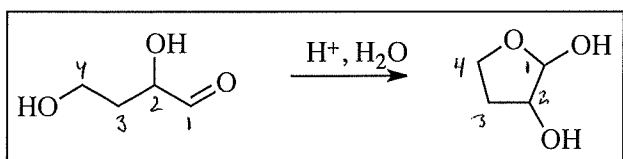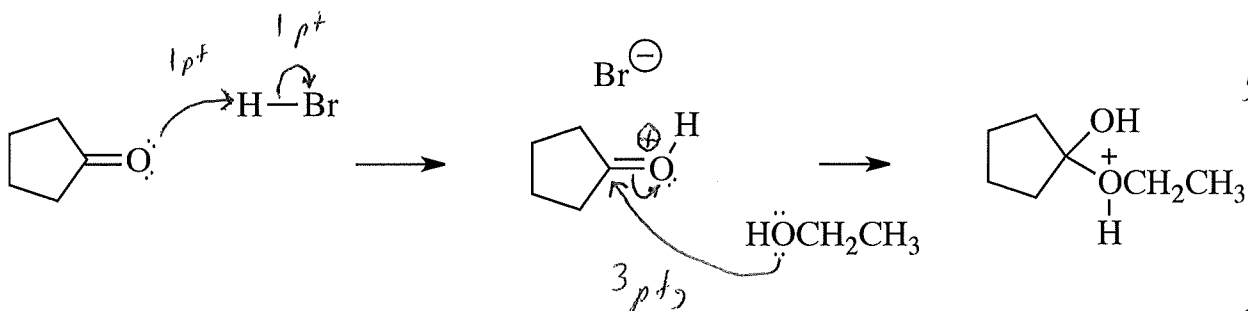

(c) (5 pts) Draw **4** curved **arrows** and show **1 charge** missing in the following mechanism (1 pt each arrow or charge):
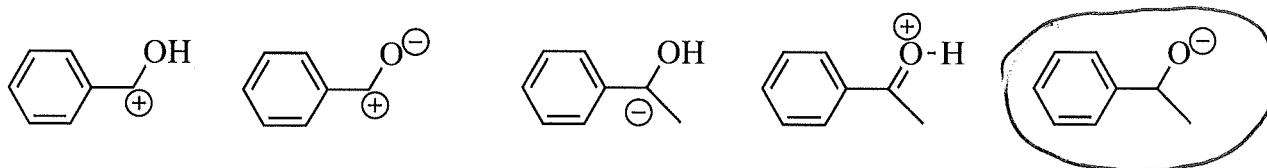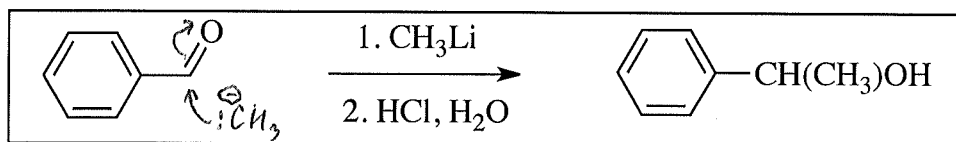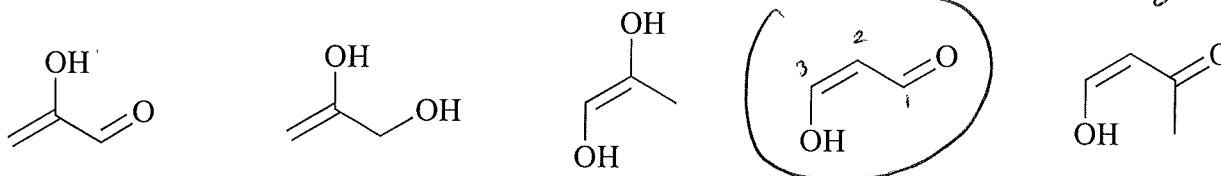
2. (16 pts) Answer the following questions.

**(a) (4 pts)** Circle the structure of the **intermediate** for the reaction in the box:

$$\text{PhCHO} + \text{CH}_3^{\ominus}\text{Li} \xrightarrow[\text{2. HCl, H}_2\text{O}]{\text{1. CH}_3\text{Li}} \text{Ph}-\text{CH(CH}_3)\text{OH}$$

(Structures of intermediates shown; the rightmost one, PhCH(O⁻)CH₃, is circled.)

(b) (4 pts) Which one of the following compounds is the **enol** form of **3-oxopropanal**?

(The fourth structure, (Z)-3-hydroxy-2-propenal with OH, is circled.)

(c) (8 pts) Circle the correct **IUPAC name** of the compounds in the boxes (2 pts each):
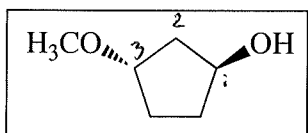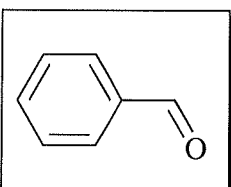
cis-3-methoxycyclopentanol   cis-1-hydroxy-3-methoxycyclopentane
(*trans*-3-methoxycyclopentanol) circled   trans-1-hydroxy-3-methoxycyclopentane
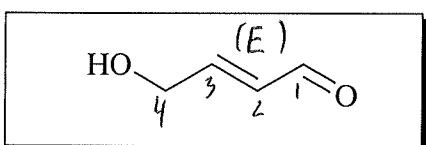
((E)-4-hydroxy-2-butenal) circled   (Z)-4-hydroxy-2-butenal
(E)-1-hydroxy-2-buten-4-al   (Z)-1-hydroxy-2-buten-4-al
(E)-4-oxo-2-butenol   (Z)-4-oxo-2-butenol
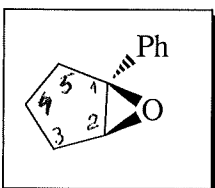
1-phenylcyclopentane epoxide   2-phenylcyclopenteneoxirane
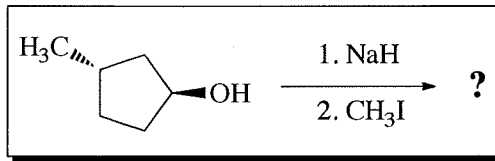(1-phenyl-1,2-epoxycyclopentane) circled   1-phenylcyclopentaneoxide

phenylcarbaldehyde   cyclohexenecarbaldehyde
(benzaldehyde) circled   benzophenone   benzenal

16 pts

3. (26 pts) Answer the following questions:

(a) Circle the name of a **major product** in each of the following reactions **(5 pts each)**:

H₃C,,, (cyclopentane) OH ⟶ 1. NaH / 2. CH₃I ⟶ **?**
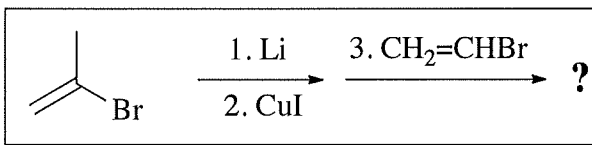
trans-1-methoxy-3-methylcyclopentane   3-methoxycyclopentene

trans-3-methoxycyclopentanol   *cis*-3-methoxycyclopentanol   5

3-methylcyclopentene   *cis*-1-methoxy-3-methylcyclopentane

(cyclohexenone) ⟶ 1. LiAlH₄, ether / 2. H₃O⁺ ⟶ **?**
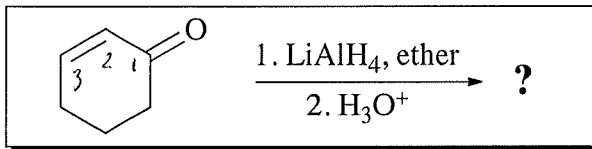
1-cyclohexenol   cyclohexanol   cyclohexanone

cyclohexene   2-cyclohexenol   cyclohexane   5

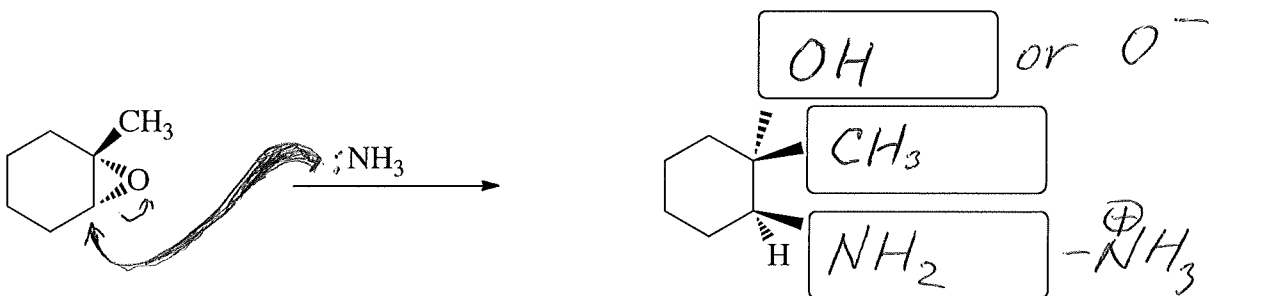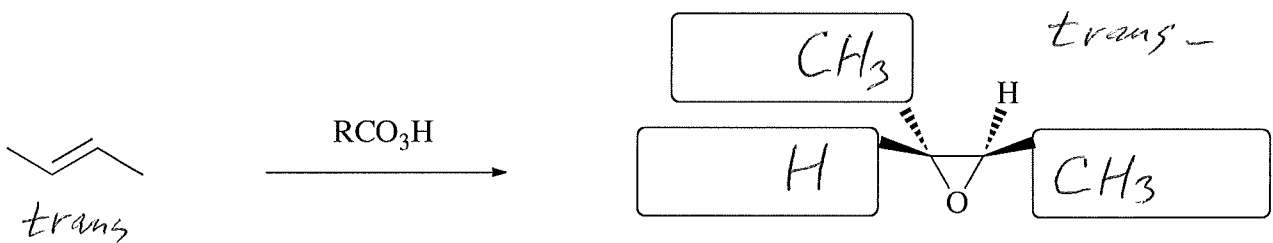(allyl bromide) Br ⟶ 1) Li / pentane   2) H₂CO   3) H⁺, H₂O ⟶ **?**
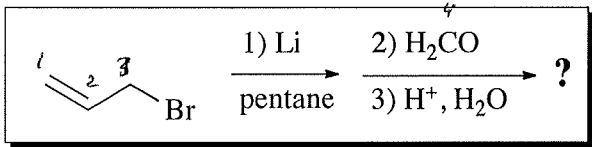
(Z)-2-buten-1-ol   (E)-2-buten-1-ol   3-buten-1-ol   5

2-propen-1-ol   (Z)-3-penten-1-ol   (E)-3-penten-1-ol

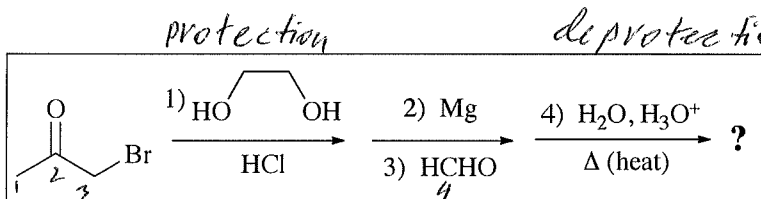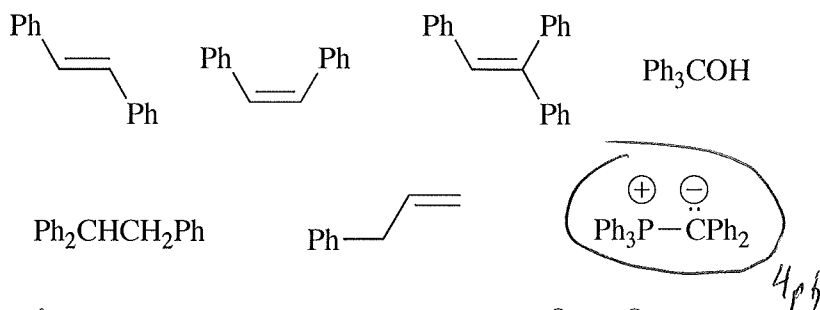(isopropenyl bromide) Br ⟶ 1. Li / 2. CuI   3. CH₂=CHBr ⟶ **?**
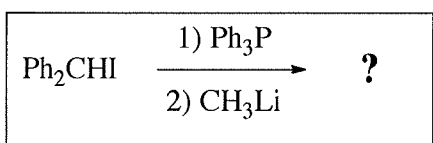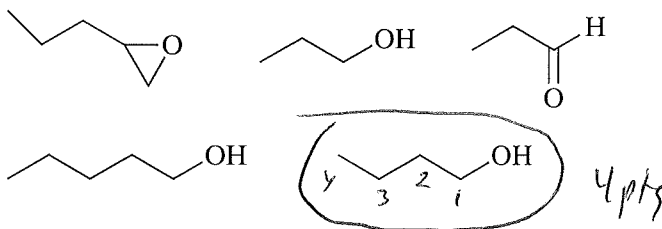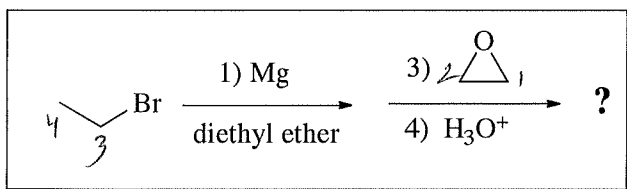
2-methyl-1,4-pentadiene   2-methyl-1,3-butadiene   5

2-methyl-1,5-hexadiene   2-methyl-1,4-hexadiene

(b) (6 pts) Finish drawing the main product for each the following reactions by placing appropriate substituents in the boxes; 1 pt each.

(trans-2-butene) ⟶ RCO₃H ⟶

$\boxed{CH_3}$ *trans*-

$\boxed{H}$ (epoxide) H / $\boxed{CH_3}$

(cyclohexene oxide with CH₃) ⟶ ; NH₃ ⟶

$\boxed{OH}$ or O^-

$\boxed{CH_3}$

H $\boxed{NH_2}$ $-NH_3^⊕$

26 pts

4. (21 pts) (a) Circle the structure of a **major product** in each of the following reactions (4 pts each):

Reaction 1 box: structures shown, with the 4-carbon chain diol circled. **4 pts**

Reaction 2: Ph₂CHI → 1) Ph₃P 2) CH₃Li → ? with Ph₃P–CPh₂ ylide circled. **4 pts**

Reaction 3 (protection/deprotection): product circled. **4 pts**

Reaction 4: Ag₂O, NH₃ / H₂O: HO-CH₂CH₂-CO₂H circled. **4 pts**
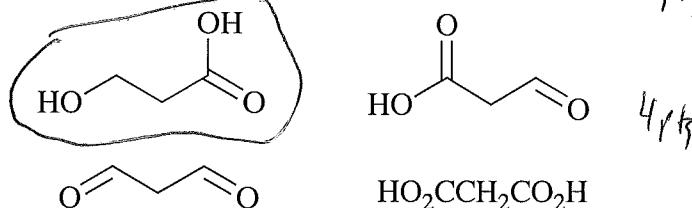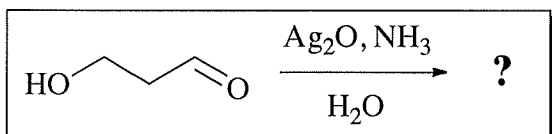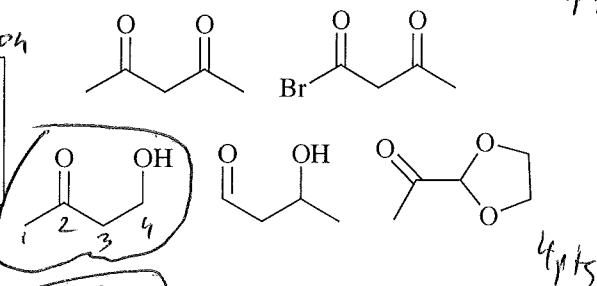
(b) (5 pts) Which pair of reactants is required to synthesize the compound in the box (circle the answer):
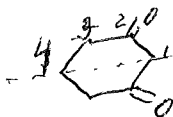
(A), (B) circled, (C), (D). **5 pts**
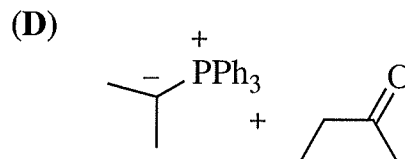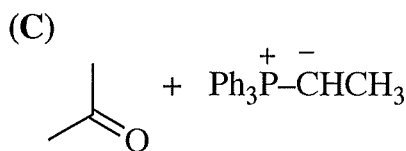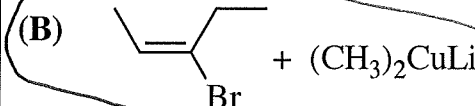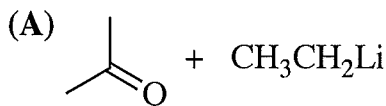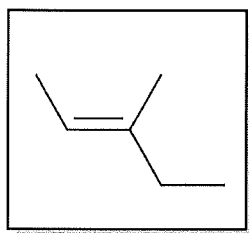
21 pts

5. (10 pts) Answer the following spectroscopy questions:

(a) (4 pts) Circle the structure of the compound which has a broad, strong IR absorption at 3200-3500 cm^{-1} and the following ^{1}H NMR spectrum:
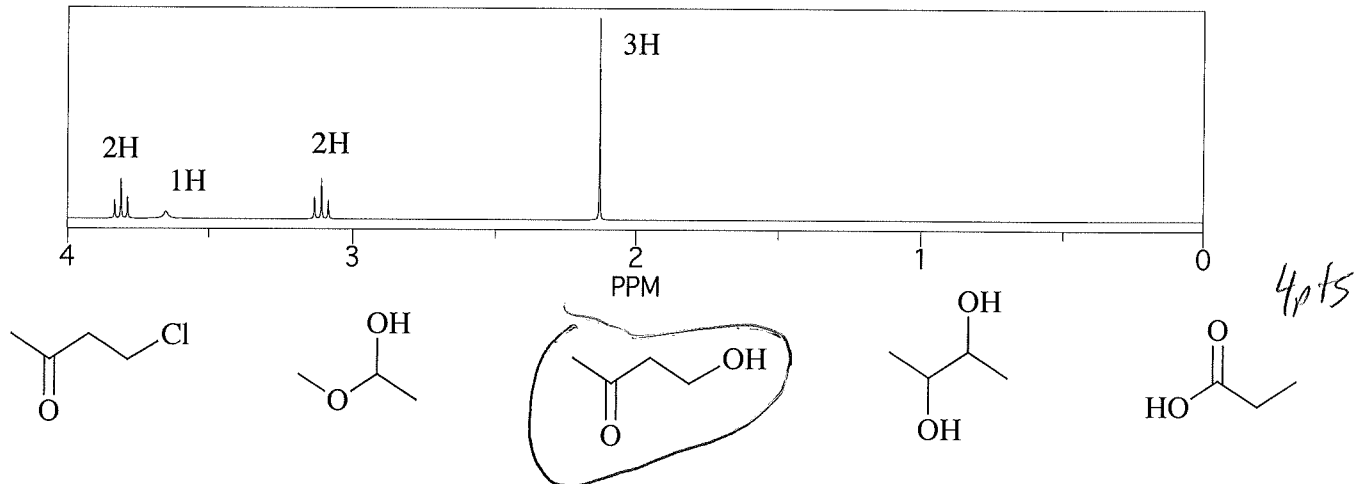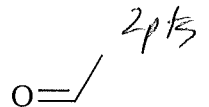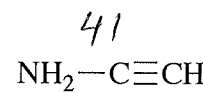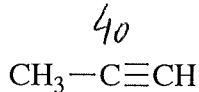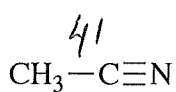

(b) (2 pts) How many signals would you expect to observe in the ^{13}C NMR spectra of the molecule of **1,3-cyclohexanedione** (put the number in the box):


4

2 pts

(c) (2 pts) Which of the following compounds will have the *characteristic* **IR** peak at about 2150 cm^{-1} **and** the molecular peak M$^+$ = 44 in the mass spectrum (atomic weight of C is 12, N 14, F 19, H 1)?
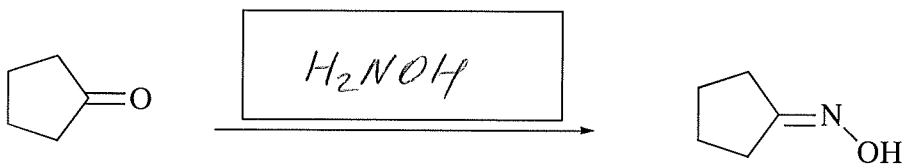
41   40   44
$CH_3-C\equiv N$ $CH_3-C\equiv CH$ $F-C\equiv CH$ ▷ $NH_2-C\equiv CH$ O=⟨
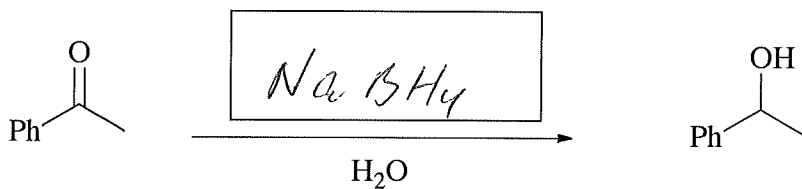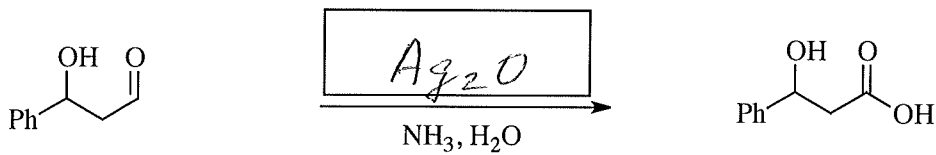
41   2 pts

(d) (2 pts) Which of the following compounds will have the most de**shielded** carbon atom? (Circle one structure)

CH_3Cl (structure with OH, O) CH_3Br CH_3I C_2H_6 (structure with two C=O)
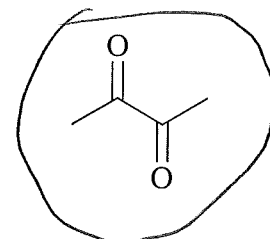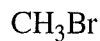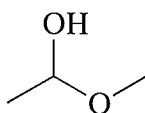
2 pts

10 pts

6. (12 pts) Place in each box the molecule of a reagent that is required to perform each of the following reactions (2 pts each box):

or $CH_3 Mg Br$ or HCl, or $H^{\oplus}$

| $CH_3 Li$ | H_3O^+ |

ether

or $Ph_3P^{\oplus} - \overset{\ominus}{C}(CH_3)_2$

| Ag_2O |

NH_3, H_2O

| $Na BH_4$ |

H_2O

| H_2NOH |

$12 pts$