

1. _____

4. _____

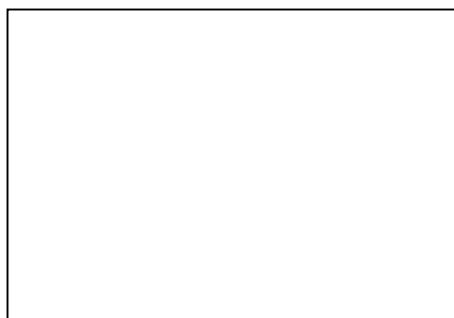
2. _____

5. _____

3. _____

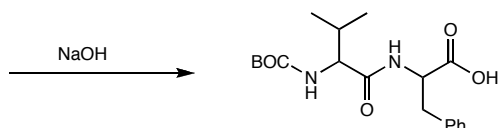
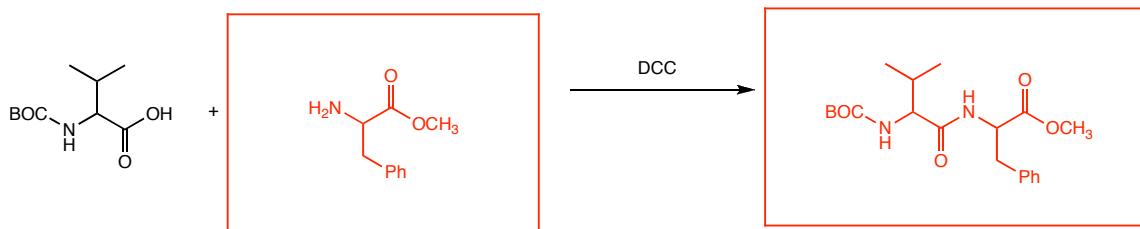
6. _____

7. _____

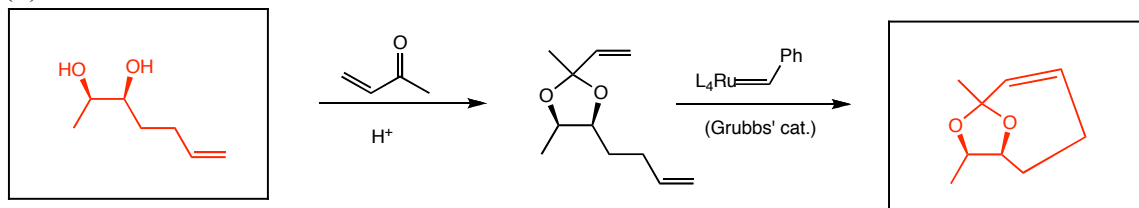


1. Assume a single equivalent of reagent and that all reactions are quenched. (40 pts)

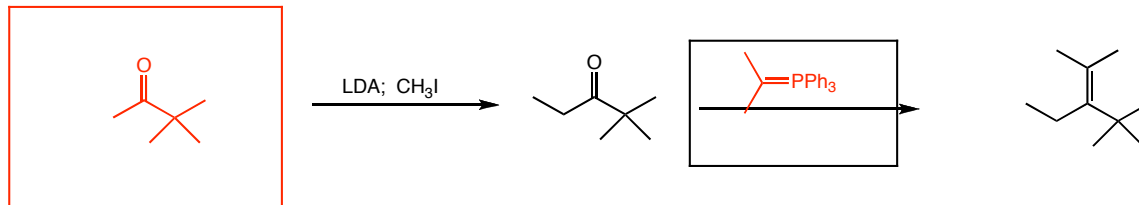
(a)



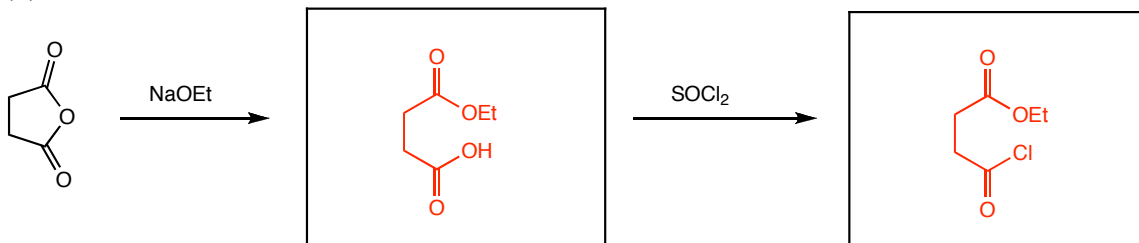
(b)



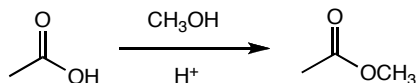
(c)



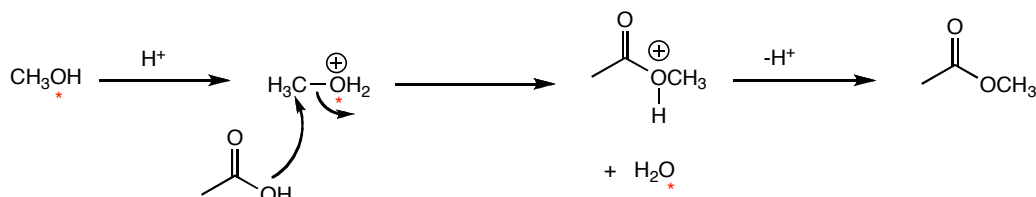
(d)



2. A generic Fischer esterification is shown below.

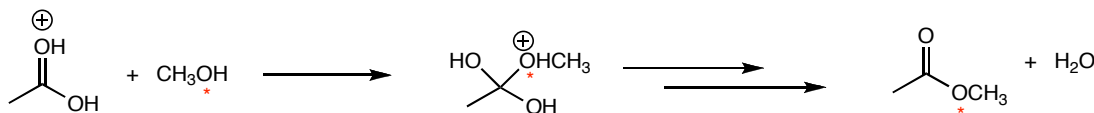


The currently accepted mechanism is the one you learned from this exam. However, an alternative mechanism was originally proposed:

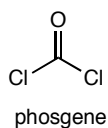


The two mechanisms can be distinguished by using methanol that is isotopically labelled with ^{18}O . How? (8 pts)

In the mechanism shown above, an isotopic label on methanol would appear in the final product as water (see stars above). In the currently accepted mechanism, the label would appear in the methoxy group of the product (see below).

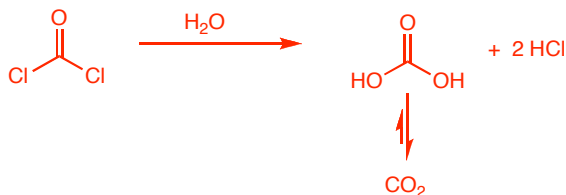


3. Phosgene was used as a chemical weapon in World War I, but it is also very useful for the preparation of many different organic compounds.

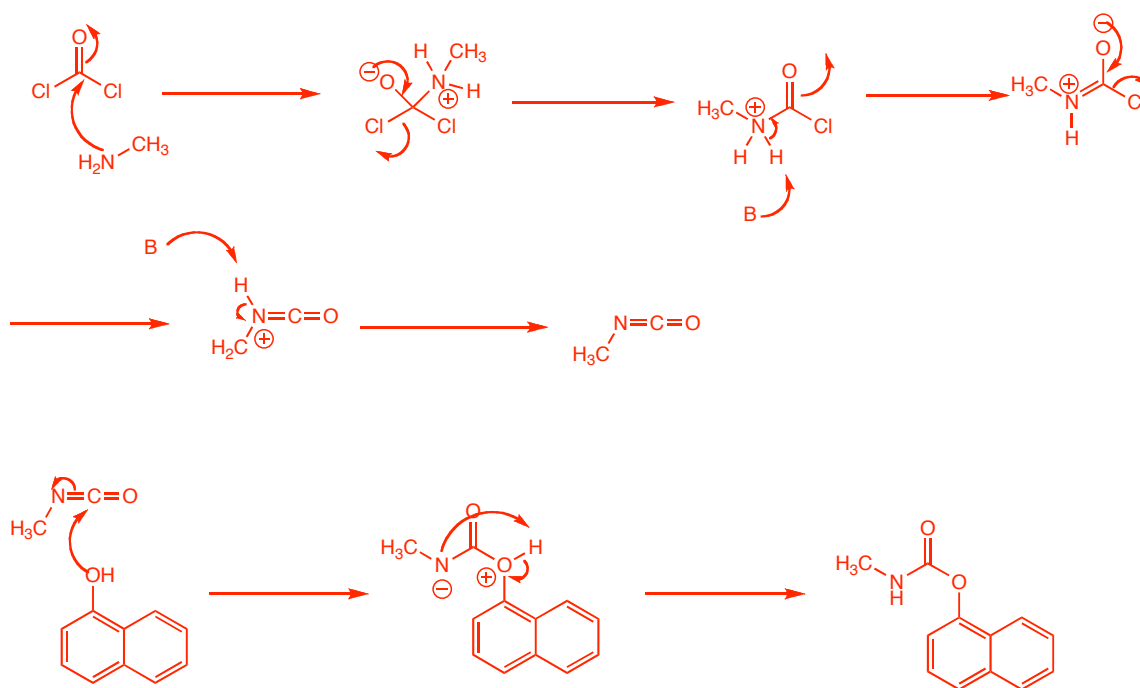
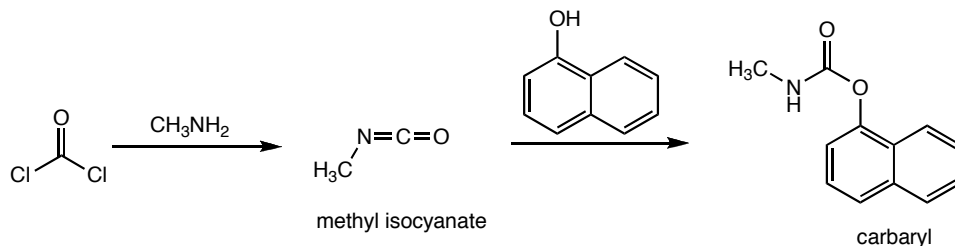


(a) Explain why inhaling phosgene significantly increases the acidity of the lungs. Keep in mind that lungs are very damp places. (6 pts)

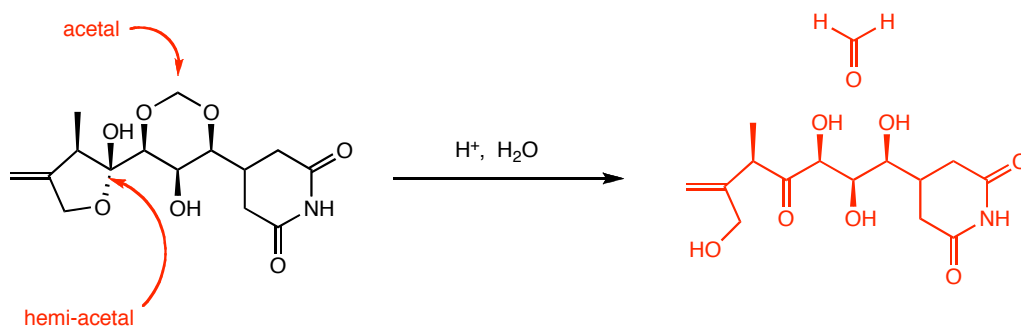
Phosgene reacts with water as follows. For every molecule of phosgene, two molecules of HCl are formed (carbonic acid is also formed, but the acidity is mostly due to HCl, since the preferred form of carbonic acid is carbon dioxide).



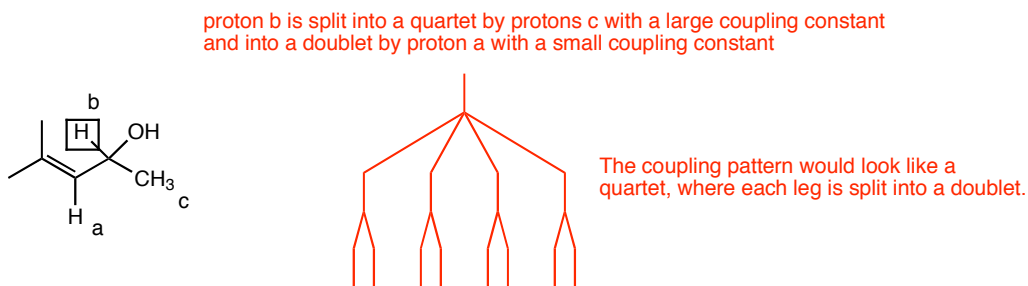
(b) In 1984, a Union Carbide pesticide plant in Bhopal, India accidentally released 40 tons of methyl isocyanate which killed at least 3,000 people. Methyl isocyanate is prepared from phosgene and converted into pesticides such as carbaryl. Propose a mechanism for the formation of methylisocyanate and for the formation of carbaryl. (12 pts)



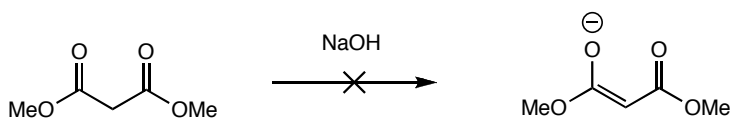
4. Draw all products formed from hydrolysis of the natural product sesbanimide A. (6 pts)



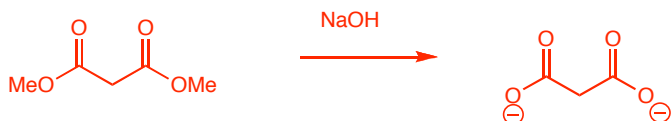
5. Sketch the coupling pattern you would expect for the boxed proton below (labelled b) with the following stipulations: $J_{ab} < J_{bc}$. (8 pts)



6. Sodium hydroxide is not typically used to form the enolate of dimethyl malonate, even though it is a strong enough base to completely deprotonate. Why not? Which base could you use instead that would alleviate the problem? (8 pts)

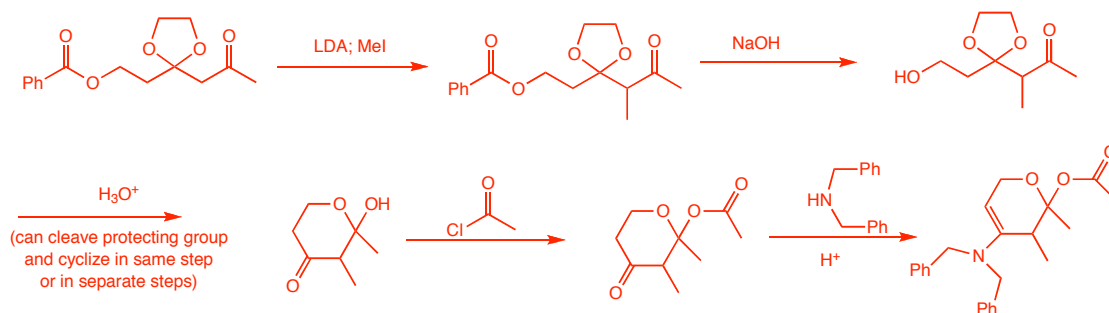
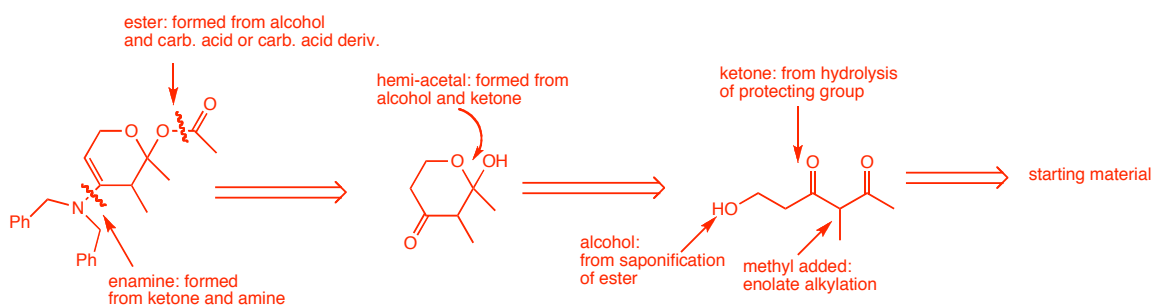
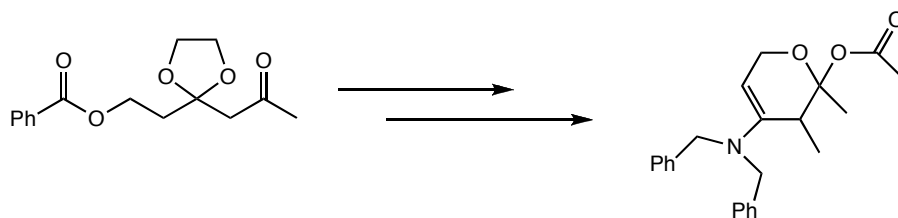


NaOH would saponify the esters to give the di-acid :



Two problems: (1) In the presence of NaOH, the di-acid is actually the dianion, making the α -protons much less acidic and (2) It destroys the starting ester. Instead, match the base to the ester, and use NaOMe or use a much stronger, non-nucleophilic base such as NaH or LDA.

7. Propose a synthesis of the target molecule from the starting material provided. You may use any organic or inorganic reagent necessary. (12 pts)



The following are actual acronyms for reagents or experiments. What do you think they stand for?

DEAD (a reagent):

HOHAHA (an NMR experiment):