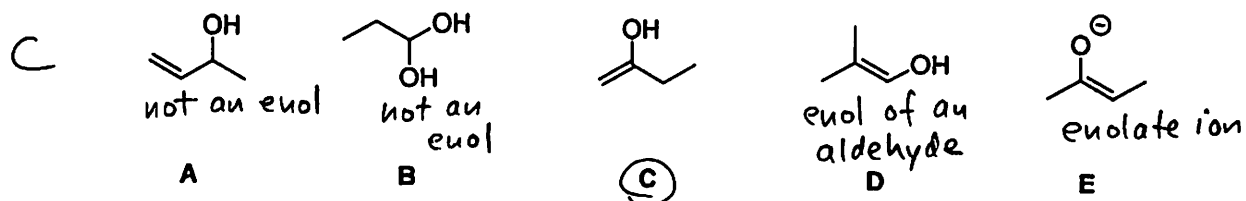
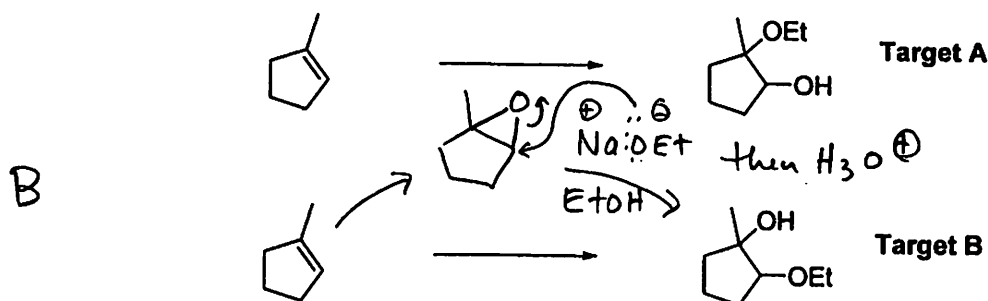




1. Select the structure that is the enol of a ketone.



2. Here are two multi-step syntheses:



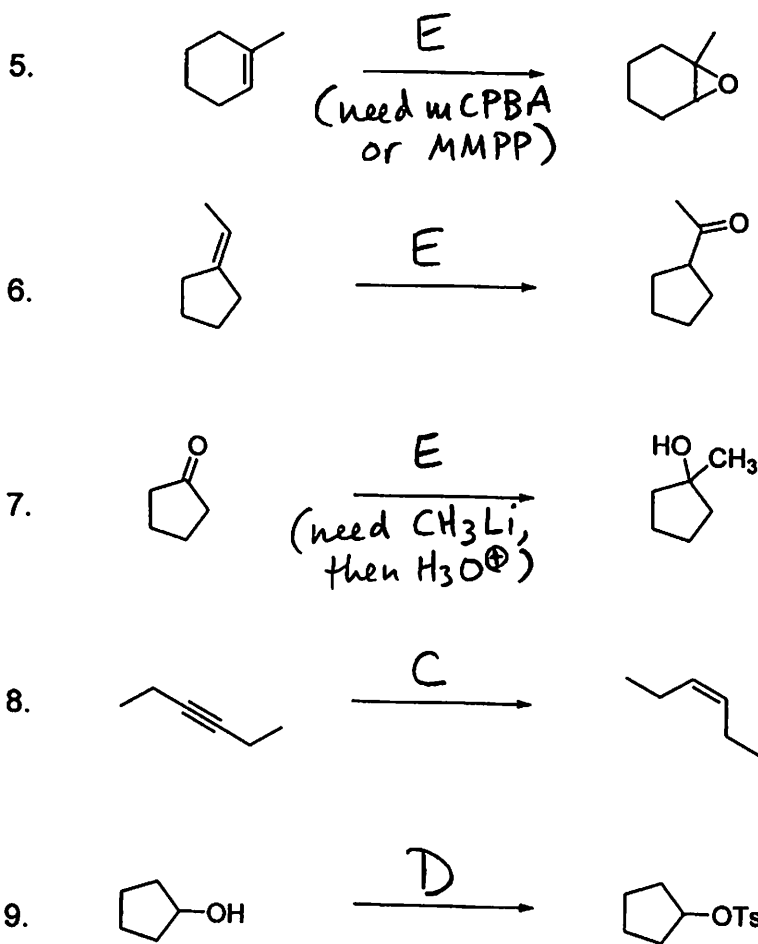
In which of these synthetic pathways would you use sodium ethoxide?

- a. Synthesis of Target A  
 b. Synthesis of Target B  
 c. Both syntheses  
 d. Neither synthesis
3. Which statement best describes one of the chemical (mechanistic) roles of  $\text{NH}_3$  in the dissolving metal reduction of an alkyne?
- A
- a. It donates a proton to a radical anion  
 b. It donates an electron to a sodium cation  
 c. It donates a pair of electrons to the alkyne  
 d. It is a nucleophilic source of hydride ion,  $\text{H}^-$ , which reduces the alkyne
- 

4. The keto and enol forms of a carbonyl compound are related as tautomers. Tautomers are
- B
- a. Stereoisomers  
 b. Constitutional isomers  
 c. Different conformations of the same molecule  
 d. None of the above

For questions 5 through 9, use the following list to identify the reagent(s) that you would use to accomplish each transformation in one synthetic operation (includes workup). Choices may be used more than once, or not at all. (Assume that the appropriate workup follows each of the choices "a" through "d".)

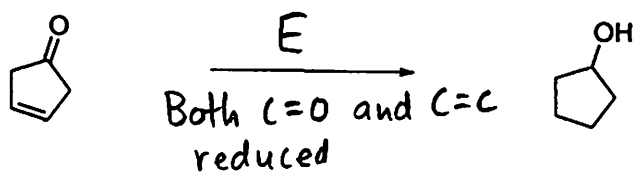
- a. PCC
- b.  $\text{CH}_3\text{I}$  (methyl iodide)
- c.  $\text{H}_2$ /Lindlar catalyst
- d.  $\text{TsCl/pyr}$
- e. Can't be accomplished in one operation using any of these choices



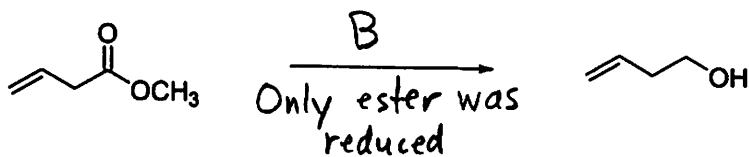
For questions 10 through 14, select the best reagent from the list. Assume appropriate aqueous workup after all reactions. Choices may be used more than once, or not at all.

- a. Only  $\text{NaBH}_4$  would work
- b. Only LAH would work
- c. Either  $\text{NaBH}_4$  or LAH would work
- d.  $\text{H}_2/\text{Pd}$
- e.  $\text{H}_2/\text{Raney Ni}$

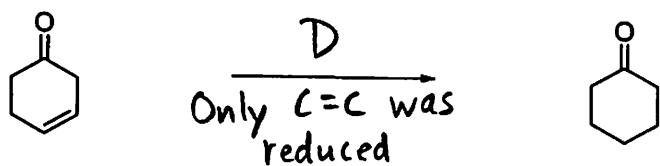
10.



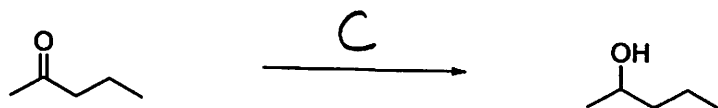
11.



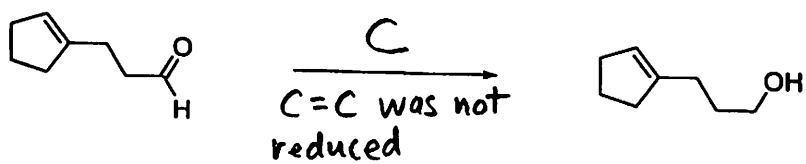
12.



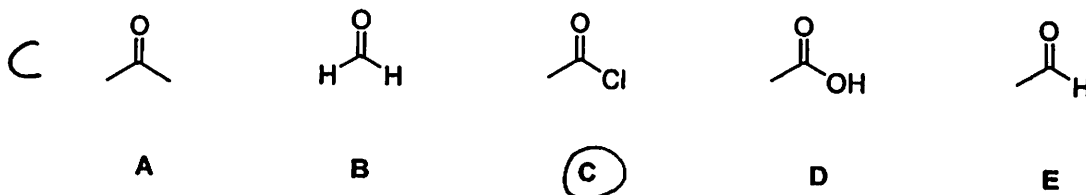
13.



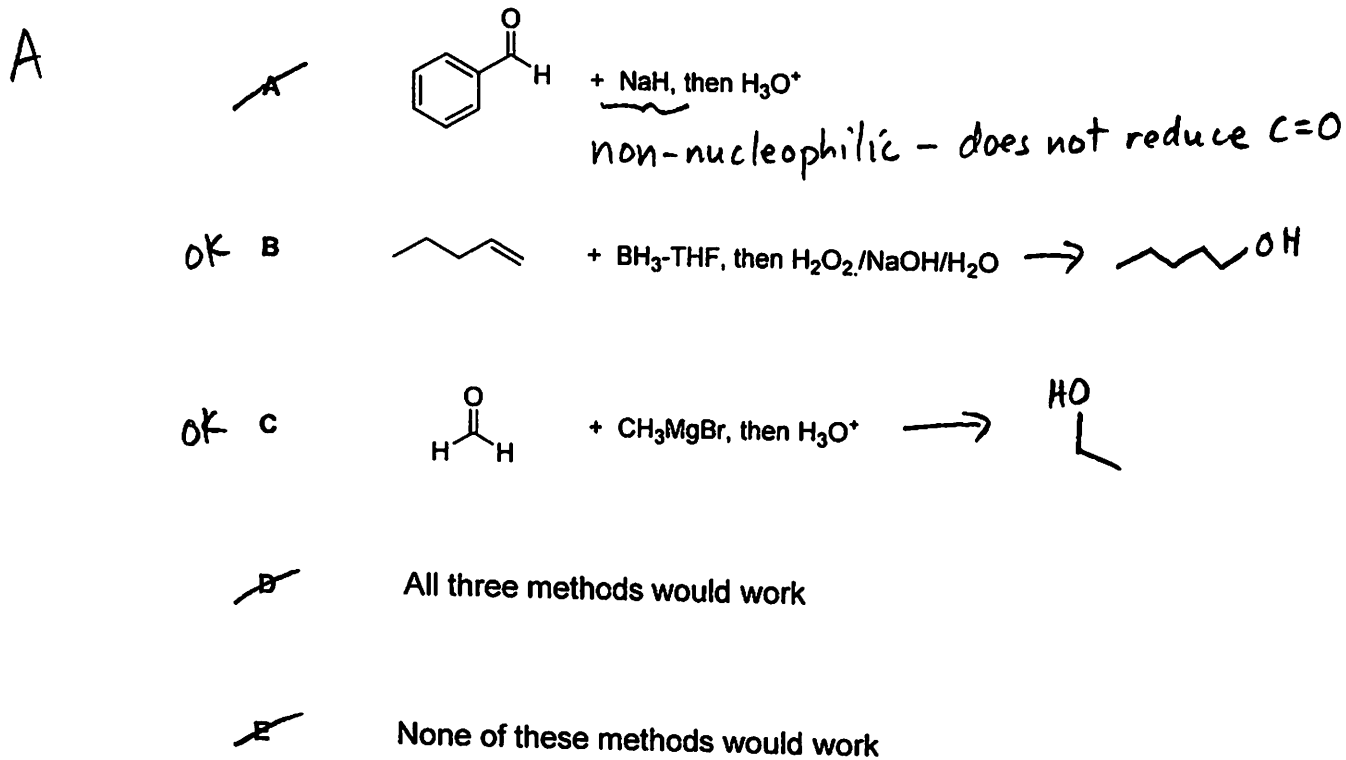
14.



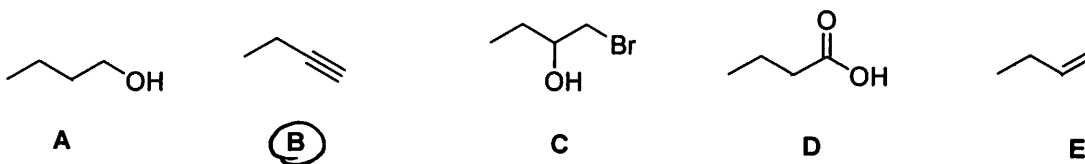
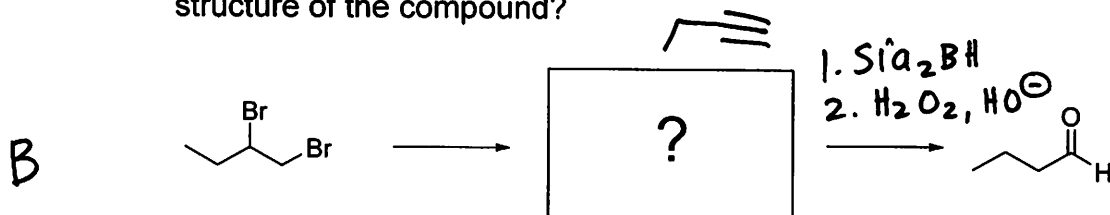
15. Which of the following requires 2 equivalents of a Grignard reagent (followed by aqueous acid) to produce a tertiary alcohol?



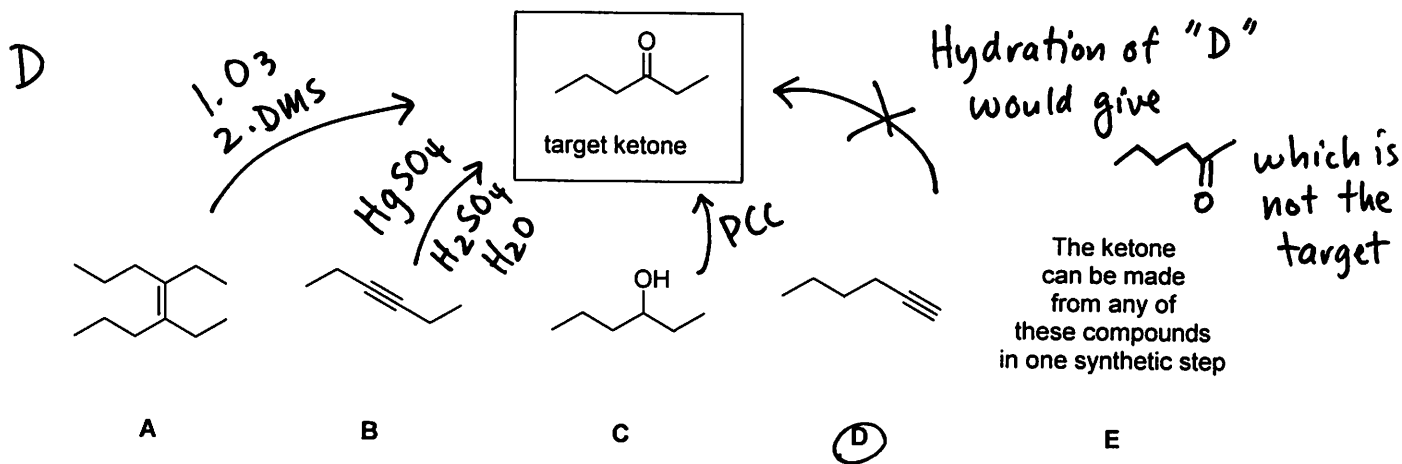
16. You need to make a primary alcohol. Which of the following methods would not work?



17. A certain compound can be synthesized from the vicinal dibromide shown in one synthetic operation. This same compound can then be used to synthesize the aldehyde at the right in one synthetic operation. What is the structure of the compound?

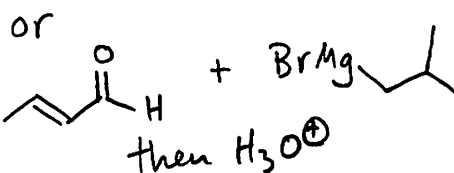
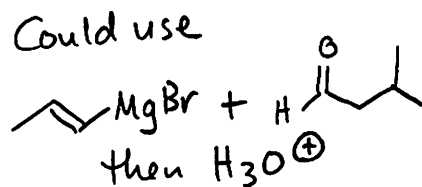
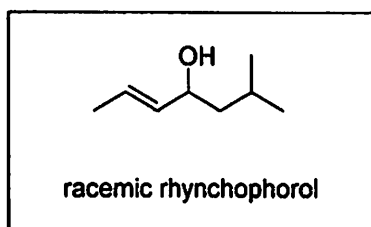


18. From which of these compounds can the target ketone NOT be made in one synthetic operation (including workup)?

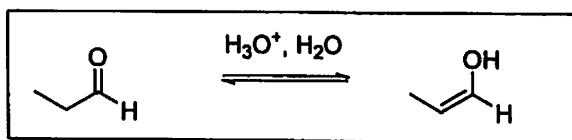


19. A molecule called rhynchophorol is a aggregation pheromone of the American palm weevil. Aggregation pheromones are involved in assembling groups of insects in one location. The organizers of the popular weevil music festival "Burning Weevil" are interested in attracting throngs of concertgoers by synthesizing rhynchophorol. They will use a reaction between a Grignard or organolithium reagent and a carbonyl compound. What type of carbonyl compound will they use?

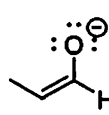
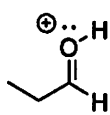
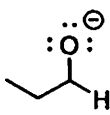
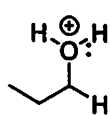
B



- a. Formaldehyde,  $\text{CH}_2\text{O}$   
**b.** An aldehyde other than formaldehyde  
 c. A ketone  
 d. An acid chloride  
 e. An ester
20. Select the structure that is a mechanistic intermediate in the tautomerization of this aldehyde in aqueous acid.



C



None of these structures are mechanistic intermediates

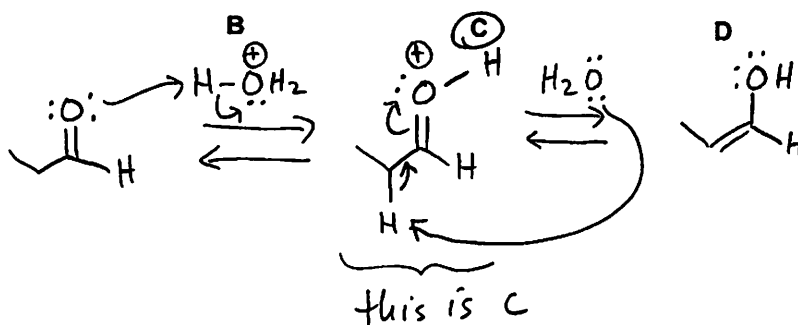
A

B

C

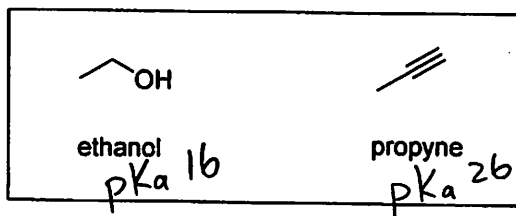
D

E

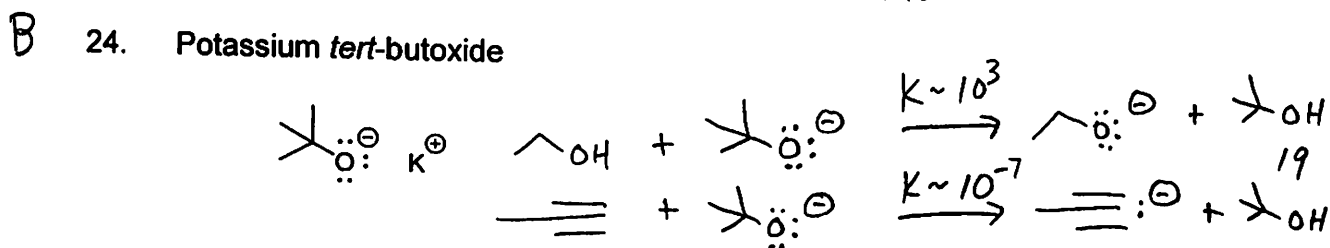
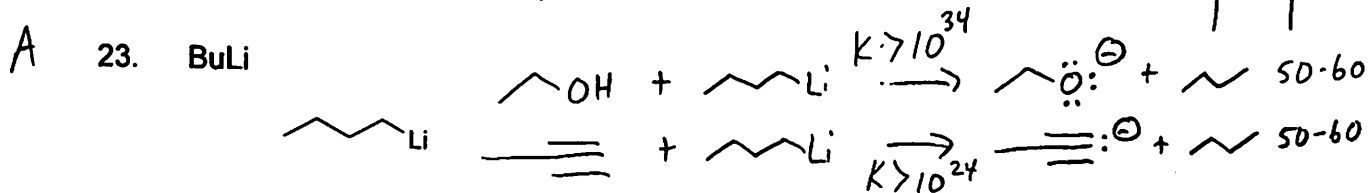
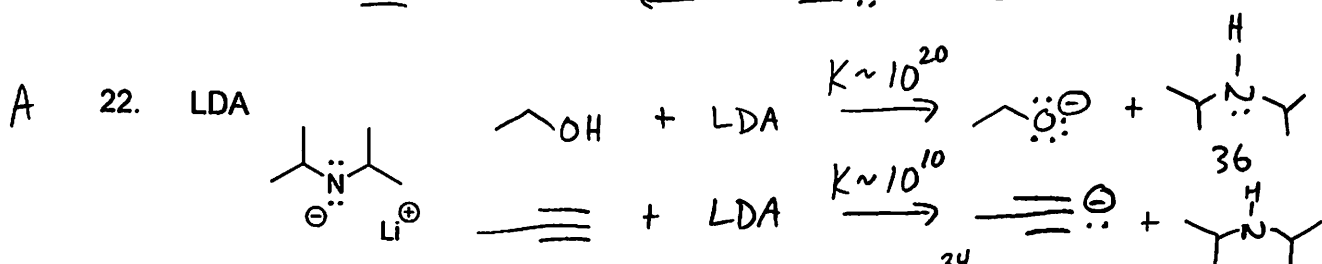
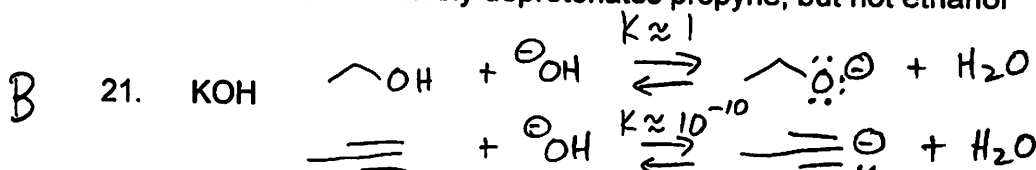


For questions 21, 22, 23, and 24: "Quantitative deprotonation" means that essentially 100% of your starting material (the acid) is deprotonated by a base. Assume that an acid will be quantitatively deprotonated if the equilibrium constant for the reaction,  $K$ , is  $10^5$  or greater.

Consider the following pair of compounds and select the appropriate statement from this list for each base in questions 21-24. Some of the base structures are shown.



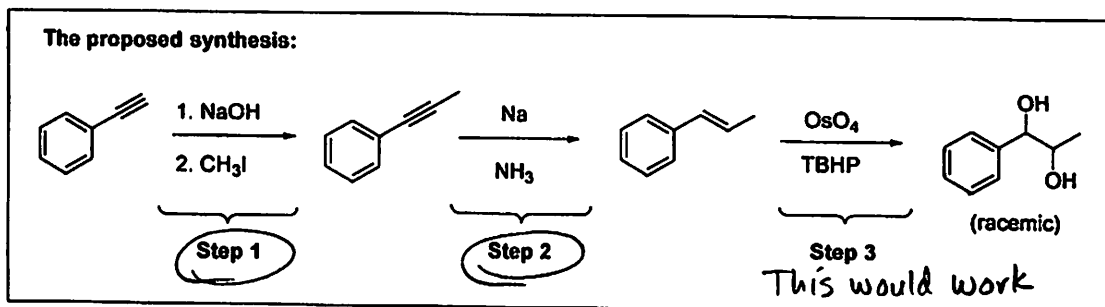
- Quantitatively deprotonates ethanol AND propyne
- Quantitatively deprotonates neither ethanol nor propyne
- Quantitatively deprotonates ethanol, but not propyne
- Quantitatively deprotonates propyne, but not ethanol





25. In April, a judge in Argentina issued an arrest warrant for Justin Bieber based on his alleged involvement in an altercation in a Buenos Aires nightclub in 2013. The arrest warrant also states that Bieber is to be charged with designing a multistep synthesis that has at least one incorrect step. This type of chemical negligence is taken quite seriously in Argentina and is punishable with life imprisonment in solitary confinement.

The multistep synthesis proposed by Bieber is the following:



According to the judge, Bieber "designed a synthesis that has at least one step that would not work, or that would give other undesired products". To which step(s) is the judge referring?

- a. Step 1
- b. Step 2
- c. Step 3
- d. Steps 1 and 2
- e. Steps 1, 2 and 3

Step 1: NaOH is not a strong enough base to deprotonate the terminal alkyne.

Step 2: Na, NH<sub>3</sub>, dissolving metal reduction conditions, will also cause benzene to react.