

Please read and sign the Honor Code statement below:

I pledge that on my honor, as a University of Colorado at Boulder student, I have neither given nor received unauthorized assistance on this exam.

Signature

General Instructions: There are 25 questions. Be sure you have them all. Read each question carefully so that you know exactly what is being asked.

Each multiple choice question (1-25) is worth **4 points** and has **only one correct answer**. Bubble in your answers to these questions on the Scantron provided. **Only the Scantron will be graded, not anything that you write on the exam.**

At the end of the exam, turn in your Scantron and this signed cover sheet. You may keep the rest of the exam to check your answers against the key later. Grades will be uploaded to D2L.

Good luck!

1A 2A 3A 4A 5A 6A 7A 8A

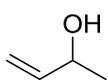
hydrogen 1 H 1.0079																	helium 2 He 4.0026				
lithium 3 Li 6.941	beryllium 4 Be 9.0122															boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305															aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80				
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	paladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29				
caesium 55 Cs 132.91	barium 56 Ba 137.33	lanthanum 57-70 * Lu 174.97	hafnium 71 Hf 178.49	tantalum 72 Ta 180.95	tungsten 73 W 183.84	rhenium 74 Re 186.21	osmium 75 Os 190.23	iridium 76 Ir 192.22	platinum 77 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]				
francium 87 Fr [223]	radium 88 Ra [226]	89-102 * * La [227]	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [257]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]	unnilium 110 Uu [271]	ununium 111 Uu [272]	ununilium 112 Uu [277]	ununquadium 114 Uu [285]	

* Lanthanide series

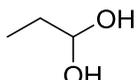
lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [257]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

** Actinide series

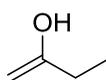
1. Select the structure that is the enol of a ketone.



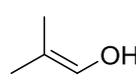
A



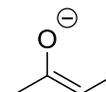
B



C

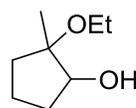
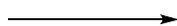
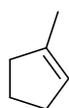


D

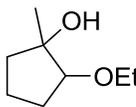
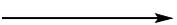
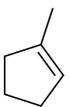


E

2. Here are two multi-step syntheses:



Target A



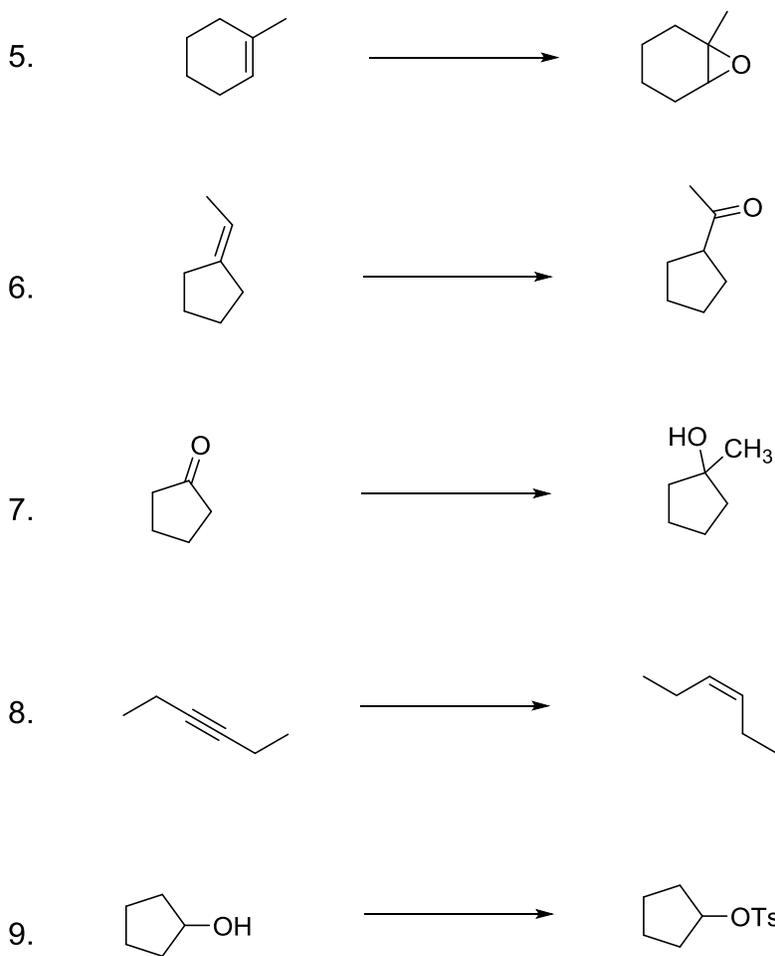
Target B

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

- Synthesis of Target A
 - Synthesis of Target B
 - Both syntheses
 - Neither synthesis
3. Which statement best describes one of the chemical (mechanistic) roles of NH_3 in the dissolving metal reduction of an alkyne?
- It donates a proton to a radical anion
 - It donates an electron to a sodium cation
 - It donates a pair of electrons to the alkyne
 - It is a nucleophilic source of hydride ion, H^- , which reduces the alkyne
4. The keto and enol forms of a carbonyl compound are related as tautomers. Tautomers are
- Stereoisomers
 - Constitutional isomers
 - Different conformations of the same molecule
 - 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. CH_3I (methyl iodide)
- c. $\text{H}_2/\text{Lindlar catalyst}$
- d. TsCl/pyr
- e. Can't be accomplished in one operation using any of these choices



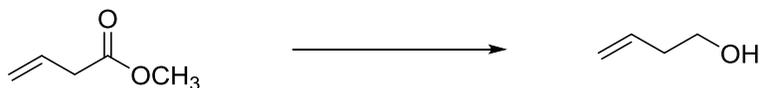
For questions 10 through 14, select the best reagent from the list. Assume appropriate aqueous workup after all reactions. Choices may be used more than once, or not at all.

- a. Only NaBH_4 would work
- b. Only LAH would work
- c. Either NaBH_4 or LAH would work
- d. H_2/Pd
- e. $\text{H}_2/\text{Raney Ni}$

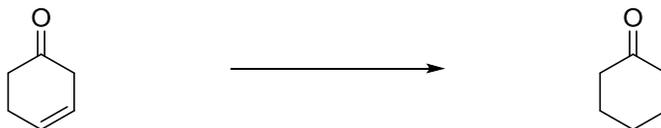
10.



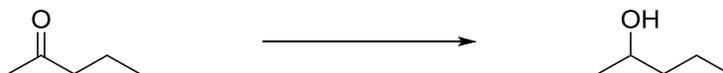
11.



12.



13.



14.



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



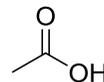
A



B



C

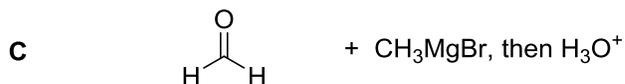
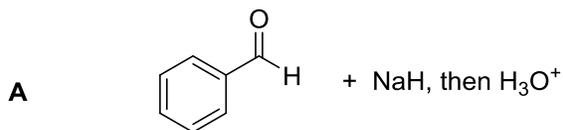


D



E

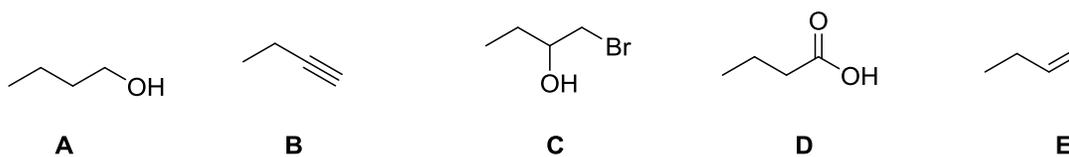
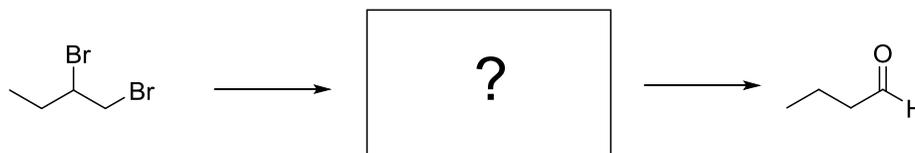
16. You need to make a primary alcohol. Which of the following methods would not work?



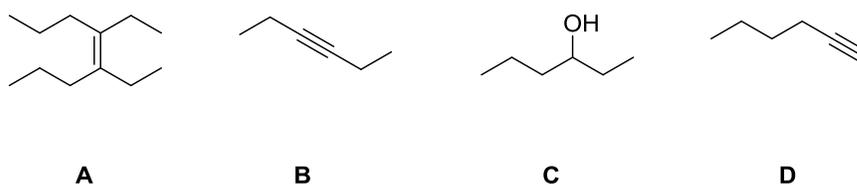
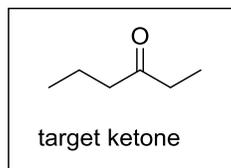
D All three methods would work

E None of these methods would 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?



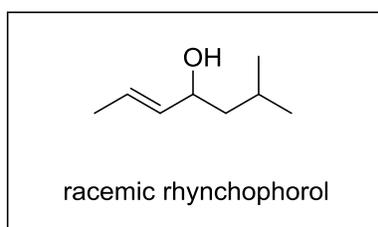
18. From which of these compounds can the target ketone NOT be made in one synthetic operation (including workup)?



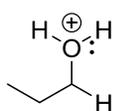
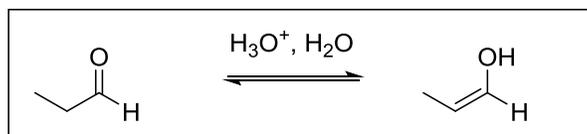
The ketone can be made from any of these compounds in one synthetic step

A B C D E

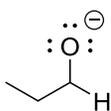
19. A molecule called rhynchophorol is a aggregation pheromone of the American palm weevil. Aggregation pheromones are involved in assembling groups of insects in one location. The organizers of the popular weevil music festival "Burning Weevil" are interested in attracting throngs of concertgoers by 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?



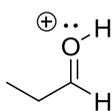
- a. Formaldehyde, CH_2O
 b. An aldehyde other than formaldehyde
 c. A ketone
 d. An acid chloride
 e. An ester
20. Select the structure that is a mechanistic intermediate in the tautomerization of this aldehyde in aqueous acid.



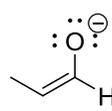
A



B



C



D

None of these structures are mechanistic intermediates

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.

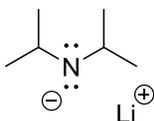
Consider the following pair of compounds and select the appropriate statement from this list for each base in questions 21-24. Some of the base structures are shown. Helpful pK_a values: butane, 50-60; *tert*-butanol, 19.



- a. Quantitatively deprotonates ethanol AND propyne
- b. Quantitatively deprotonates neither ethanol nor propyne
- c. Quantitatively deprotonates ethanol, but not propyne
- d. Quantitatively deprotonates propyne, but not ethanol

21. KOH

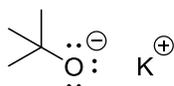
22. LDA



23. BuLi

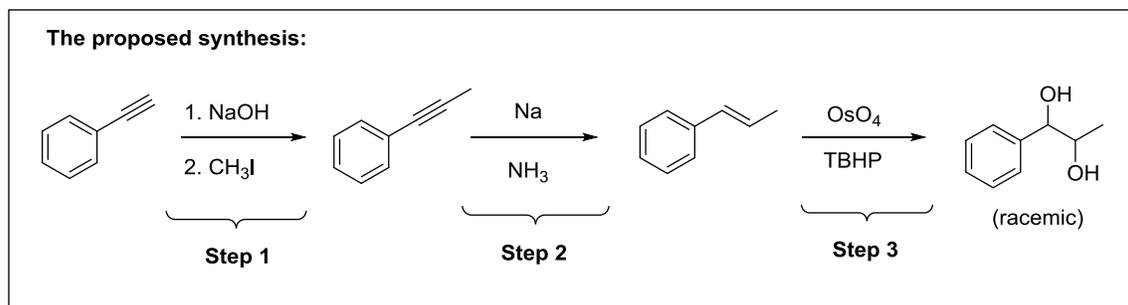


24. Potassium *tert*-butoxide



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?

- Step 1
- Step 2
- Step 3
- Steps 1 and 2
- Steps 1, 2 and 3