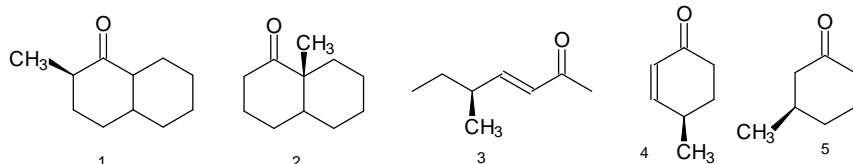


Problem Set 4 Chem 232

1. Some of the ketones below racemize very rapidly in acidified water while the other ones retain their optical purity. Which ones racemize? (hint: some can form achiral tautomers)

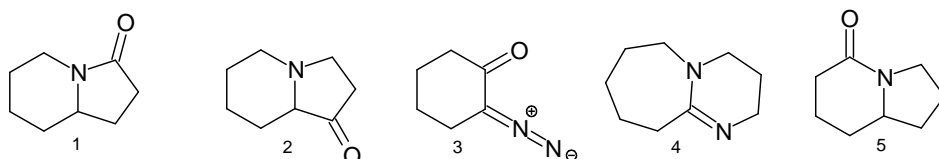


- A. 1 and 2 B. only 1 C. 1,3 and 4 D. 1,3 and 5 E. only 5

2. What is the correct order of acidities for the following acids: 1. ethanol, 2. trifluoroacetic acid 3. formic acid 4. acetic acid 5. propanoic acid?

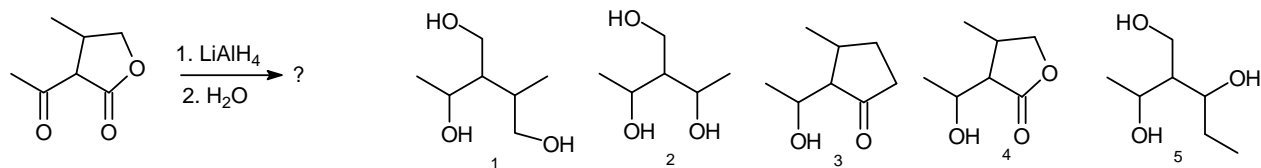
- A. $1 < 2 < 4 < 5 < 3$ B. $1 < 5 < 4 < 3 < 2$ C. $5 < 4 < 3 < 2 < 1$ D. $5 < 4 < 1 < 3 < 2$
E. $1 < 2 < 5 < 3 < 4$

3. How many of the compounds below are lactams?



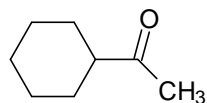
- A. 1 B. 2 C. 3 D. 4 E. all

4. What is the result of the reduction below?



- A. 1 B. 2 C. 3 D. 4 E. 5

5. The ketone below can be prepared conveniently, starting with the alkylation of a suitable β -dicarbonyl precursor. Which organic chemicals might be appropriate for this synthesis?

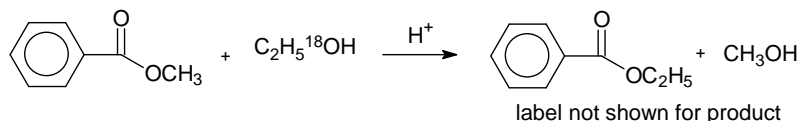


- A. ethyl acetoacetate, 1,4-dibromobutane, and sodium ethoxide
B. diethyl malonate, 1,4-dibromopentane, and sodium ethoxide
C. ethyl acetoacetate, 1,5-dibromopentane, and sodium ethoxide
D. diethyl malonate, 1,5-dibromopentane, and sodium ethoxide
E. ethyl acetoacetate, 1-bromopropane, and sodium ethoxide

6. The trans-3-methyl-3-hexene can be made by Wittig reaction, starting with a suitable ketone and a suitable alkyl halide. Which ketone and which alkyl halide might be appropriate?

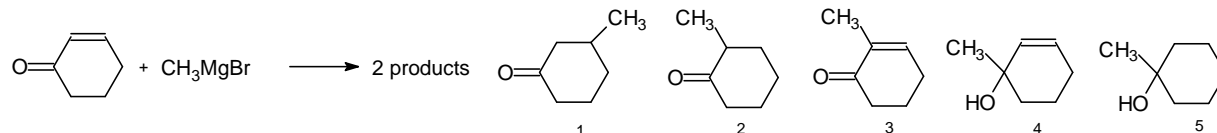
- A. butanone and 1-bromopropane
B. 2-pentanone and bromoethane
C. 3-pentanone and bromoethane
D. 2-pentanone and 1-bromopropane
E. butanone and 2-bromopropane

7. The mechanism for acid catalyzed transesterification of methyl benzoate to ethyl benzoate can be confirmed by using ^{18}O labeled ethanol. Sketch out the mechanism: where would you expect the ^{18}O label to show up? (8 pts)



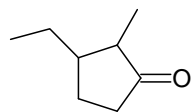
- A. Both oxygens of ethyl benzoate will have ^{18}O incorporated
 B. all three oxygens of the two products will have ^{18}O incorporated
 C. only the carbonyl oxygen of ethyl benzoate will have ^{18}O incorporated
 D. only the $-\text{OC}_2\text{H}_5$ oxygen of ethyl benzoate will have ^{18}O incorporated
 E. only the $-\text{OH}$ group of methanol will have ^{18}O incorporated
8. One of the reactions below does **not** generate acetophenone. Which one?
 A. The reaction of methylmagnesium bromide with benzonitrile, followed by aqueous workup
 B. The oxidation of 1-phenylethanol with PCC
 C. The acetylation of benzene with acetylchloride/aluminum chloride
 D. The reaction of benzoylchloride with lithium dimethyl copper, followed by aqueous workup
 E. The reaction of phenylethyne with borane, followed by treatment with sodium hydroxide/ H_2O_2
9. What is the most plausible molecular formula for the mixed aldol condensation of cyclohexanone with benzaldehyde?
 A. $\text{C}_{12}\text{H}_{18}\text{O}$ B. $\text{C}_{13}\text{H}_{14}\text{O}$ C. $\text{C}_{13}\text{H}_{15}\text{O}_2$ D. $\text{C}_{13}\text{H}_{12}\text{O}_2$ E. $\text{C}_{13}\text{H}_{18}\text{O}$
10. One of the reactions below does **not** generate methyl 3-nitrobenzoate. Which one?
 A. The reaction of bis(3-nitrobenzoic) anhydride with methanol
 B. The reaction of 3-nitrobenzoylchloride with methanol
 C. Fisher esterification of 3-nitrophenylbenzoic acid with methanol
 D. Electrophilic nitration of methyl benzoate
 E. The reaction of 1-bromo-3-nitrobenzene with sodium acetate
11. Commercially, most acetic acid sold today is manufactured from two common gases following a two step synthesis. Which ones?
 A. CO_2 and H_2 B. CO and CO_2 C. CO and NH_3 D. CO and H_2 E. Cl_2 and CH_4

12. The reaction of methylmagnesium bromide with 2-cyclohexenone results in the formation of a mixture of two products, one resulting from direct addition at the carbonyl carbon, the other (and major) one from conjugate addition. Which compounds form?



- A. 1 and 4 B. 2 and 5 C. 1 and 5 D. 3 and 4 E. 3 and 5

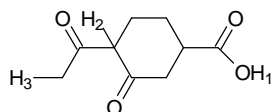
13. Select the best (highest yield) way to generate the ketone below!



- A. From 2-methyl-2-cyclopentenone and ethylmagnesium bromide
 B. From 3-ethyl-2-cyclopentenone and methylmagnesium bromide
 C. From 2-methyl-2-cyclopentenone and lithium diethylcopper
 D. From 2-methylcyclopentanone and ethylmagnesium bromide

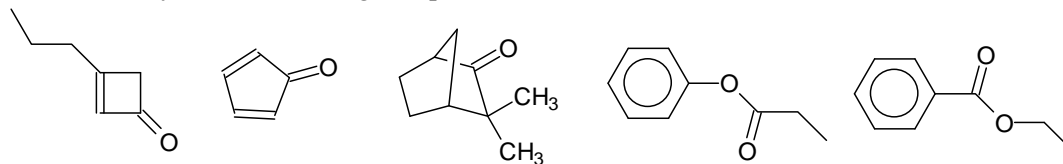
E. From 2-methylcyclopentanone and lithium diethylcopper

14. Rank the highlighted hydrogens according to their acidities



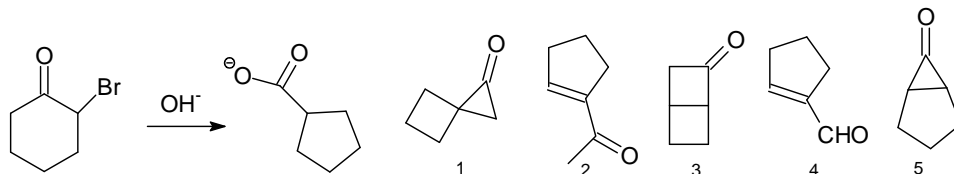
- A. $H_2 < H_1 < H_3$ B. $H_1 < H_3 < H_2$ C. $H_1 < H_2 < H_3$ D. $H_3 < H_2 < H_1$ E. $H_3 < H_1 < H_2$

15. How many of the following compounds are enolizable?



- A. none B. 1 C. 2 D. 3 E. 4

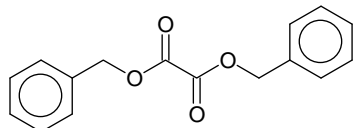
16. A common reaction (Favorskii rearrangement) converts 2-halocyclohexanones into salts of cyclopentanecarboxylic acids, using sodium hydroxide solution (Br^- is eliminated)



Sketch out a plausible mechanism for this reaction and select one of the structures 1-5 as a plausible intermediate. Which one?

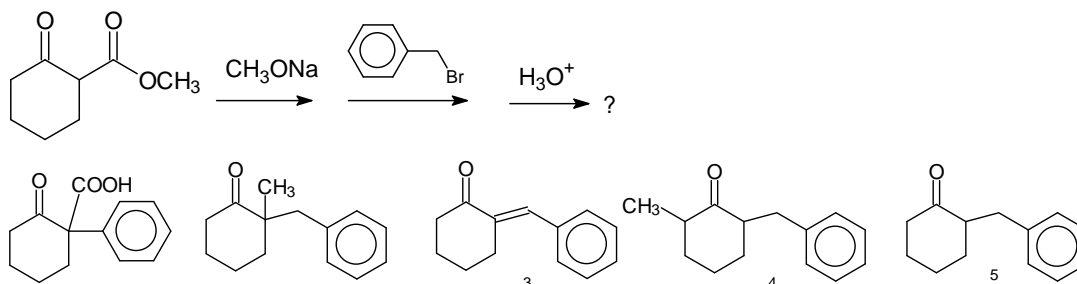
- A. 1 B. 2 C. 3 D. 4 E. 5

17. What names are appropriate for the following compound?



- A. either diphenyl oxalate or dibenzyl carbonate
 B. only diphenyl malonate
 C. either diphenyl oxalate or diphenyl benzenedioate
 D. only dibenzyl carbonate
 E. either dibenzyl oxalate or dibenzyl ethanedioate

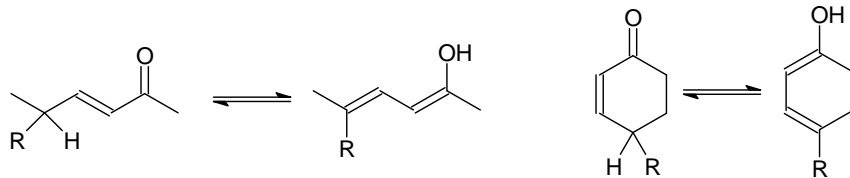
18. What is the most plausible product of the following reaction sequence?



- A. 1 B. 2 C. 3 D. 4 E. 5

Key pr232_4_101:

1. C



2. B

3. B (1 and 5)

4. A

5. C

6. A

7. D

8. E

9. B

10. E

11. D (step 1: methanol from $H_2 + CO$; step 2: acetic acid from methanol and CO by rhodium catalyzed formylation)

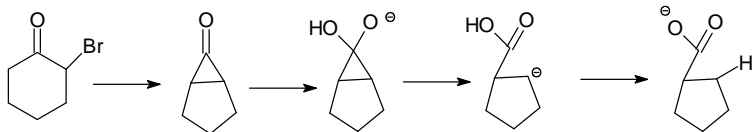
12. A

13. C

14. D

15. B (only phenyl propanoate)

16. E



17. E

18. E