

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.

Good luck!

1A 2A

3A 4A 5A 6A 7A 8A

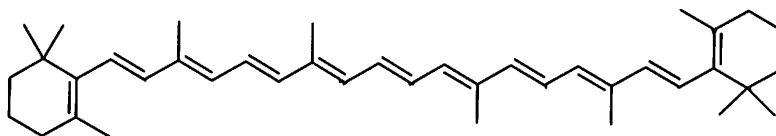
1 H																	2 He	
3 Li	4 Be															10 Ne		
11 Na	12 Mg													15 P	16 S	17 Cl	18 Ar	
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	
55 Cs	56 Ba	57-70 *	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89-102 **	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub	113 Uuq	114 Uuq	115 Uuq	116 Uuq	117 Uuq	118 Uuq

\* Lanthanide series

\*\* Actinide series

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

1. How many pi molecular orbitals are there in  $\beta$ -carotene?



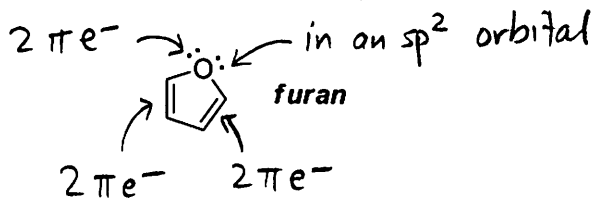
$\beta$ -carotene

D

- a. 9
- b. 11
- c. 18
- d. 22
- e. None of these

22 p orbitals  $\rightarrow$  22  $\pi$  MO's  
 Atomic orbitals used = Molecular orbitals created

2. How many pi electrons are there in furan?

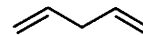
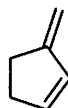
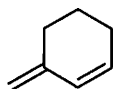


C

- a. 2
- b. 4
- c. 6
- d. 8
- e. None

Furan is aromatic - It is able to include one of the lone pairs on O (by hybridizing O as  $sp^2$ ) in the  $\pi$  system to give a total of  $6 \pi e^-$

3. Which of these compounds will react fastest as a diene in a Diels Alder reaction?



C

~~A~~  
Does not react!

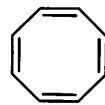
B  
 Locked in S-trans  
 Can't react

C  
 Locked in S-cis  
 (Reactive conformation)

D  
 Locked in S-trans  
 Can't react

E  
 Not a conjugated diene -  
 Will not react as a diene in DA

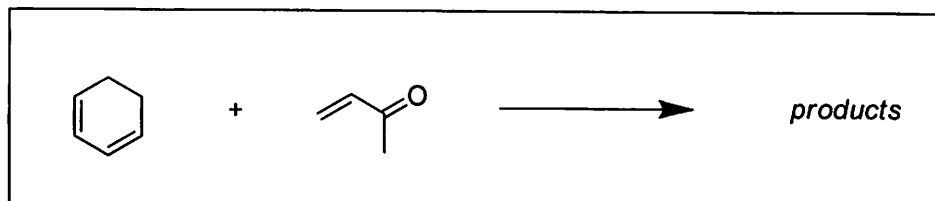
4. Which of these statements best describes cyclooctatetraene?



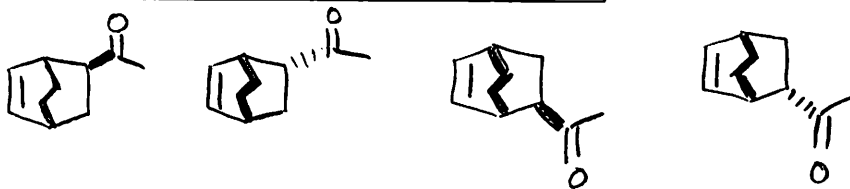
- E
- a. Planar and aromatic
  - b. Nonplanar and aromatic
  - c. Planar and antiaromatic
  - d. Nonplanar and antiaromatic
  - e. Nonplanar and nonaromatic

Has  $8 \pi e^-$ ,...  
adopts a "tub shaped"  
conformation to avoid  
antiaromaticity

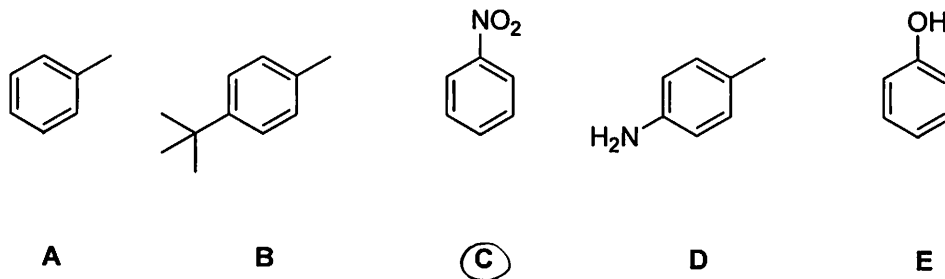
5. How many different stereoisomers will form in this Diels Alder reaction?  
(Include all possible stereoisomers; don't worry about "major" or "minor"  
product arguments.)



- C
- a. 2
  - b. 3
  - c. 4
  - d. 6
  - e. Too many to count

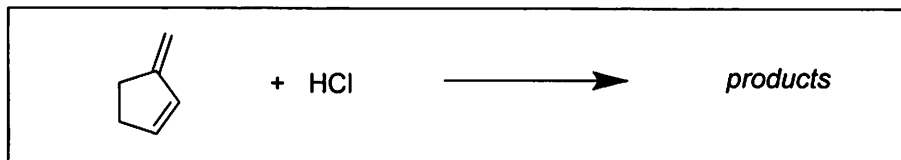


6. Which of these substituted benzenes will not undergo a Friedel-Crafts alkylation?

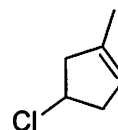
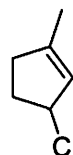
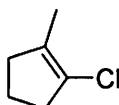
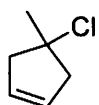
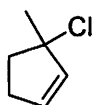


Deactivated

For questions 7 and 8, consider the following reactants:

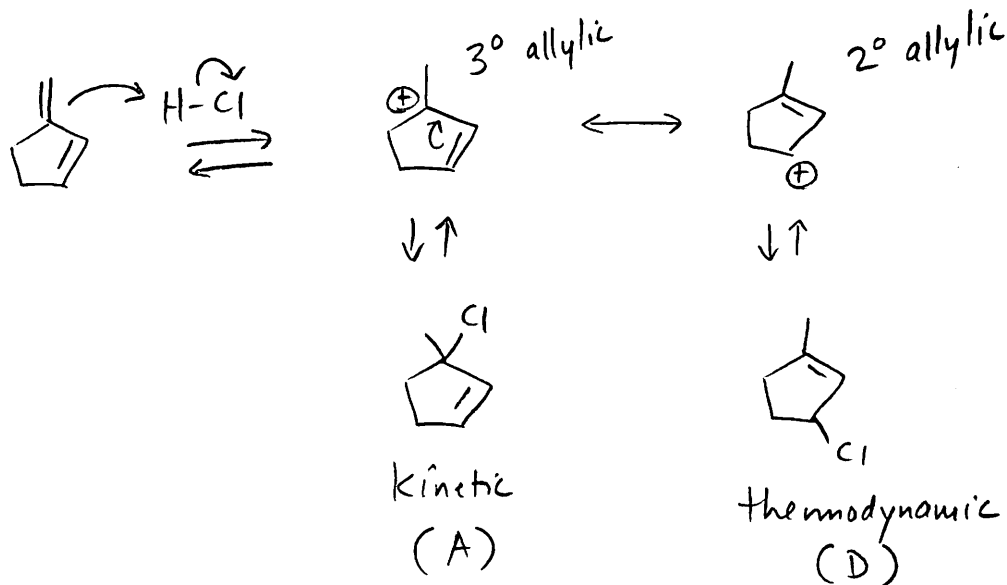


and the following answer choices (again, these apply to both 7 and to 8):

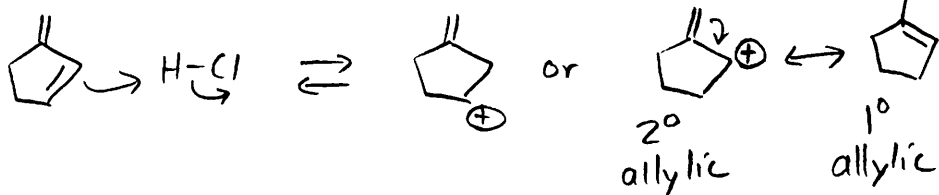


**A** 7. You combine the reactants and allow them to react for a short period of time at a low temperature. Which compound do you expect to be the major product? *Kinetic conditions*

**D** 8. You combine the reactants and allow them to react for a long period of time at a high temperature. Which compound do you expect to be the major product? *Thermodynamic conditions*



Note that the cation formed is more stable than protonating the other alkene:

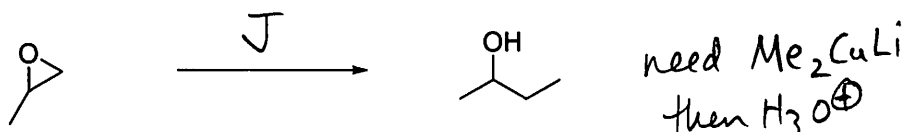




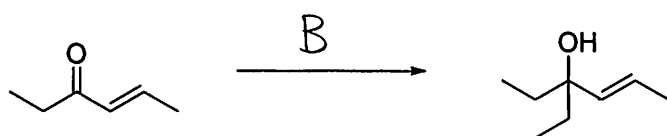
For questions 10-14, select from the following answer choices. Answer choices may be used once, more than once, or not at all.

- |          |  |          |   |
|----------|--|----------|---|
| <b>A</b> | Et <sub>2</sub> CuLi, followed by H <sub>3</sub> O <sup>+</sup> workup | <b>F</b> | Either "D" or "E"   |
| <b>B</b> | EtLi, followed by H <sub>3</sub> O <sup>+</sup> workup                 | <b>G</b> | NaH   |
| <b>C</b> | Either "A" or "B"  | <b>H</b> | NBS, AIBN, CCl <sub>4</sub> , heat                        |
| <b>D</b> | LAH, followed by H <sub>3</sub> O <sup>+</sup> workup                  | <b>I</b> | KMnO <sub>4</sub>   |
| <b>E</b> | NaBH <sub>4</sub>  | <b>J</b> | None of these.<br>The reagent needed is not on this list. |

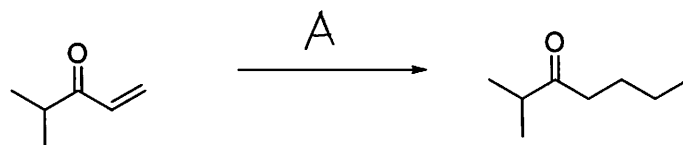
10.



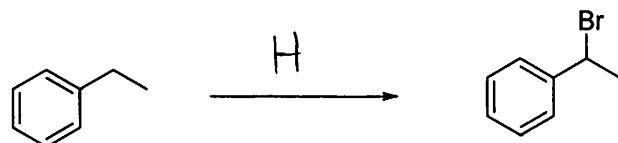
11.



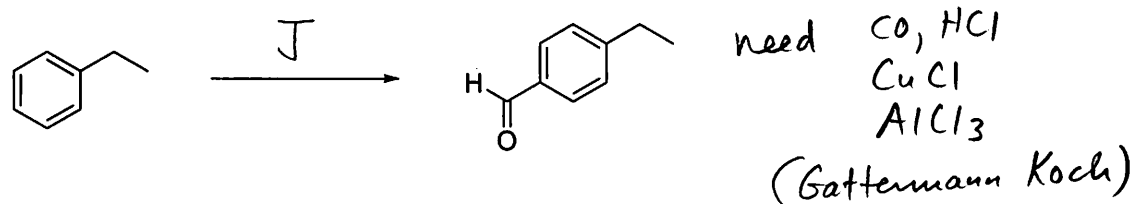
12.



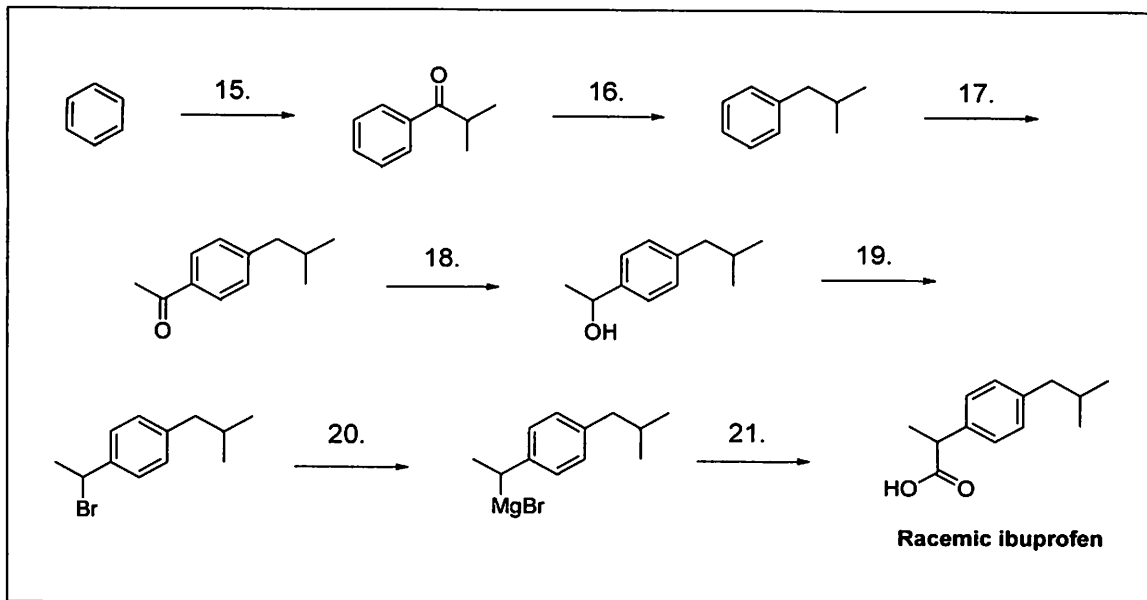
13.



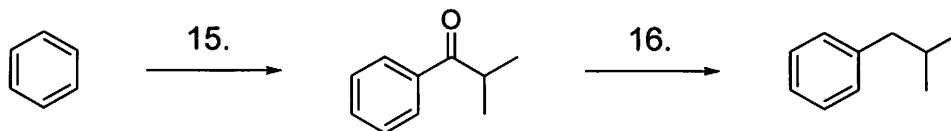
14.



Questions 15 through 21 relate to the multi-step synthesis of racemic ibuprofen from benzene, shown in the following scheme:



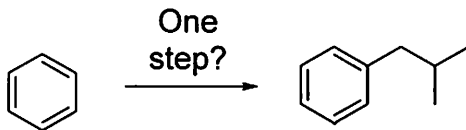
15. Benzene is transformed in two steps to sec-butyl benzene in the synthesis:



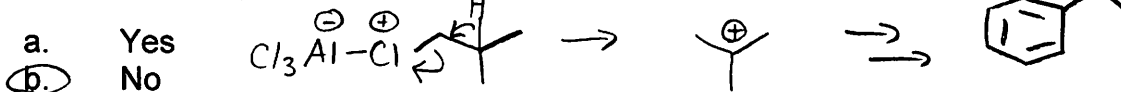
Can this transformation be successfully accomplished instead in ONE step, using a Friedel Crafts alkylation?

So;  $\text{Cl-CH(CH}_3)_2 + \text{AlCl}_3 \dots?$

B



There would be a rearrangement:



16. Of these choices, what reagent should be used for the step labeled "16"?

- a. Clemmensen reduction ( $\text{HCl}$ ,  $\text{H}_2\text{O}$ ,  $\text{Zn/Hg}$ )  
 b. Gattermann Koch formylation ( $\text{CO}$ ,  $\text{HCl}$ ,  $\text{CuCl}$ ,  $\text{AlCl}_3$ )  
 c. LAH - reduces ketones to alcohols  
 d. NaH - doesn't reduce  $\text{C=O}$   
 e. Either "a" or "b" would work

A

17. The step labeled "17" is referred to as

- B
- a. Alkylation
  - b. Acylation
  - c. Reduction
  - d. Addition
  - e. None of these

18. Of these choices, what reagent should be used for the step labeled "18"?

- C
- a. Clemmensen reduction (HCl, H<sub>2</sub>O, Zn/Hg)
  - b. Wolff-Kishner reduction (H<sub>2</sub>NNH<sub>2</sub>, KOH, heat)
  - c. LAH
  - d. NaH - Does not reduce ketones
  - e. Either "a" or "b" would work
- } Do not form alcohols


19. What reagent should be used in the step labeled "19"?

- D
- a. Br<sub>2</sub>, heat
  - b. NBS, AIBN, CCl<sub>4</sub>, heat
  - c. Br<sub>2</sub>, FeBr<sub>3</sub>
  - d. PBr<sub>3</sub>
  - e. None of these

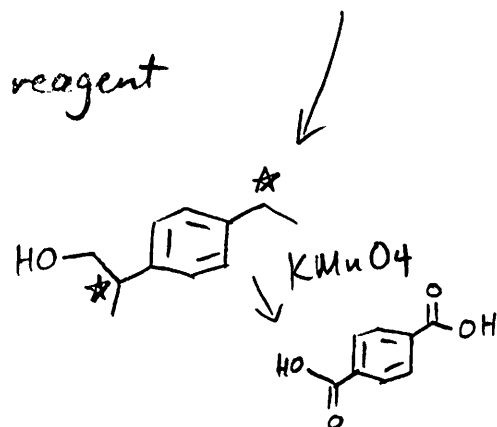
20. In the step labeled "20", which is the most appropriate solvent to use?

- D
- a. Water
  - b. Methanol
  - c. Ethanol
  - d. Diethyl ether
  - e. Any of these solvents would be fine

21. The transformation labeled as "21" should be accomplished using what reagents?

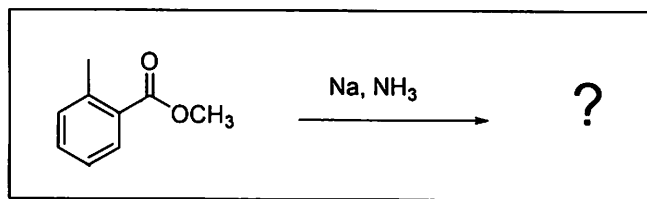
- B
- a. Oxirane  then H<sub>3</sub>O<sup>+</sup>, then KMnO<sub>4</sub>
  - b. CO<sub>2</sub>, then H<sub>3</sub>O<sup>+</sup>
  - c. H<sub>2</sub>O/H<sub>3</sub>O<sup>+</sup>
  - d. Any of these would work fine

Would protonate Grignard reagent



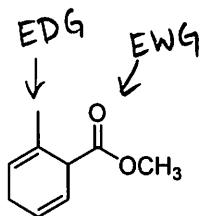


22. Select the correct product of the reaction conditions.

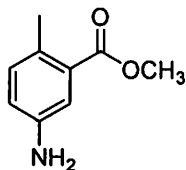


Birch reduction

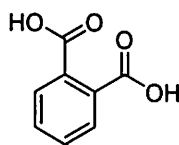
A



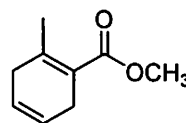
**A**



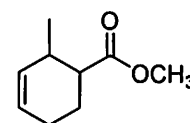
B



C



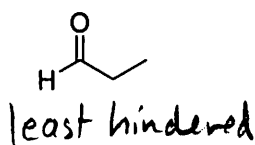
D



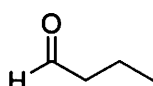
E

23. Select the compound that you expect to have the *largest* value of  $K_{\text{hydration}}$ .

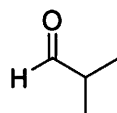
A



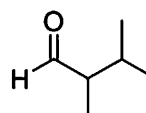
**A**



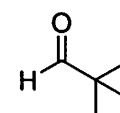
B



C

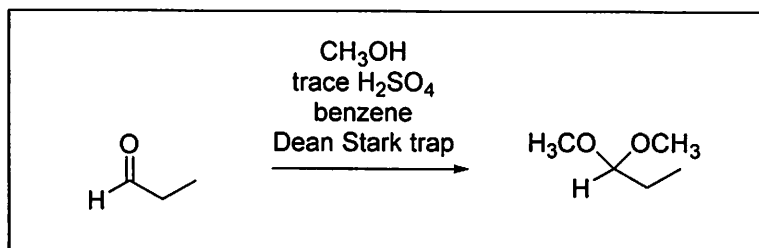


D

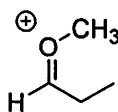


E

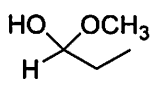
24. Which of the following is a hemiacetal intermediate in this acetal formation reaction? (Lone pairs are omitted for clarity.)



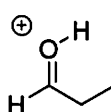
B



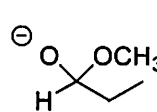
A



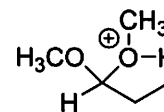
**B**



C

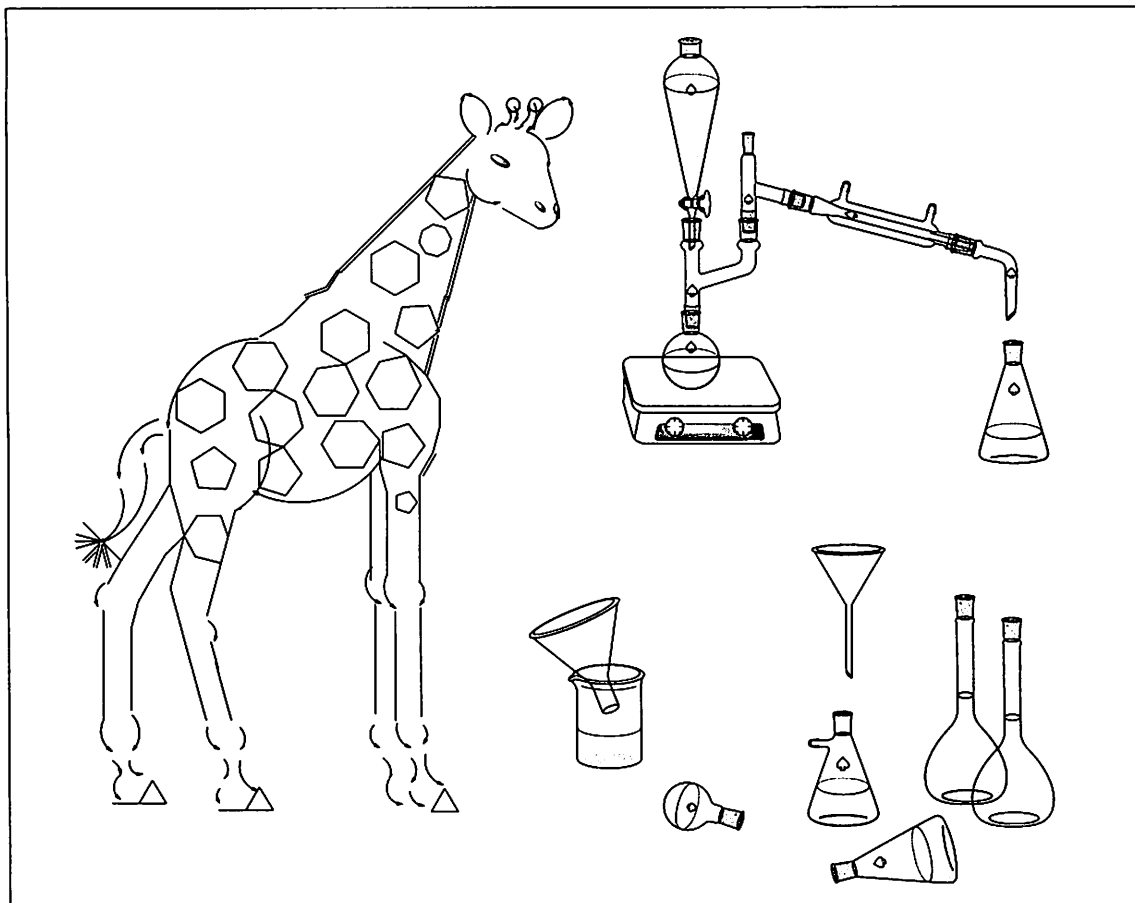


D

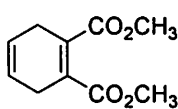


E

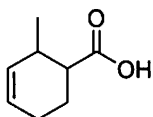
25. The ChemDraw Giraffe is in the house! Here it is in its lab, working on some reactions. (Notice that the giraffe's technique is poor: It has not clamped its distillation apparatus to a ring stand.)



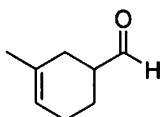
The giraffe is an accomplished organic chemist and claims that it has published many complicated scientific papers. However, it has a very narrow research focus: It insists on only performing multi-step syntheses that involve the use of the Diels Alder reaction. Which of these molecules would the giraffe be LEAST likely to make using a Diels Alder reaction as part of the synthetic plan?



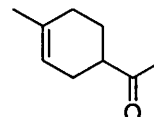
A



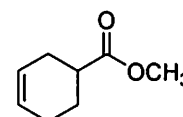
B



**C**



D



E

1,3 product  
not observed in  
DA