

NAME (Print): _____

SIGNATURE: _____

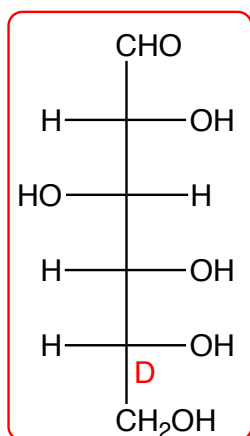
**Chemistry 320N
Dr. Brent Iverson
Final Practice
April 23, 2024**

**Please print the
first three letters
of your last name
in the three boxes**

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Score: _____

For the following carbohydrates, draw a circle around all of the D-carbohydrate(s), and draw a rectangle around all of the L-carbohydrate(s). On the two first two lines below the four structures, indicate whether each is an aldose or ketose, and whether each is a pentose or hexose, respectively. On the third line below each structure, construct a compound name from all of these elements. For example, answers might be L-ketopentose or L-aldohexose. Finally, on the fourth line under each structure write the specific name (i.e. D-glucose) for each structure. You should use table 25.1 or other structures named in the book to identify these exact sugar names. (You will NOT need to know them for the test).

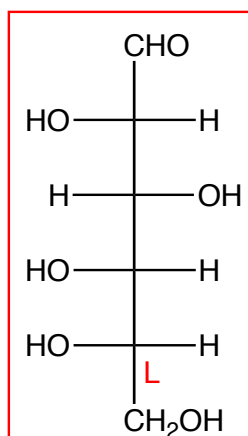


aldose

hexose

D-aldohexose

D-glucose

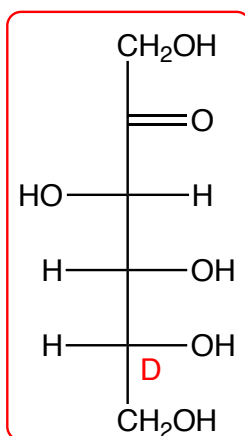


aldose

hexose

L-aldohexose

L-glucose

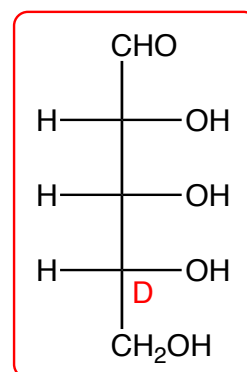


ketose

hexose

D-ketohexose

D-fructose



aldose

pentose

D-aldopentose

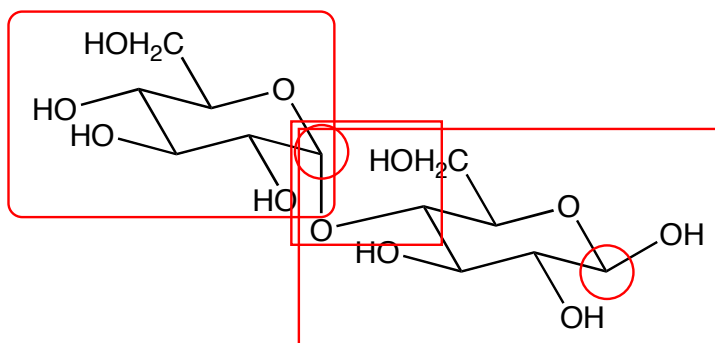
D-ribose

(aldose or ketose?)

(pentose or hexose?)

(compound name)

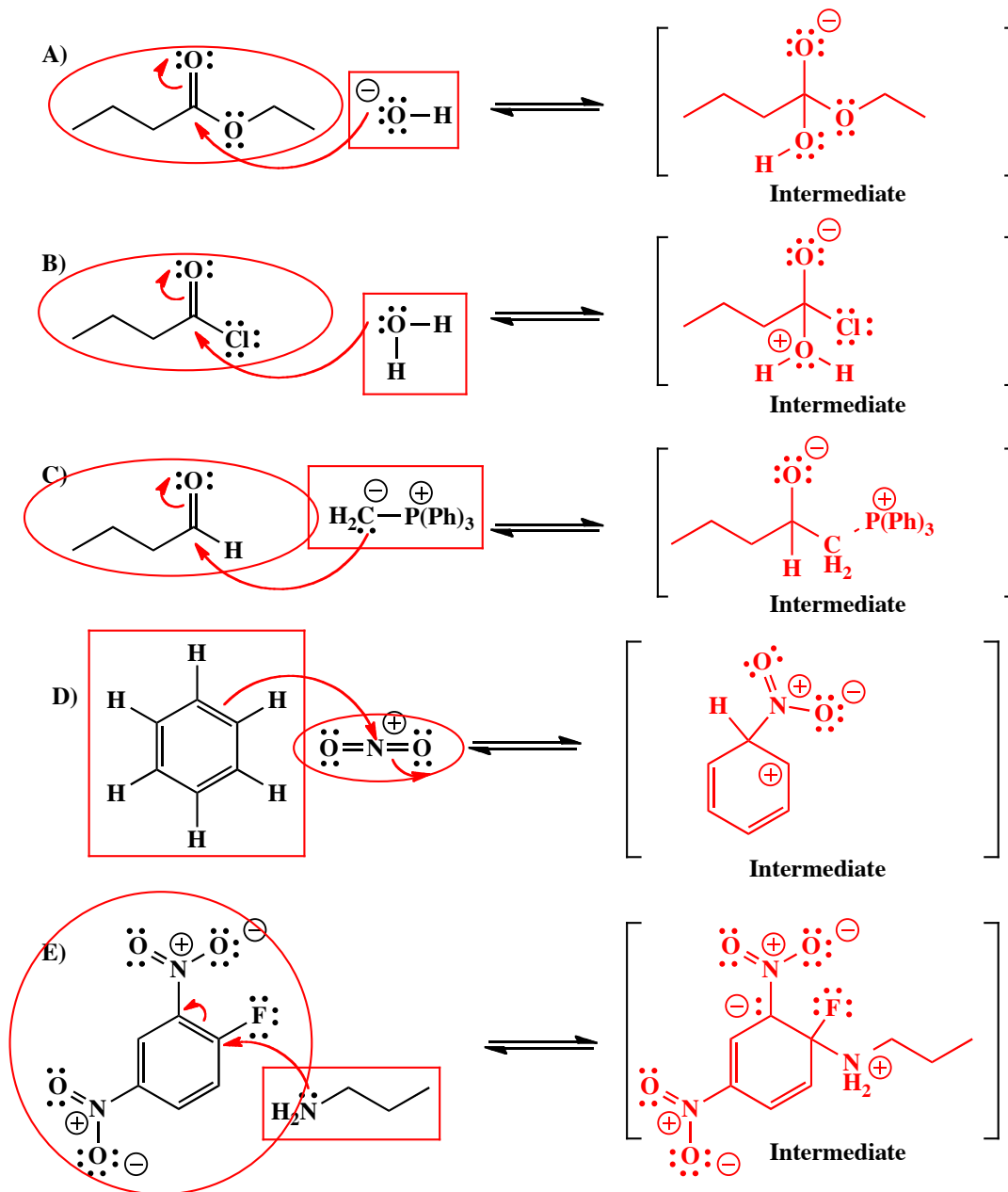
(exact name)
(look up but don't memorize)



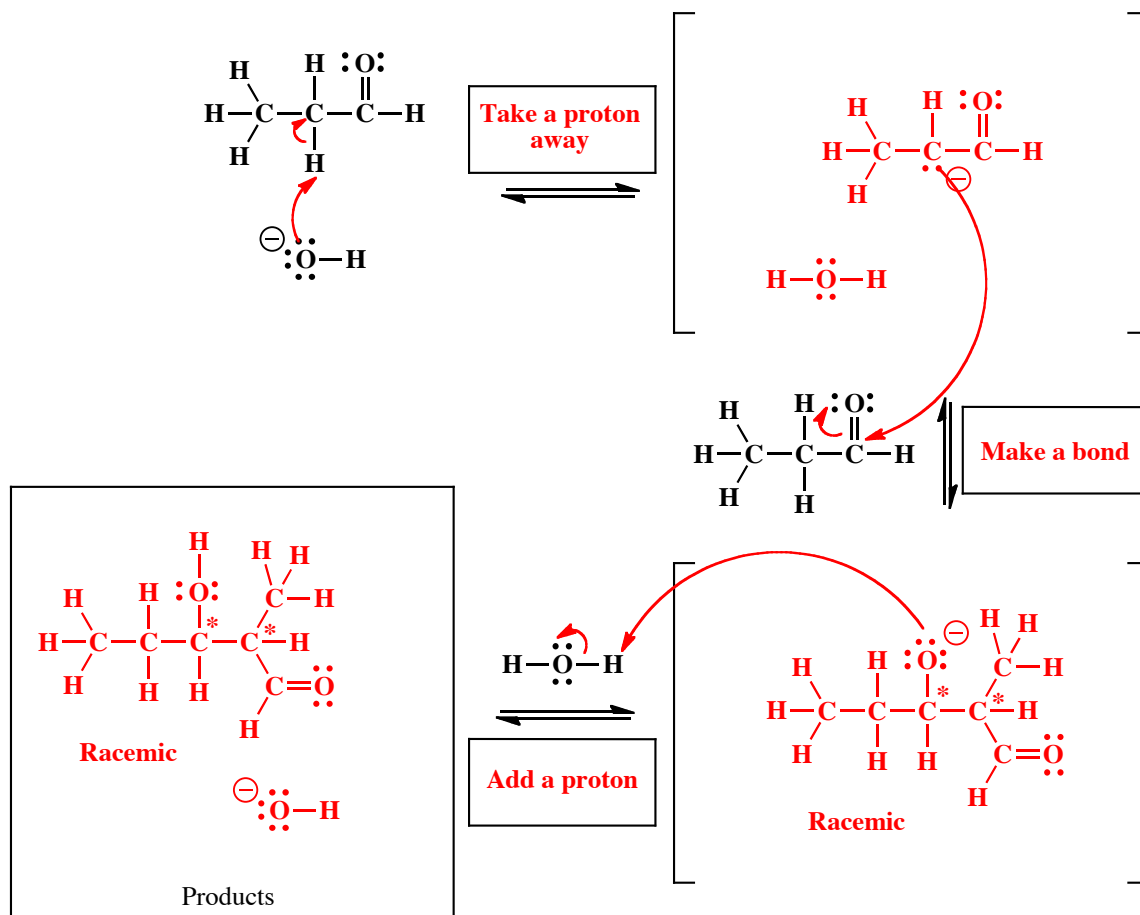
For the disaccharide of glucose on the left, draw a circle around any glucose residue that is/are α . Draw a box around any glucose residue that is/are β . Next, draw a box around the glycosidic bond linkage. Finally, circle all anomeric carbon atoms.

Describe the above linkage using the terminology presented in class: α -1,4 glycosidic bond

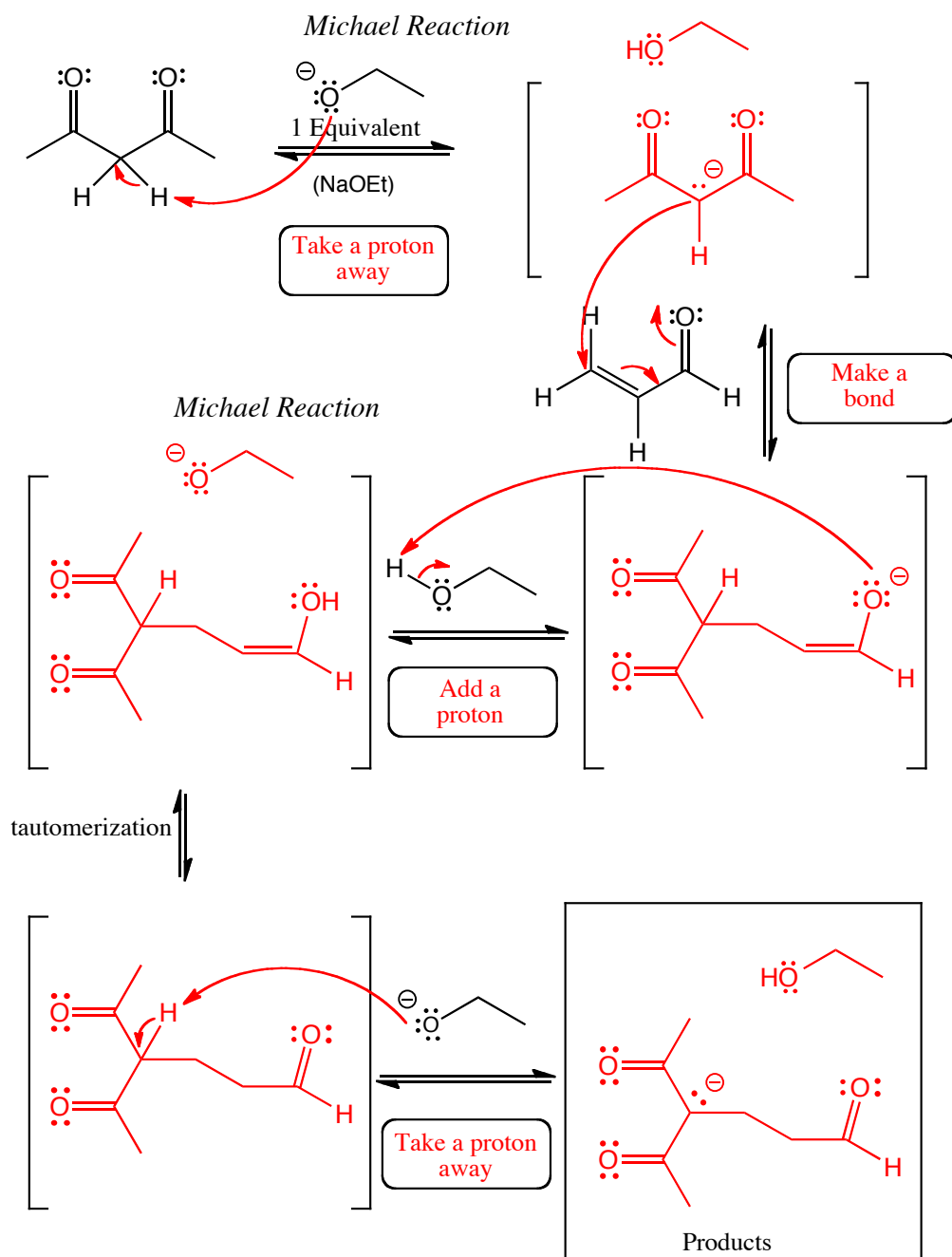
1. Many of the reactions we have learned this semester involve steps with nucleophiles reacting with electrophiles. For the following examples of steps in mechanisms we have seen this semester, 1) Draw the intermediate that will be formed when the two molecules react. 2) Draw all formal charges and lone pairs on the intermediates. 3) Draw arrows on the starting materials to indicate the flow of electrons that leads to the intermediate. 4) Finally, draw a box around the nucleophile and a circle around the electrophile in each case. There is no need to draw products or any further steps of the mechanisms. You might want to read these directions again so you know what we want.



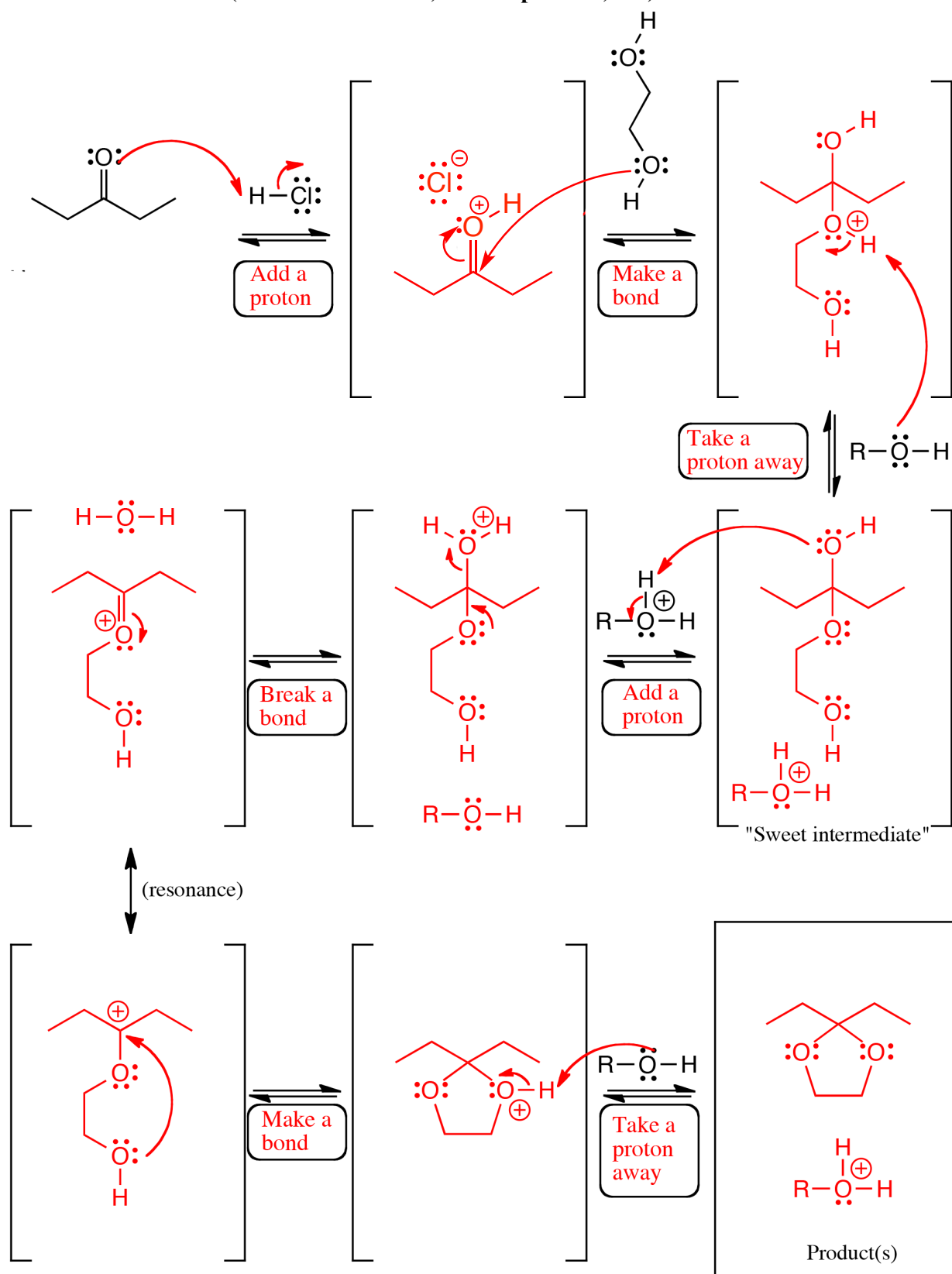
2. Complete the mechanism for the following aldol reaction. Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step. Remember, I said all the products for each step. IF A NEW CHIRAL CENTER IS CREATED IN AN INTERMEDIATE OR THE PRODUCTS, MARK IT WITH AN ASTERISK and WRITE RACEMIC IF RELEVANT. In the boxes provided adjacent to the first two sets of arrows, write which of the four basic mechanistic elements are involved (i.e. "Make a bond", "Add a proton", etc.)



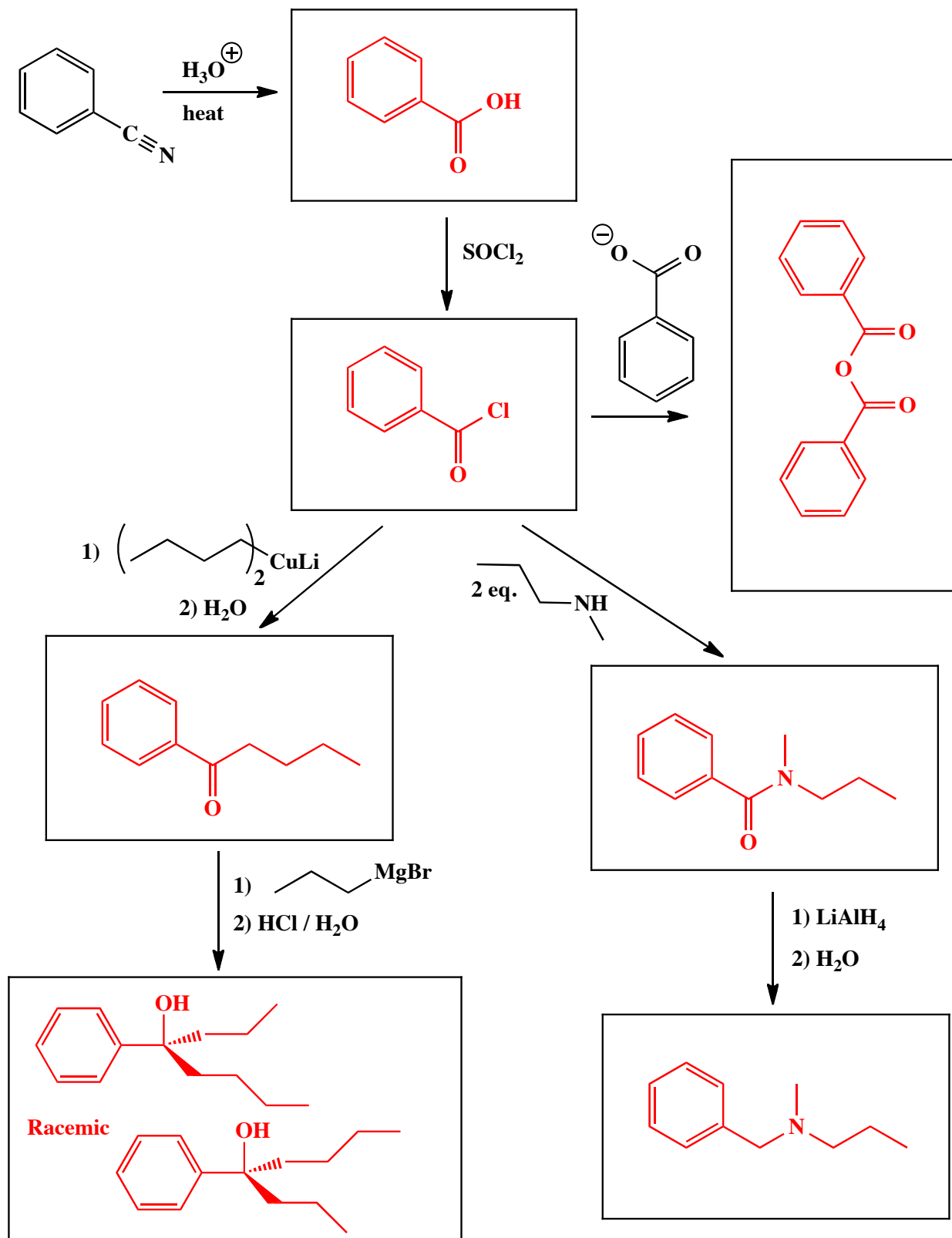
3. Complete the following mechanism for the Michael reaction. Make sure to show all lone pairs, all formal charges and use arrows to indicate the flow of all electrons. You must draw all products that are made in each step. This should look familiar, as it is identical to the mechanism sheet handed out in class.



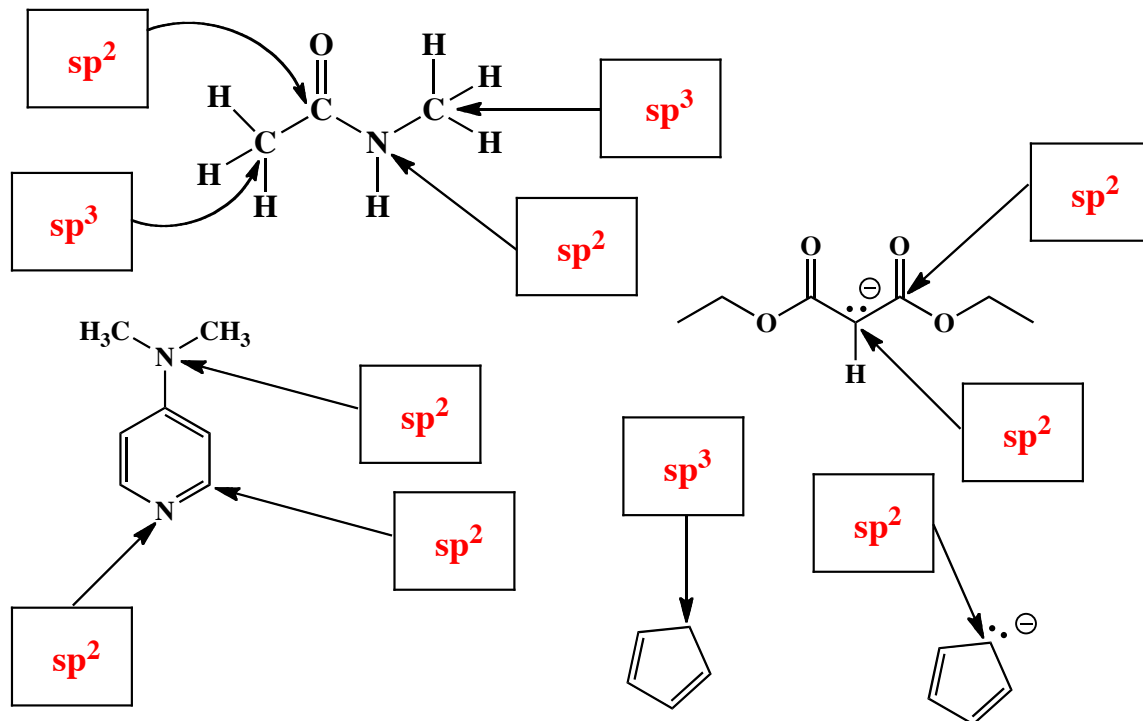
4. Complete the mechanism for the following cyclic acetal formation reaction. Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step. In the boxes provided adjacent to the arrows, write which of the four basic mechanistic elements are involved (i.e. "Make a bond", "Add a proton", etc.)



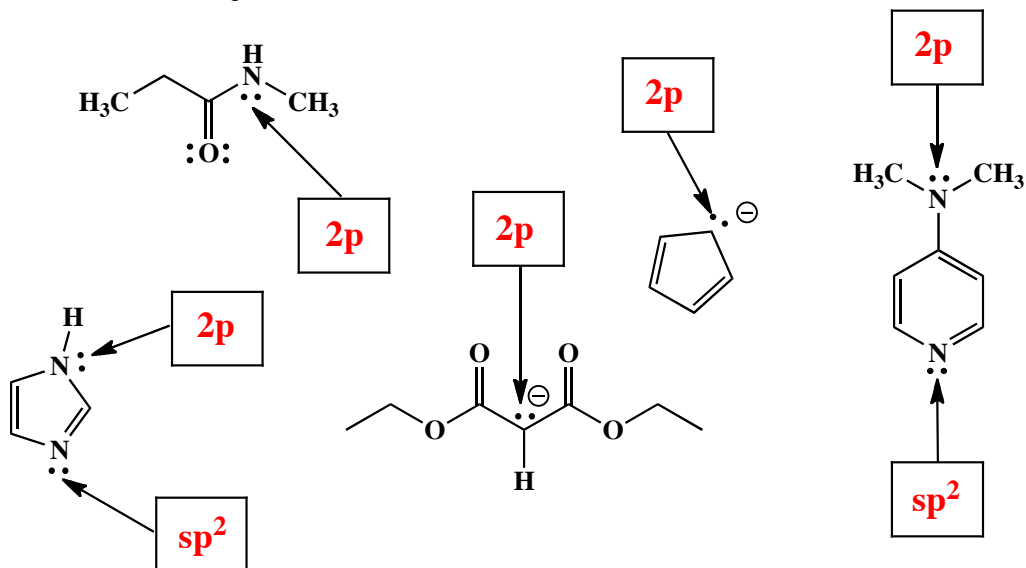
5. Fill in the box with the product or products that are missing from the following chemical reaction equations. When a racemic mixture is formed, you must write "racemic" under both structures EVEN THOUGH YOU DREW BOTH STRUCTURES.



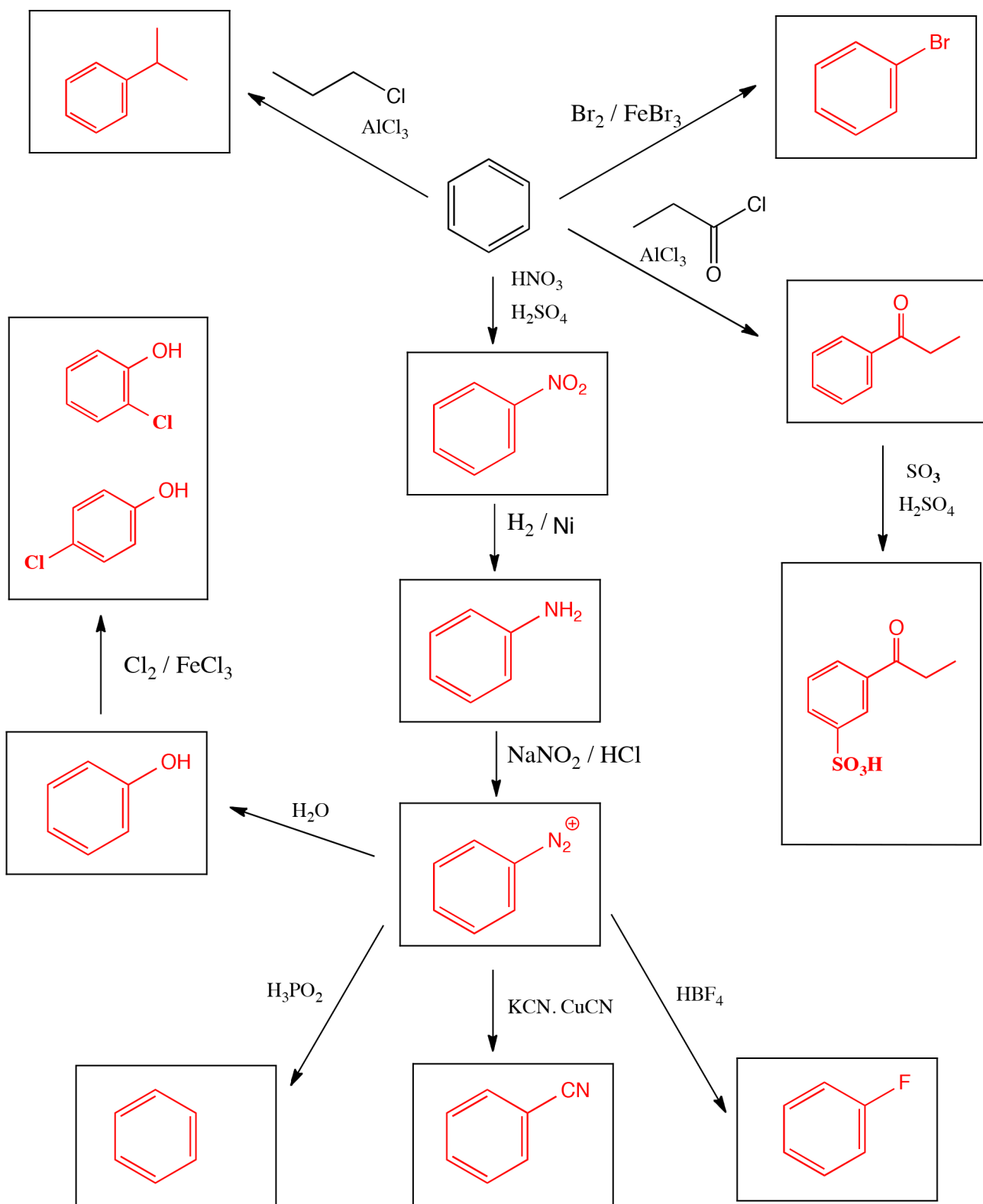
6. In the boxes provided, write the hybridization state of the given atoms.



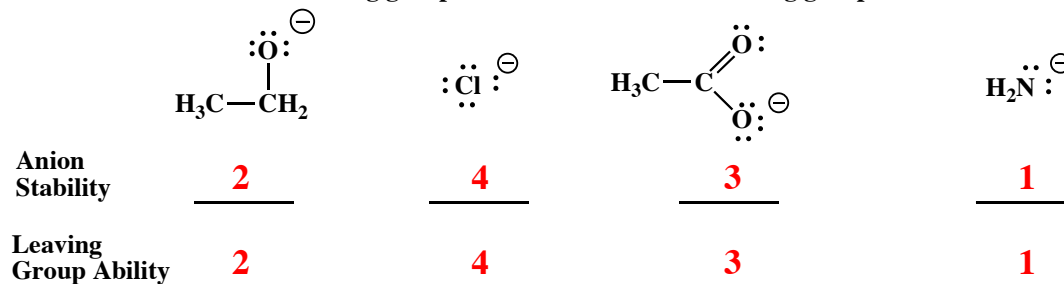
7. In the boxes provided, according to the valence bond approach, write the type of atomic orbital that contains the indicated lone pair of electrons..



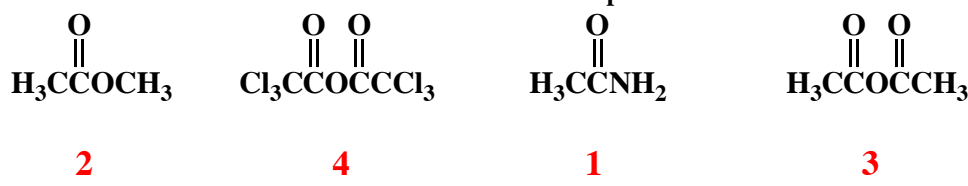
8. Write the predominant product or products that will occur for each transformation. Assume each reagent only adds once to the ring. If predominantly ortho/para products are predicted, you must draw both.



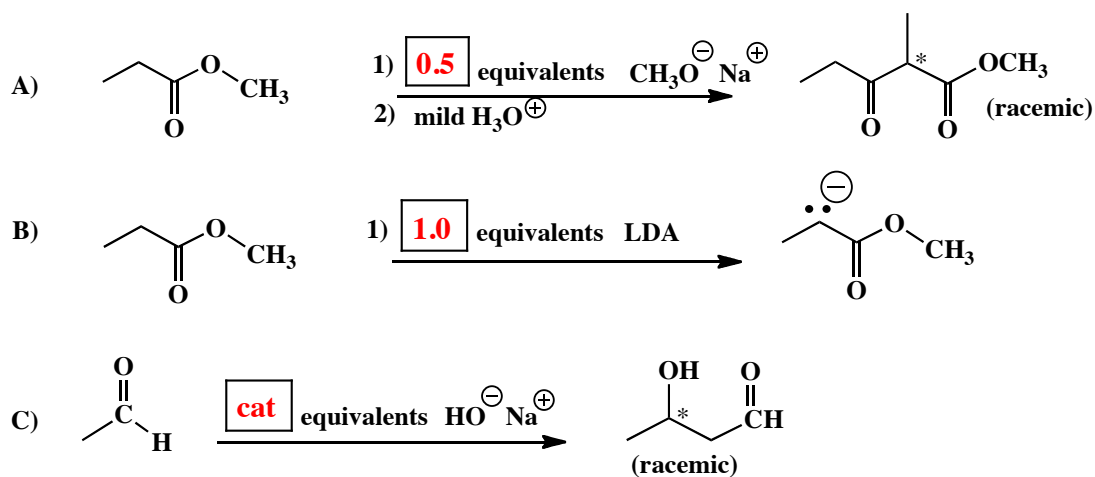
9. A) On the upper lines, rank the following with respect to relative anion stability, with a **1 under the least stable anion** (i.e. most reactive with a proton) and a **4 under the most stable anion** (i.e. least reactive with a proton). On the lower lines, rank the following with respect to leaving group ability, with a **1 under the worst leaving group**, and a **4 under the best leaving group**.



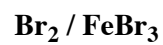
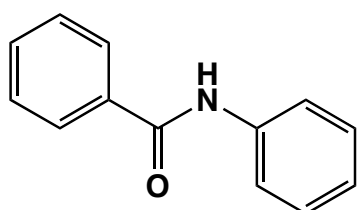
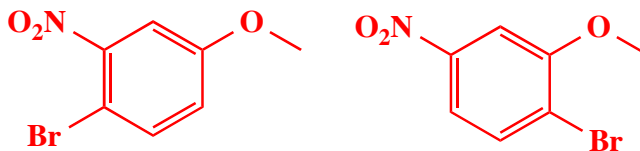
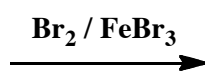
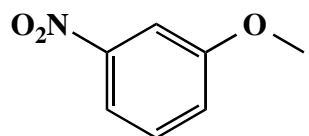
B) Rank the following in terms of **relative reactivity with a nucleophile without acid catalysis**. Place a **1 under the least reactive** and a **4 under the most reactive species**.



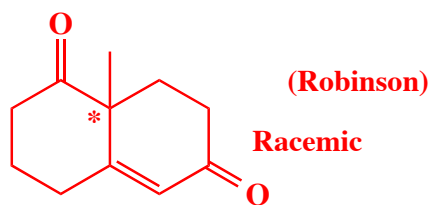
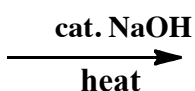
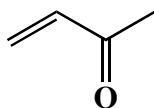
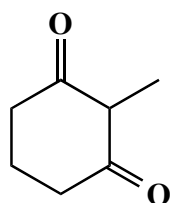
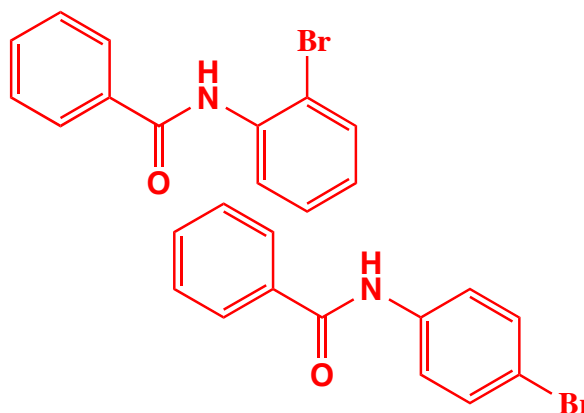
10. In each of the boxes over an arrow, write the **minimum number of equivalents** of the specified reagent required to carry out the reaction shown **to completion**. If only a catalytic amount is needed, write "CAT". Note: **You must assume the carbonyl compound starting material is initially present in an amount of 1.0 equivalent**.



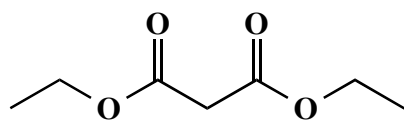
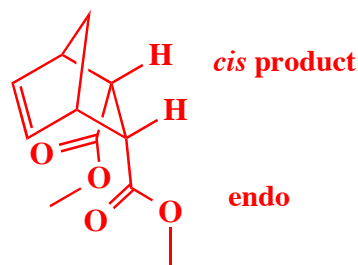
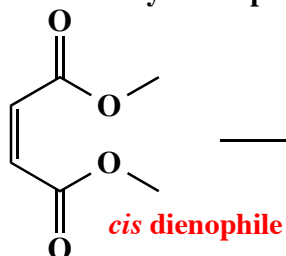
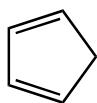
11. You might find these are harder so take your time. Write the predominant product or products that will occur for each transformation. If a new chiral center is created and a racemic mixture is formed, mark the chiral center with an asterisk "*" and write "racemic" under the structure. If ortho/para products are made, you must draw both. Note, for this problem, aldols can dehydrate if heated in dilute acid.



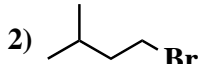
Assume only one Br atom adds



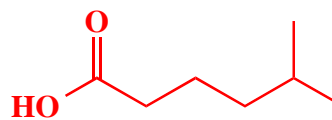
Be sure to indicate stereochemistry of the products on this next one.



1) 1.0 Eq. NaOEt

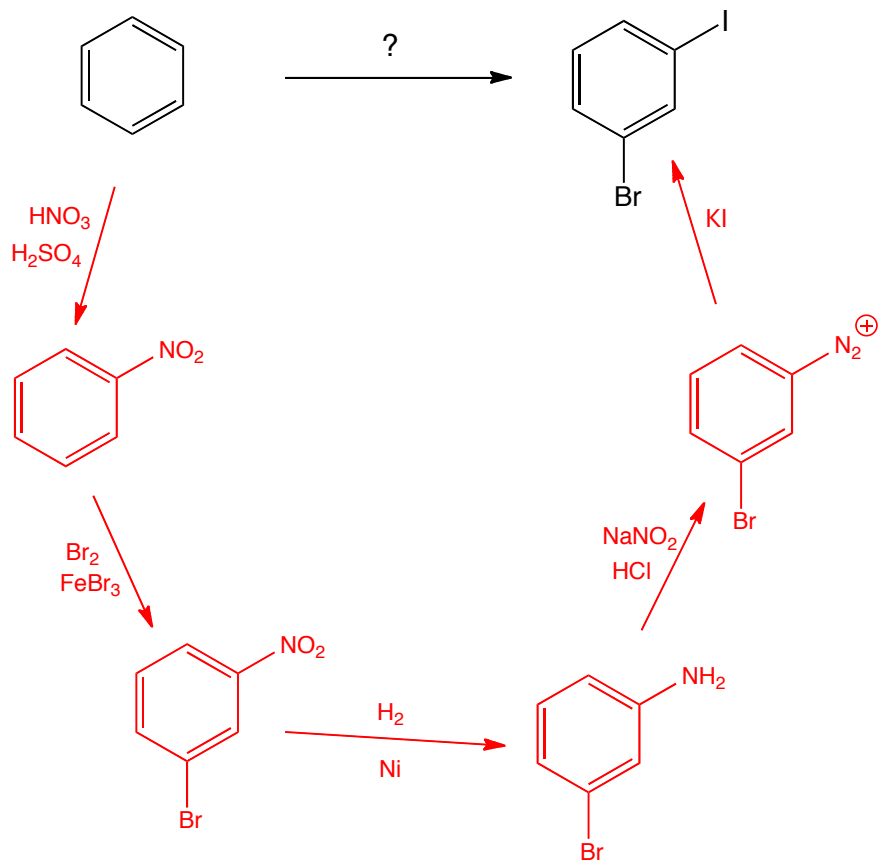


3) H_3O^+ / heat

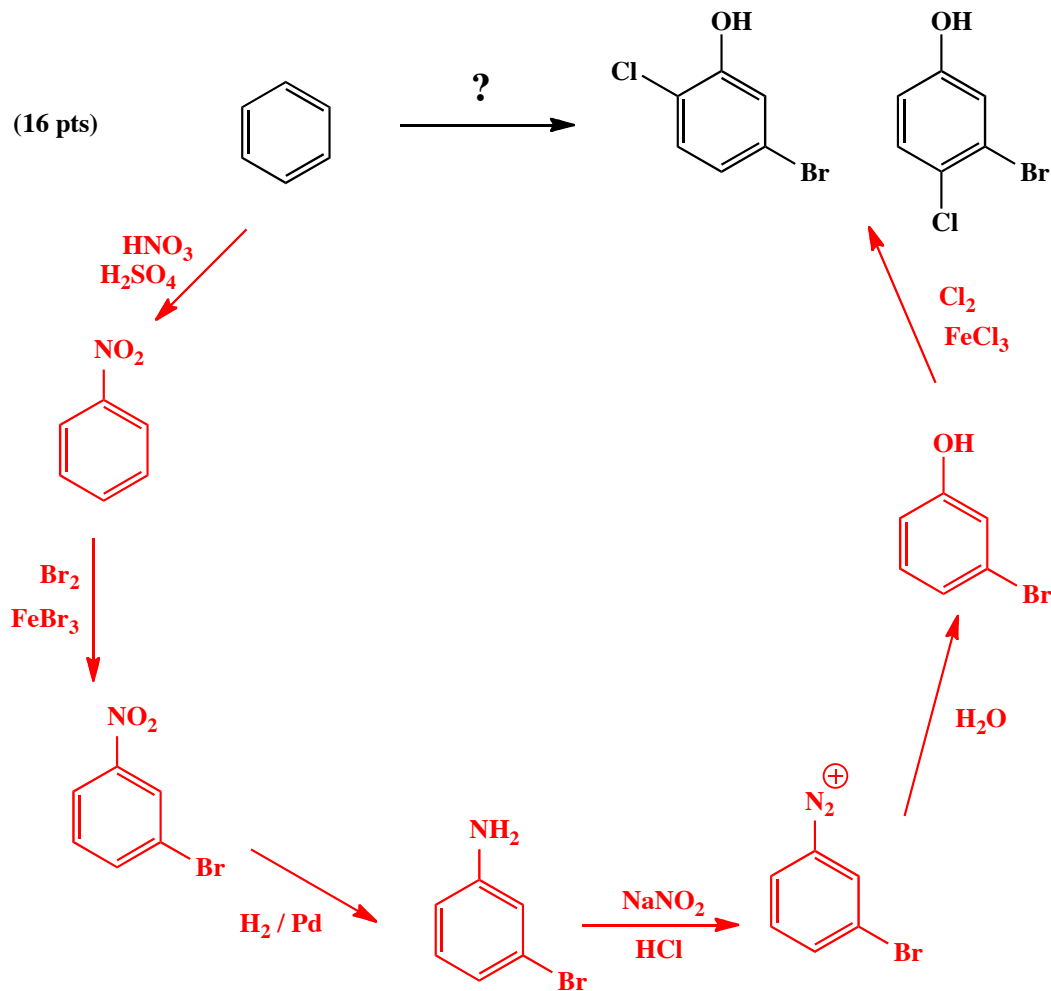


Malonic ester synthesis

12. (13 pts) Show reagents and intermediates synthesized along the way that allow you to produce the product from the given starting material. Assume you can isolate either the ortho or para product in pure form, even though both are usually produced together.



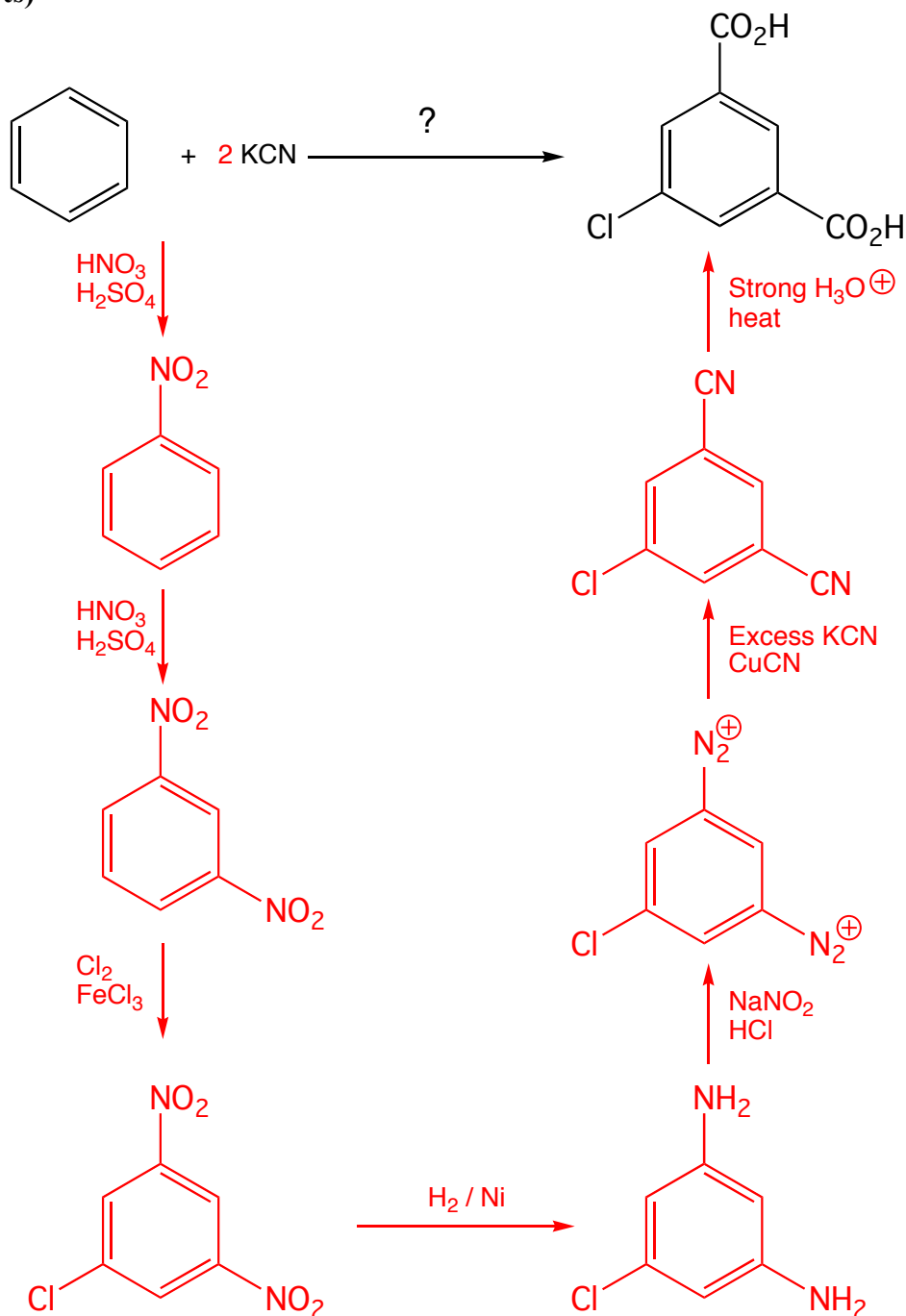
12. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule! **NOTE: For this one, you are not allowed to separate complex mixtures along the way and pull out just the isomers you want. In other words, the product isomers shown must be the only predominant isomers you make during your synthesis.**



Recognize that the last reaction had to be the chlorination reaction of the meta bromophenol. This is because we see both the ortho and para chlorination products. **Recognize** that both the OH and Br groups of meta bromophenol are ortho/para directors, so their meta relationship must derive from nitrobenzene, followed by the bromination reaction, followed by the Mr. Bill reaction and conversion to the phenol with H_2O .

15. Show reagents and intermediates synthesized along the way that allow you to produce the product from the given starting material. Assume you can isolate either the ortho or para product in pure form, even though both are usually produced together.

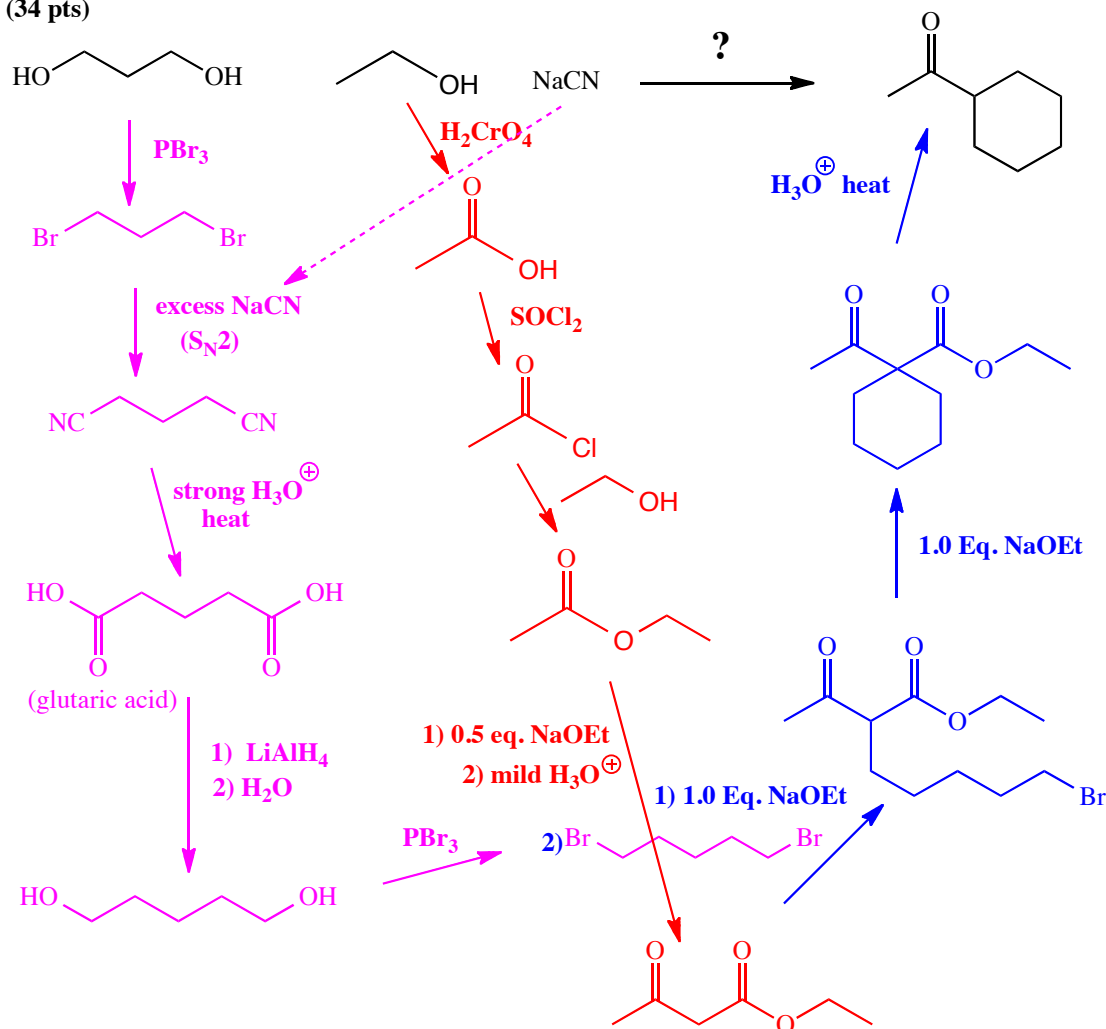
(19 pts)



Note that the reaction with Cl_2 and FeCl_3 could be carried out as the step shown, or following addition of the two cyano groups or even as the very last step starting with the diacid.

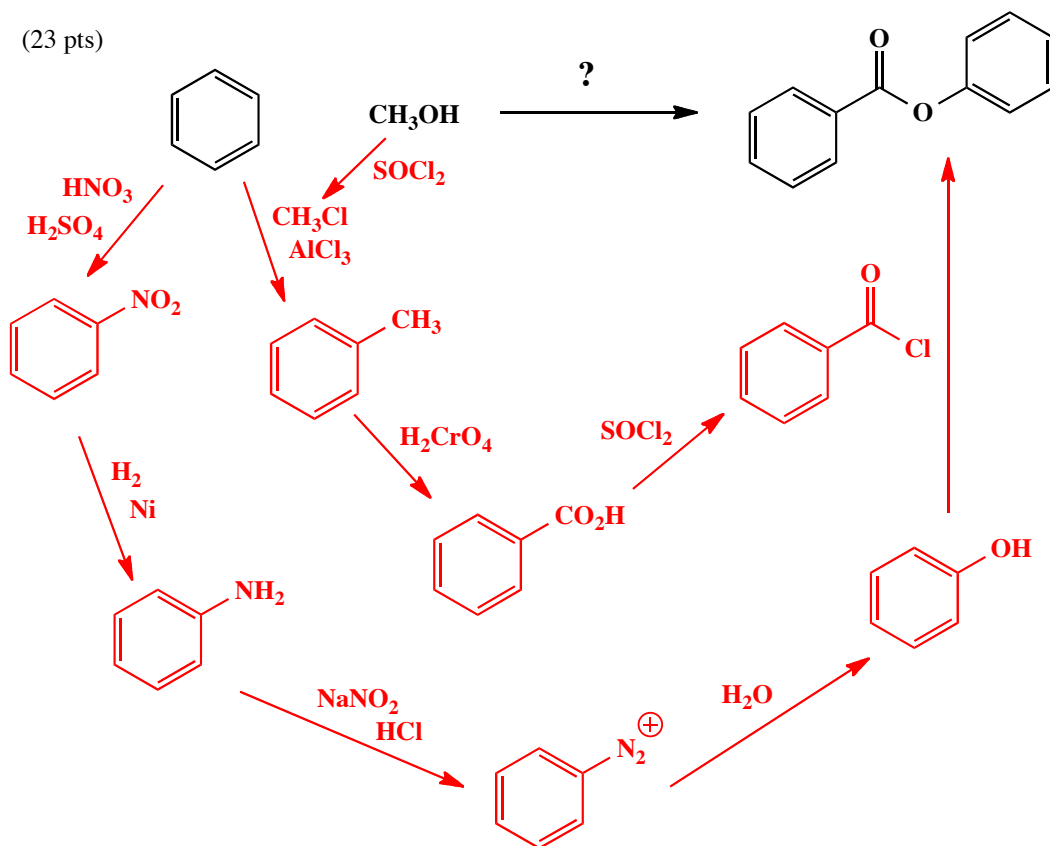
13. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule! Note, for these last two, you might not need to use all three starting materials

(34 pts)



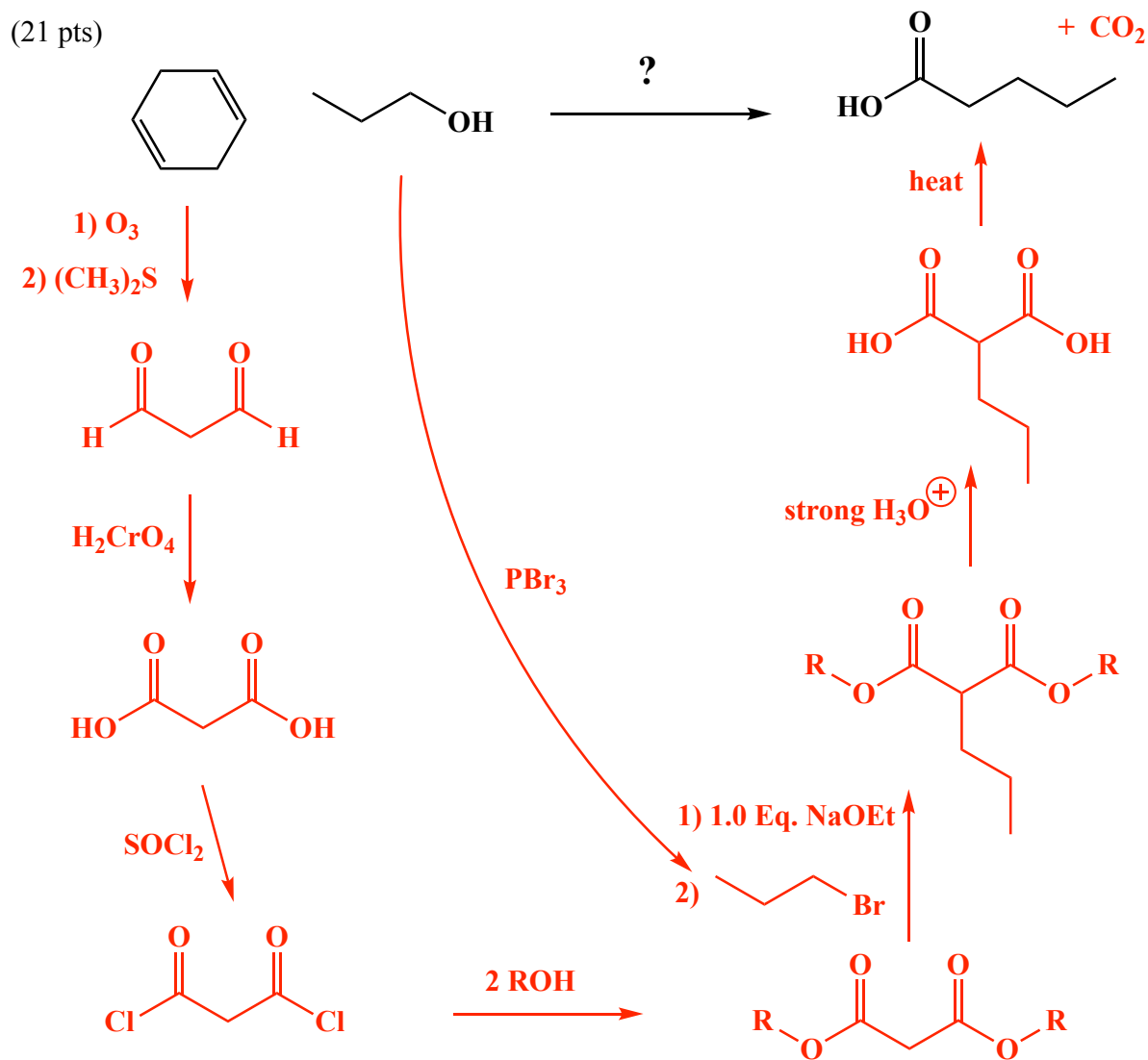
Recognize the product as coming from an acetoester synthesis (methyl ketone is the KRE). The tricky part of this one is **recognizing** that the ring comes from alkylation of ethyl acetoacetate in two sequential steps by 1,5-dibromopentane. **Recognize** that the ethyl acetoacetate comes from the Claisen reaction of ethyl acetate, which in turn comes from ethanol and acetic acid, the latter of which comes from chromic acid oxidation of ethanol. **Recognize** that the dibromopentane can be derived by converting the propane diol to the dibromide, $\text{S}_{\text{N}}2$ reaction with NaCN followed by hydrolysis to give glutaric acid, reduction to give 1,5-pentanediol, and finally conversion to the desired 1,5-dibromopentane using PBr_3 .

14. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting material or starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule!



Recognize the product as an ester, that must come from benzoyl chloride and phenol. Benzoyl chloride comes from benzoic acid, which is made from benzene via Jones oxidation of an alkyl benzene such as toluene. The phenol is derived from a diazonium species, which is made in the usual nitration reduction sequence of reactions.

15. Using any reagents turn the starting material into the indicated product. All the carbons in the product must come from the given starting material or starting materials. Draw all molecules synthesized along the way. When it doubt, draw the molecule!



If you got this congratulations!!! Recognize the product as a substituted carboxylic acid that comes from the malonic synthesis. Notice that the three carbon piece can come from the propanol via reaction with PBr_3 to give the alkyl halide. Making a malonic ester is a little more challenging. The key is to recognize that ozonolysis of the starting 1,4-cyclohexadiene followed by Jones oxidation. Reaction with SOCl_2 followed by the starting propanol gives the required dialkylmalonate.