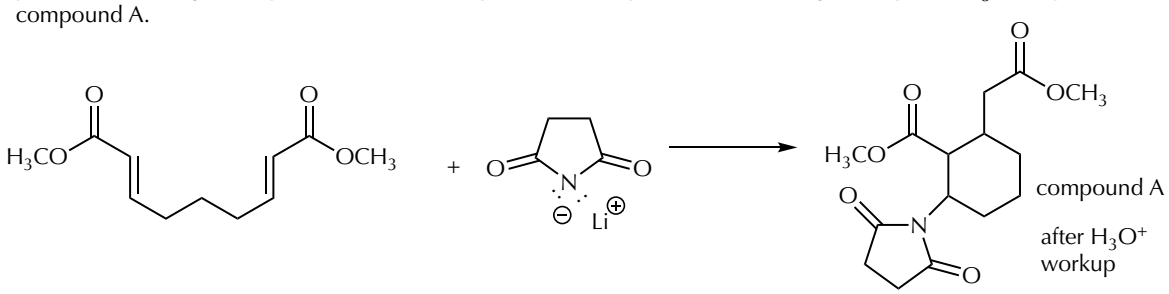
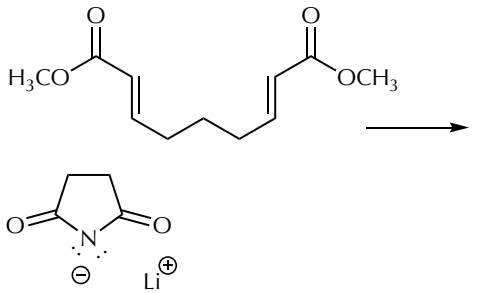
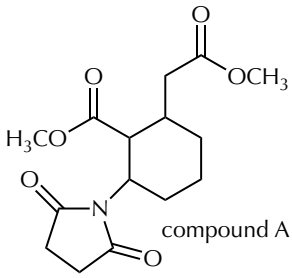
These questions do not appear in the book.

A. The following reaction involves two conjugate additions that proceed in separate steps. Show a curved arrow mechanism to explain the transformation. Include in your answer the charged structure that is made prior to protonation during workup, and also show the protonation step that occurs during workup with H_3O^+ to produce compound A.



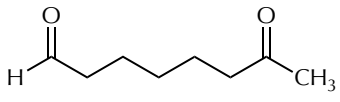




B. draw compound A with observed stereochemistry

B. The final conjugate addition occurs with a transition state that positions all of the substituents in the equatorial position. Using bold and dashed lines on the cyclohexane drawn in the box at right, predict the stereochemistry of compound A. Either enantiomer may be shown.

C. Predict the major product of the following reaction.



$NaOCH_2CH_3$

CH_3CH_2OH

+ H_2O

Chemistry 215 • Thinking in Blue • Week 09

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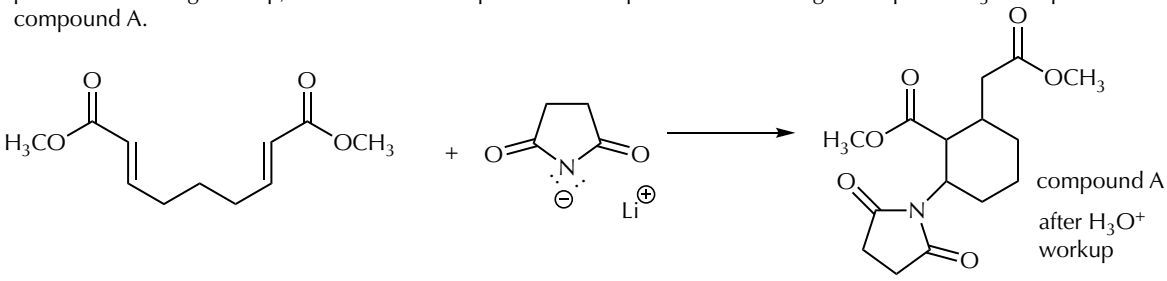
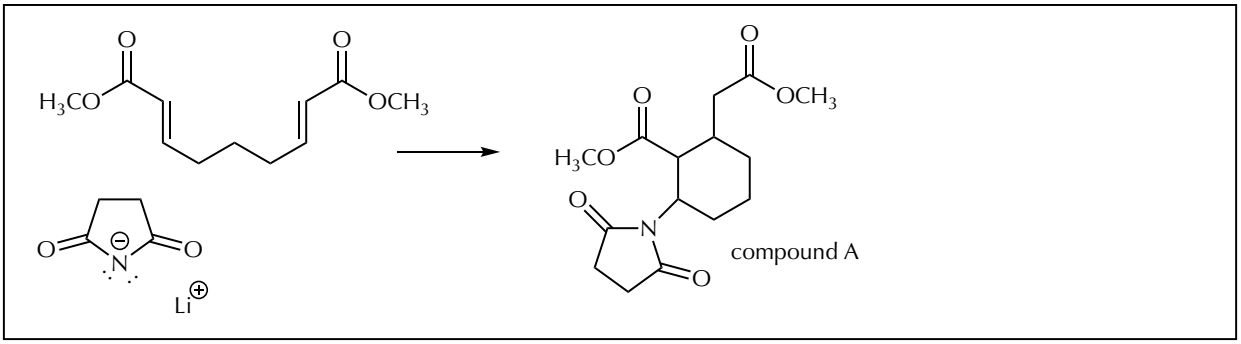
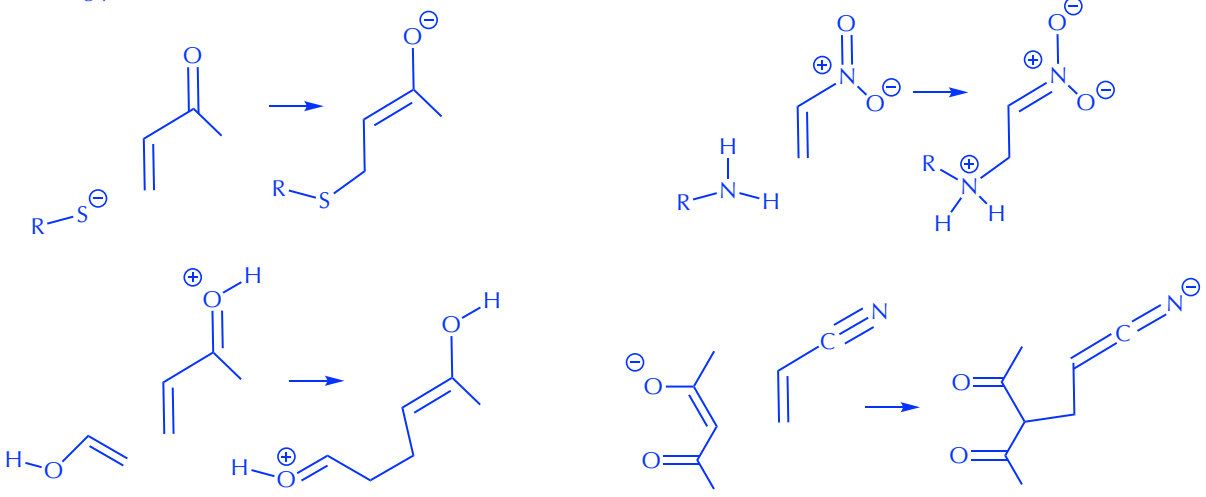




Once again, the critical identification is being provided here by the term "conjugate addition." Conjugate additions occur when nucleophiles add to the double bond of a conjugated carbonyl system (such as the one you get as the product in an aldol condensation reaction). The reaction is quite general, and many different EWG and nucleophiles can participate in a set of analogous reactions.

These are reactions that can occur under acid or base conditions, so the details of a mechanism need to be monitored accordingly.



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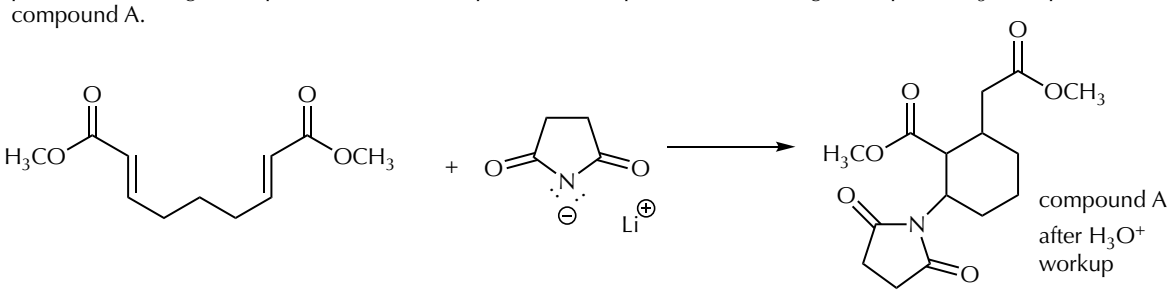
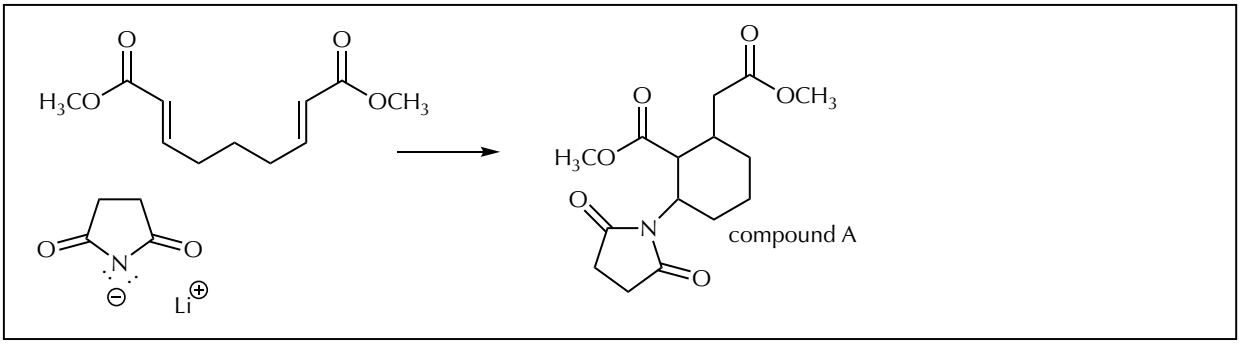
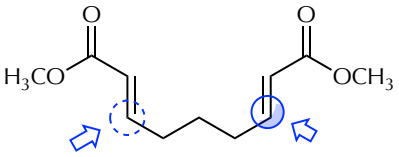
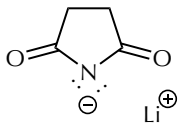




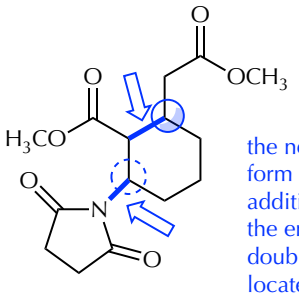
When starting materials and products are drawn quite differently, one of the things that one needs to do, mentally, is to make the correlation. Part of the identification process is not only to make the proper classification, but in a case such as this, to sketch out, in your head, the major relationships - to see the big picture. Just starting a mechanism by moving stuff around and hoping you get to the right place is not a useful strategy - particularly because a wrong move at the outset will derail the entire answer. In this question, deciding which atoms come from where and which bonds have formed is useful, because then it signals the direction to go in for the detailed mechanism. The reaction is anionic (basic) followed by a final protonation step (that information is included in the text of the question and in the equation).



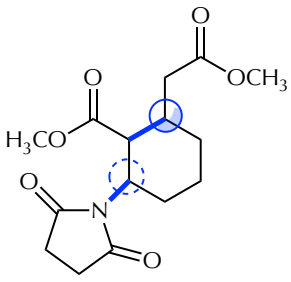
here I see a molecule with the possibility of two conjugate addition sites (as stated in the text, there are two additions)

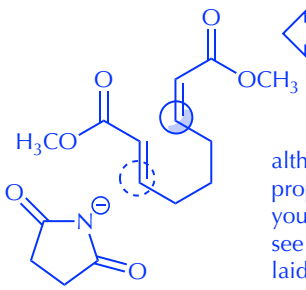


I have a single nucleophile that shows up once in the product



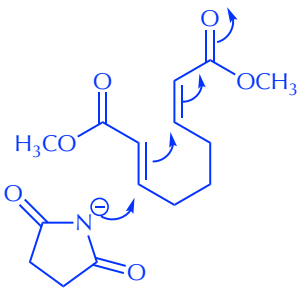
the new bonds that form in conjugate addition are where the ends of the double bonds were located





using a product's structure as a template for thinking about the starting material is common and useful

although this is not a proper mechanism, in your mind's eye you can see the sequence of steps laid out before writing anything



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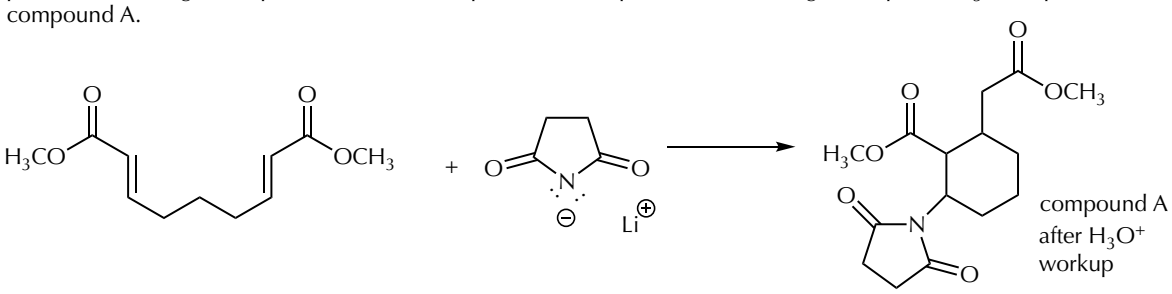
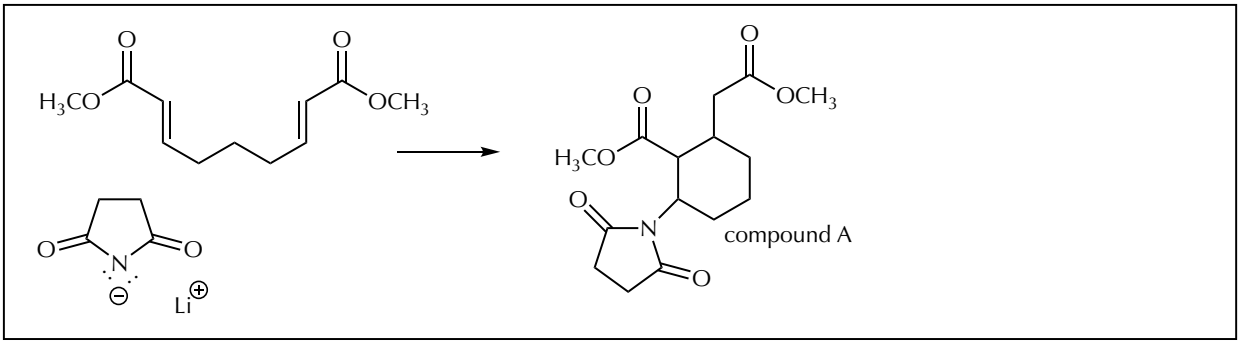
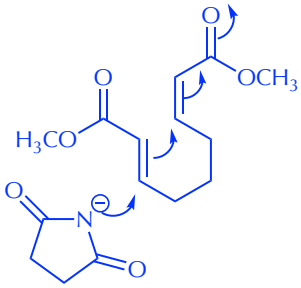
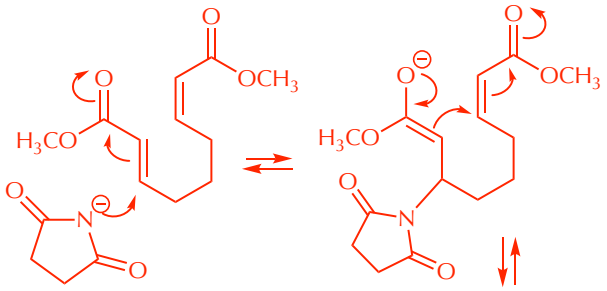






with this in mind, you can then lay down the individual steps while keeping the bigger picture to guide you; using the redrawn starting material in the shape of the product is extremely useful



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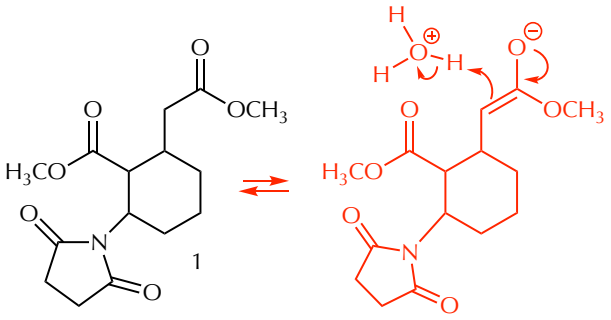
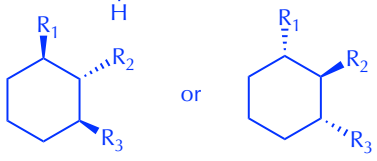
draw compound A with
observed stereochemistry

As an identification, this question asks: What is the relative stereochemistry of an all equatorial 1,2,3-trisubstituted cyclohexane?



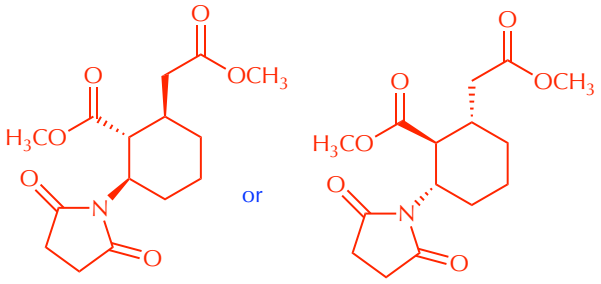
so…

means:



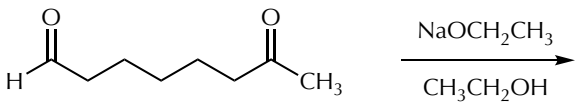
or

thus:



or

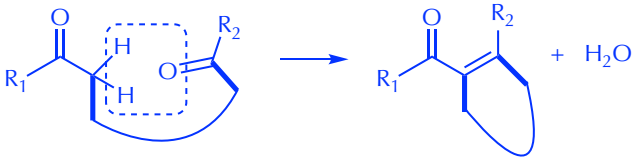
C. Predict the major product of the following reaction.



+ H_2O

The identification of this as an intramolecular aldol condensation reaction relies on (a) the two carbonyl components in one starting material, (b) the "+ H_2O" in the answer space, (c) just basic conditions (could have been acidic, but no exotic reagents), and (d) like it or not, knowing that you are in an exam related to enol and enolate chemistry.

As described previously, the general template or concept for an intramolecular aldol condensation reaction, when a detailed mechanism is not required, can be visualized according to the elements of water that are lost.



In this question, there are two sites of possible carbon acids that could give an enolate nucleophile (on either side of the ketone) as well as one site associated with the aldehyde.