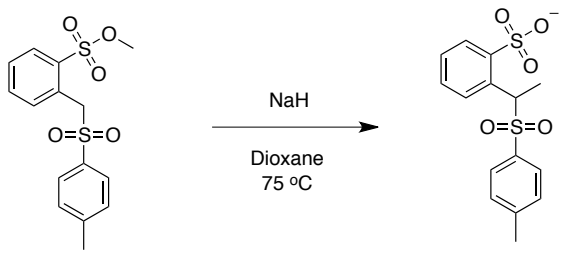
Reaction Mechanisms + Rearrangment Chemistry

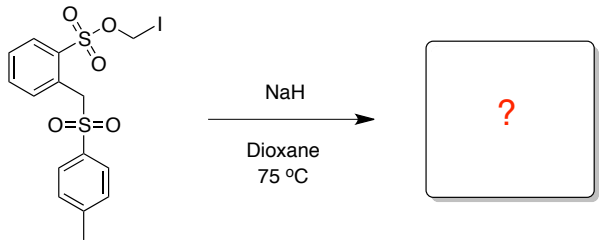
Determining reaction mechanisms conclusively is a difficult, if not impossible task. The reactions below have been studied extensively and work towards determining the mechanisms by which they occur has been undertaken at some length. Identify products where required and provide a reaction mechanism; including detail of how evidence for the proposed mechanism could be acquired.

1)



Reaction Mechanism?
Inter/Intramolecular?
How to determine this?

2)



Reaction Mechanism?
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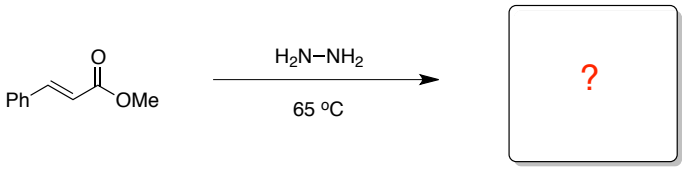
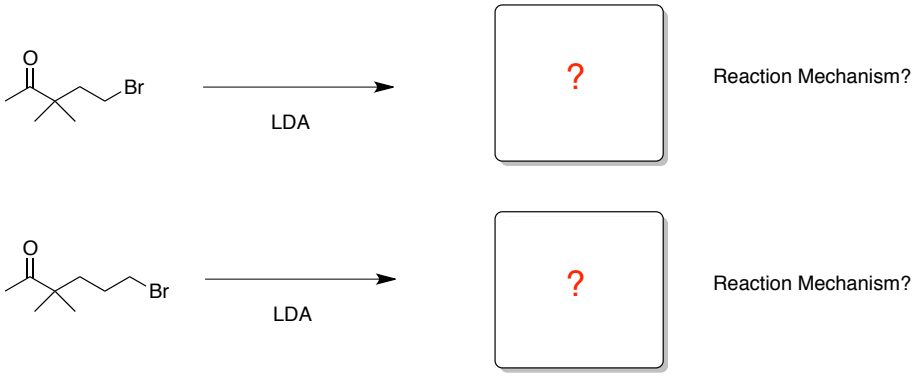
3)



Reaction Mechanism?
How to determine this?

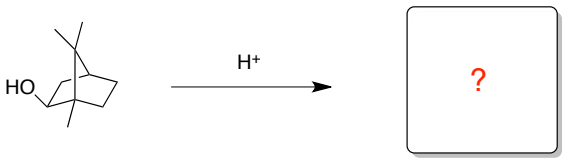
4)



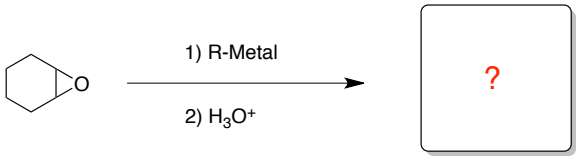
Rearrangement reactions

Reactions involving rearrangements are a useful addition to a synthetic chemists arsenal. These reactions are often overlooked as they are often not obvious when using a traditional disconnection approach. The reactions below all involve a rearrangement; identify the product (where required), propose a reaction mechanism and identify what features of the reaction (stability of intermediates, migrating groups, stereoelectronic features *etc.*) govern the mechanism by which these reactions proceed.

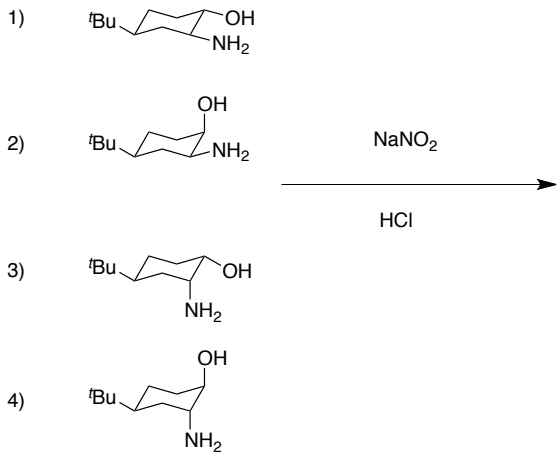
5)



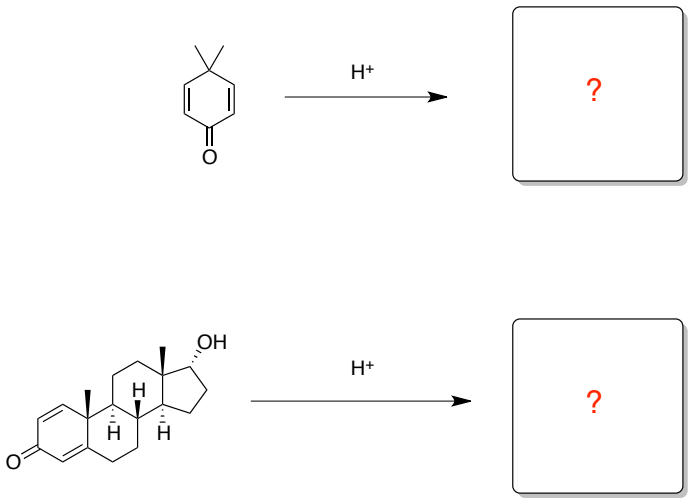
6) In the reaction below, does the choice of organometallic (R-M) effect which product is obtained? (*e.g.* Grignard *vs.* organolithium). Explain reasoning for this.



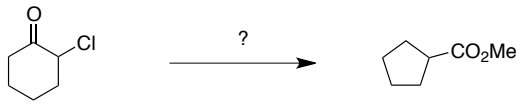
7) Do the substrates for the reaction below give the same product? If so why? If not, what determines the outcome of the reaction.



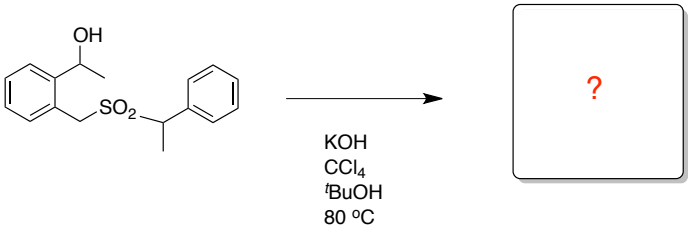
8) Identify the mechanism and product of the reaction below. What is the driving force for this reaction? The same reaction was utilised in the synthesis of a cholesterol derivative. What is the product of this reaction.



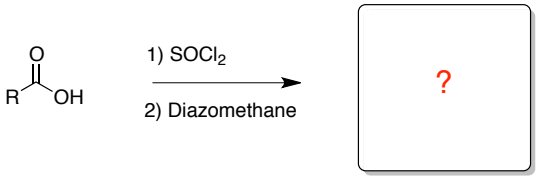
9) What reagent is required for the following transformation? Propose reaction mechanism and identify an isotopic method by which this could be confirmed. One proposed intermediate is cyclic; what is the mechanistic issue with the formation of this intermediate?



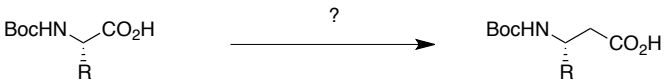
10) Identify the product of the following reaction and propose a mechanism:



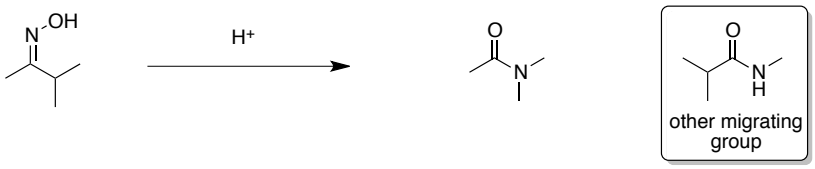
11) The reaction below is often used for the ring contraction of cyclic diazoketone substrates. However, it can also be used on carboxylic acid substrates. Identify the product and propose a mechanism for its formation.



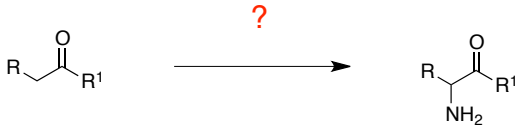
12) A similar reaction to the previous example is extremely useful in peptide synthesis for the formation of *β*-amino acids from α-amino acid derivatives. Identify the reagents required for this transformation and propose a reaction mechanism.



13) Identify the product from the reaction below and propose a mechanism for this transformation. What governs the migratory selectivity? How can the product resulting from migration of the other alkyl group be achieved? If this reaction is carried out on a symmetrical cyclic oxime (*e.g.* derived from cyclohexanone) what is the product? Does this affect the reaction mechanism?



14) Using a rearrangement, describe how the transformation below could be achieved in 3 steps. (*i.e.* not *via* catalytic α-amination).



15) **Just for fun: Do you think that the compounds below have been made? Are they stable if so? Are any of them aromatic? How would you make them?**