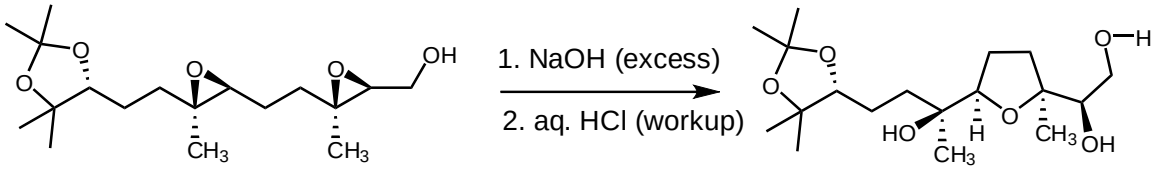
Problem 9



Ref. Y. Morimoto, T. Okita & H. Kambara, Angew. Chim. Int. Ed., 2009, 48, 2538-2541.

1. Draw all of the bonds at or near the reactive atoms in the starting materials

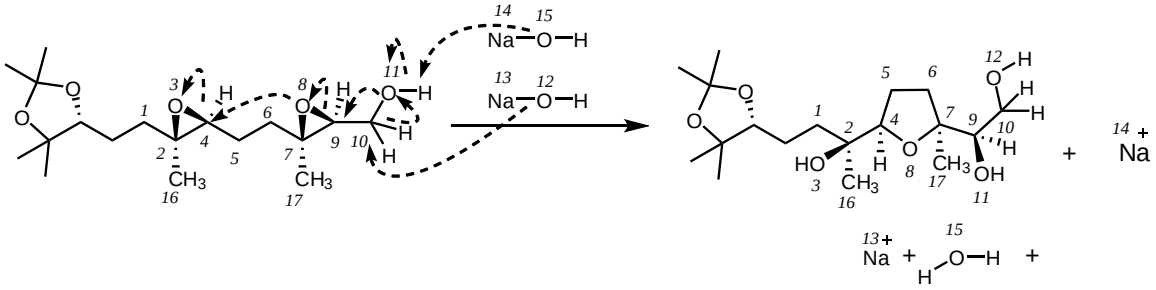
2. Draw all of the H-atoms at or near the reactive sites of the starting materials and the products

3. Balance the equation

4. Number the non-H atoms

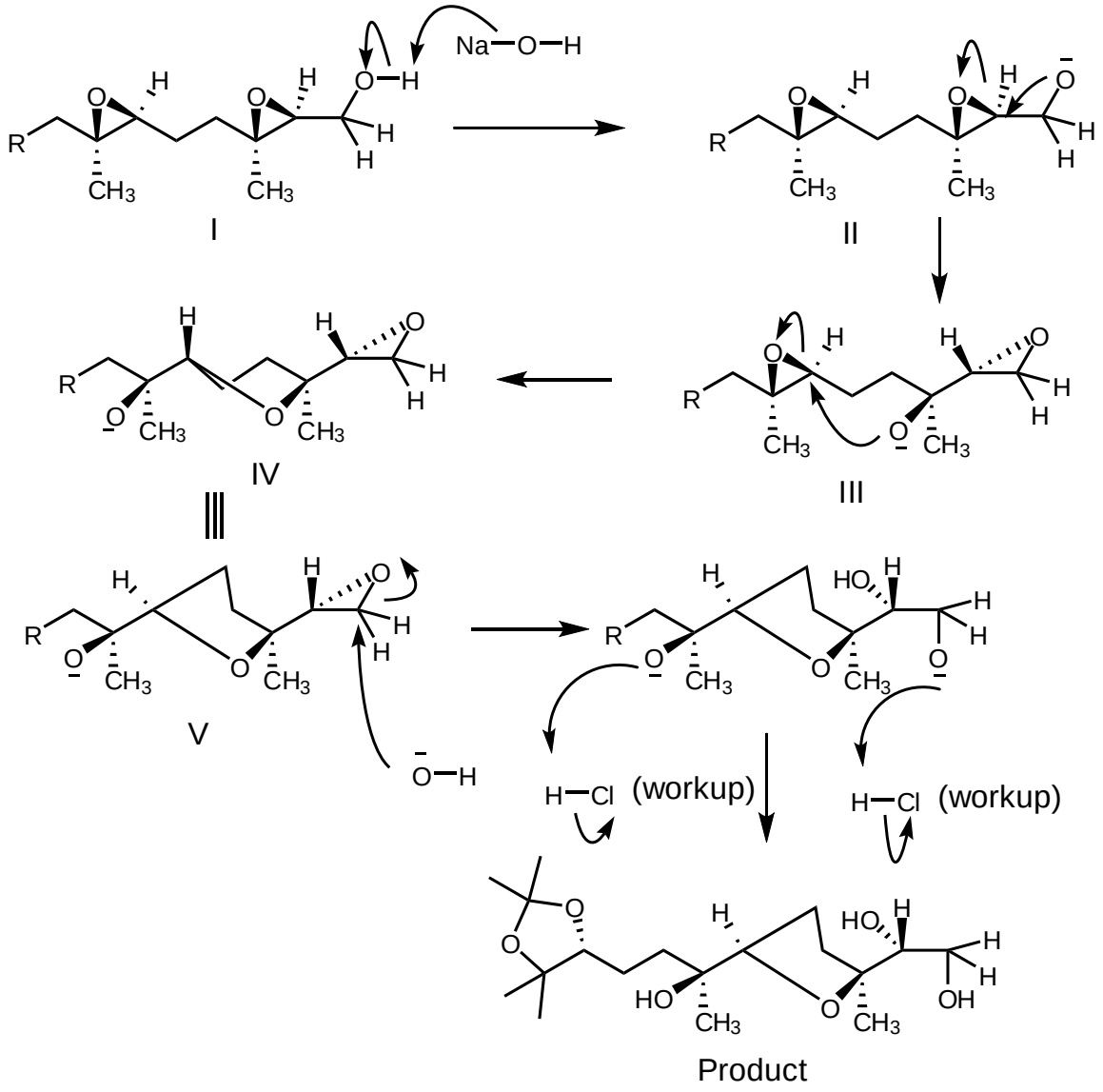
5. Identify bonds made and broken

Bonds made:3-H (workup), 4-8, 11-9, 10-12, 12-H (workup), 15-H
Bonds broken: 3-4, 8-9, 10-11, 13-12, 14-15.



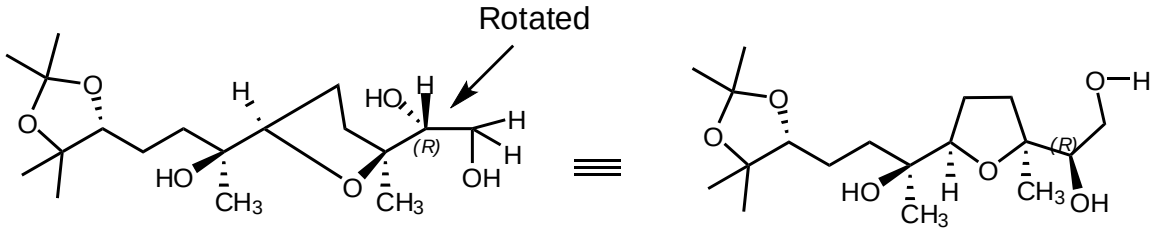
6. Conditions
Basic (does not generate strong acids)

Mechanism



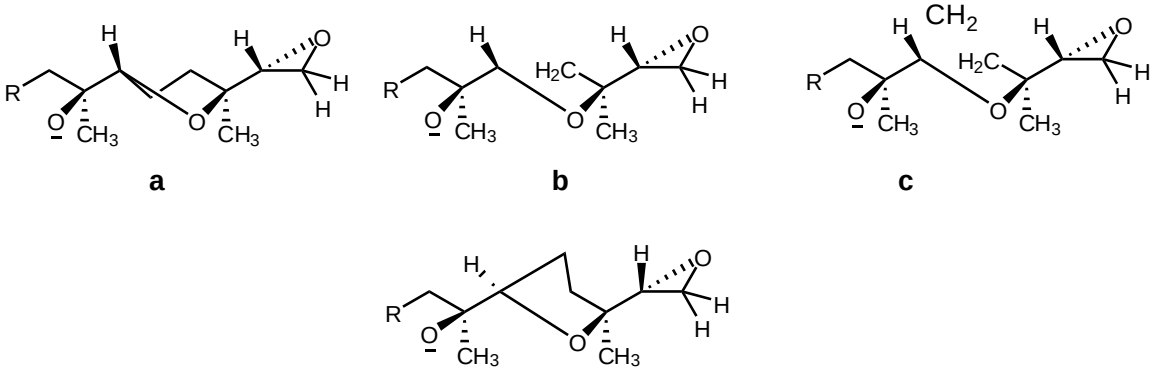
Discussion

1. The product looks different in the way it is drawn at the end. However, the two structures represent the same compound (see below). The arrow points to the C atom that is being rotated in the drawing on the right. Assignment of the absolute configuration on this C atom shows that both structures are the same compound. So, whenever you are in doubt about bond rotation, assign R/S. The two structures should have the same absolute configuration.



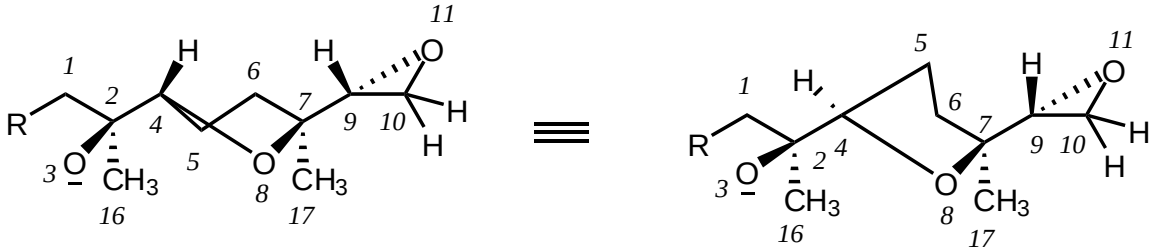
2. It is easier to make the bond first and then arrange the structure. For example, in the above mechanism, it was easier to make the O-C bond without arranging the structure of III to arrive at structure IV. Structure IV was then redrawn as V. Structure V is the better representation than IV as it does not have any overlapping bonds.

3. One easy way for the conversion of structure IV to V is as follows. First redraw structure IV (a) then erase the overlapping bond and the CH_2 group (b). Redraw the CH_2 group where it will not be overlapping with other bonds and groups (c). Attach the erased bonds to the CH_2 group (d). This procedure can be applied whenever a structure with overlapping bonds needs to be redrawn.



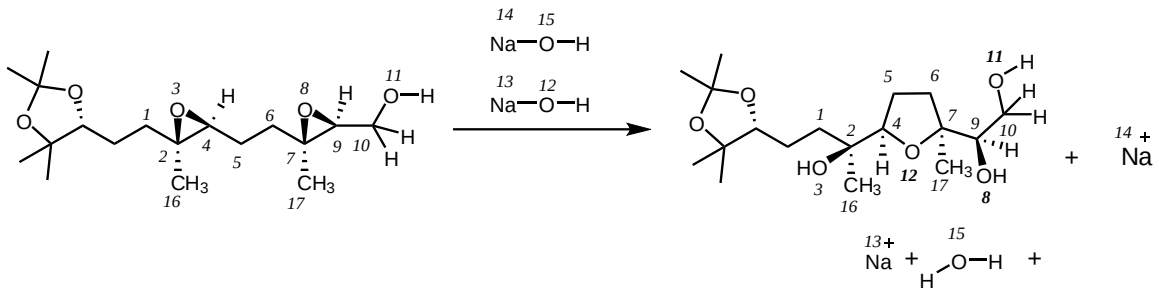
a **b** **c** **d**

4. It is easy to forget about some carbons during the redrawing. So, it is better to check the two structures by numbering them.

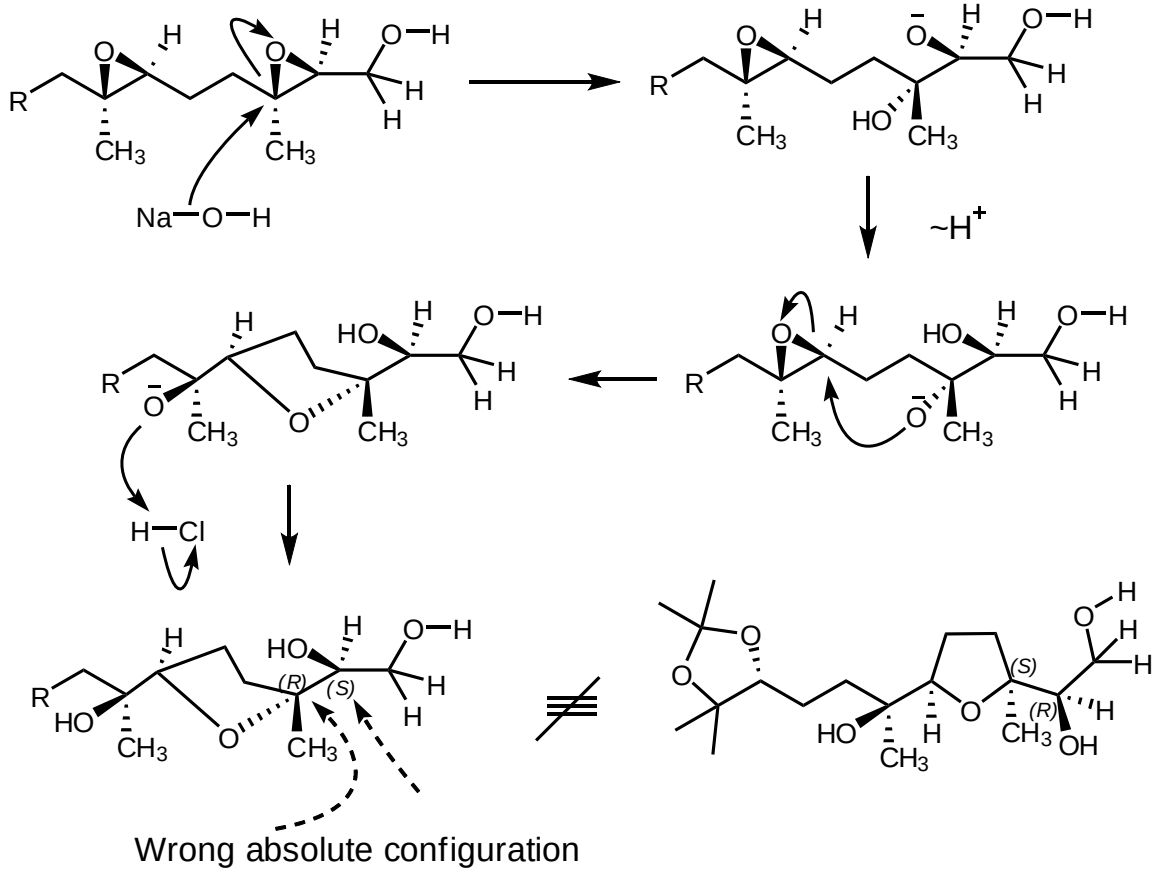


Notice that at position 4, the H atom is drawn with a thick wedged line in the left hand structure. It is drawn as dashed wedged line in the structure on the right. If we do not do this then the absolute configuration at C-4 will be inverted. Be cautious whenever you are redrawing the bonds and assign absolute configuration in both drawings at the centers that have been rearranged.

5. In a challenging problem like this, the numbering of a product could be tricky. However, if you draw all the H atoms near the reactive site and look for the easily identifiable groups, the numbering will become easy for most atoms. In this problem, 16 and 17 can be easily identified. These groups can point to the positions 2, 4, 5, 6, 7, 9 and 10. Positions 8, 11 and 12 can still be misidentified and one may arrive at the following numbering.



As such, one may draw the following mechanism.



However, this mechanism will provide the wrong diastereomer. As indicated, this compound will have an apposite absolute configuration at the two stereogenic C atoms. Such a mechanism must be incorrect. An incorrect mechanism is an indicator that the product has been numbered incorrectly.