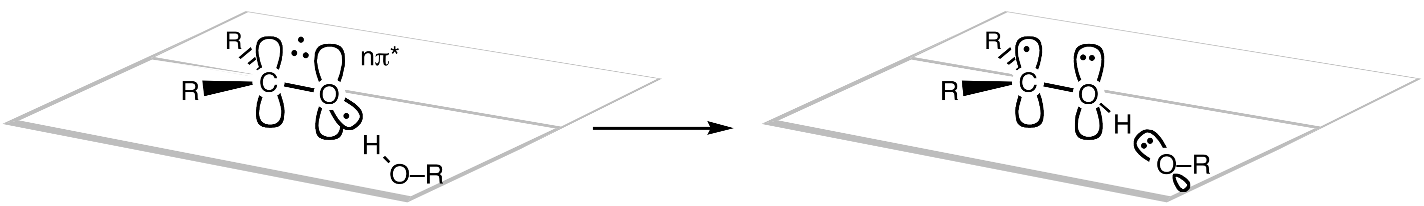
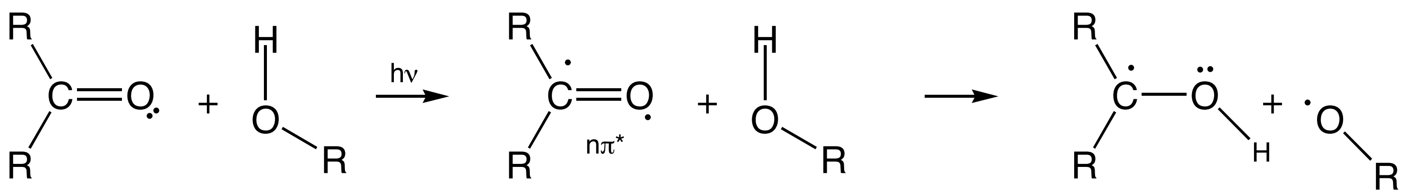
Both the $^1n\pi^*$ and $^3n\pi^*$ states of ketones are known to undergo hydrogen atom abstraction from an alcohol (even though singlet states are usually more likely to undergo 2-electron reactions). This is one reaction where it is becoming a little more difficult to analyze using orbital symmetry. Also, unlike the other reactions we have looked at, it is not a concerted reaction. If there is no symmetry element that is maintained during the ocurse of a reaction, then no meaningful orbital correlations can be drawn. In this example, we make the assumption (not a bad assumption!) that the ketone, and the H–O bond lie in the same plain, otherwise the analysis will not work. In this case, the preserved symmetry element throughout the reaction is the plane that contains the reactants.

Start by looking for the overall "big picture" of what has happened. As a result of excitation, a new O–H bond is formed using the single non-bonding electron on the oxygen of the ketone and one of the electrons in the original H–O bond. The pair of electrons comprising the C=O π bond become a non-bonding pair on oxygen, and the electron in the π* orbital becomes a single electron on carbon. of course, we can't actually track individual electrons in this fashion, but this thinking indicates where to go next.





Generate a list of the important orbitals of the reactants (those containing electrons that are actually involved in the reaction), and order them energetically. Do the same for the product. Analyze the orbitals according to the symmetry element (plane). This is started for you on the next page, complete the orbital correlation diagram. Correlate orbitals of the same symmetry and which are *obviously related to each other*. For example, the n orbital on oxygen is the atomic orbital on oxygen that is used to make the new O–H bond.

A state correlation diagram for this reaction has been started for you on the last page of this homework assignment. Assign state symmetries by multiplying the symmetries associated with the electrons involved in each case. Remember that S x S = S, S x A = A, and A x A = S. Assign zero-order state correlations based on symmetry *and* orbital assignments (make sure that the orbitals transform appropriately for each state). Note that only 4 product states are given, one of your reactant states correlates with an even higher energy product state that is not shown.

Include first-order avoided crossings. Crossings between states of different symmetry but same spin may avoid under these conditions, states with different symmetries and different spins will not undergo avoided crossing.

Draw a reaction energy diagram for the singlet reaction and the triplet reqaction based on your correlation diagrams. Make suggestions as to adiabaticity and reaction efficiency.