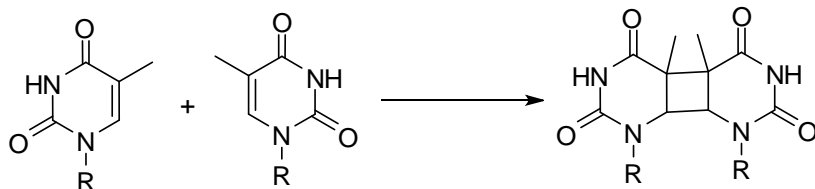


1. Skin cancer is frequently the result of UV damage to the DNA in skin cells. One important reaction that occurs to initiate carcinogenesis is the photochemical dimerization of two thymine molecules.



thymine

thymine dimer

Answer the following questions based on course discussions to date.

a) What makes the thymine alkene good at absorbing UV radiation?

b) Assuming a *syn addition*, molecular orbital analysis of the cycloaddition reaction between the two alkenes in thymine suggests the reaction will not work. Draw the alkene molecular orbital diagram (do NOT include the conjugated C=O) and explain why the reaction between the two alkenes is symmetry forbidden.

c) Show the molecular orbital diagram if UV absorption leads to electron excitation and the promotion of one electron in the alkene molecular orbitals. Label the HOMO of the resulting molecular orbital diagram.

d) This photochemical excitation allows the dimerization reaction to occur, i.e. the reaction is now symmetry allowed. Briefly explain.

2. The chemicals used in sunblock attempt to absorb UV radiation and reduce the incidence of carcinogenic photochemical reactions. As you might expect this often involves the use of chemicals with highly conjugated systems. In particular, molecules that resonate and form the quinone system shown below are good sunblocks. Using resonance, show how two popular sunblock ingredients oxybenzone and para-aminobenzoic acid have a quinone-like resonance form. Be sure to include curved electron flow arrows to indicate how you developed your resonance structure.

