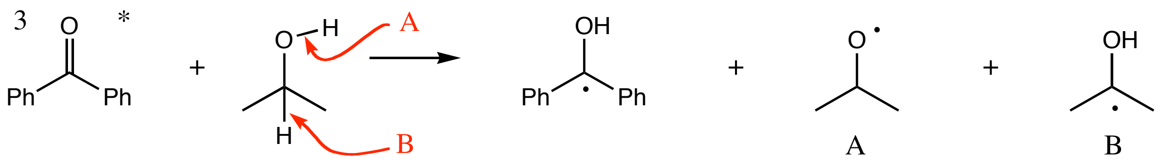
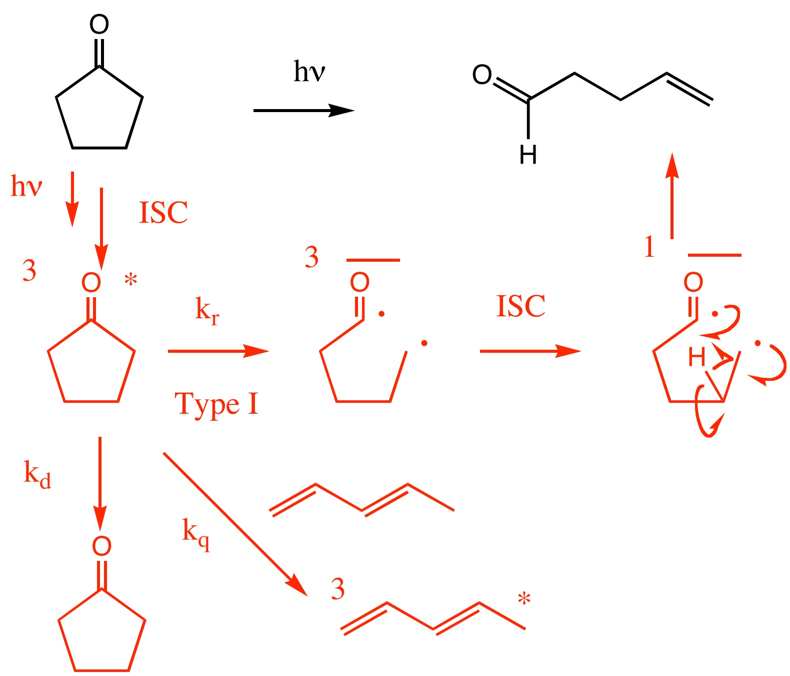
CHM 598, Photochemistry, Spring 2005, Homework 6, my answers!

**Question 1.**

The choice is between breaking bond A or bond B. Bond A is stronger than bond B for 2 reasons. First the oxygen is more electronegative than carbon, which means that the electrons in the O-H bond are lower in energy than in the C-H bond. Also, the radical formed by breaking bond B is resonance stabilized. Thus, product B, formed by breaking bond B is the more likely product.




**Question 2.**



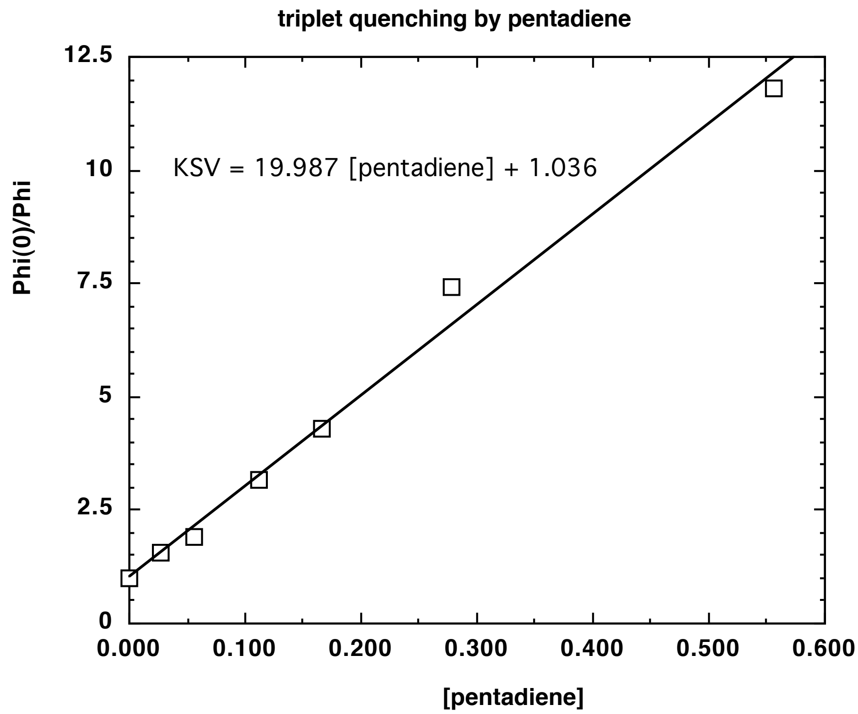

$$\Phi_{prod} = \frac{k_r}{k_r + k_d} * X$$ (X = scaling factor because yield is given in arbitrary units)

$$\Phi_{prod}^{Q} = \frac{k_r}{k_r + k_d + k_d [Q]} * X$$ (same X and here, Q = pentadiene))

$$\frac{\Phi_{prod}}{\Phi_{prod}^{Q}} = \frac{\cancel{k_r X}}{k_r + k_d} \quad \frac{k_r + k_d + k_d [Q]}{\cancel{k_r X}}$$

$$\frac{\Phi_{prod}}{\Phi_{prod}^{Q}} = \frac{k_r + k_d + k_d [Q]}{k_r + k_d} = 1 + \text{tau}\, k_d [Q]$$

tau (lifetime of triplet) = $1 / k_r + k_d$




$KSV = tau\ k_d$

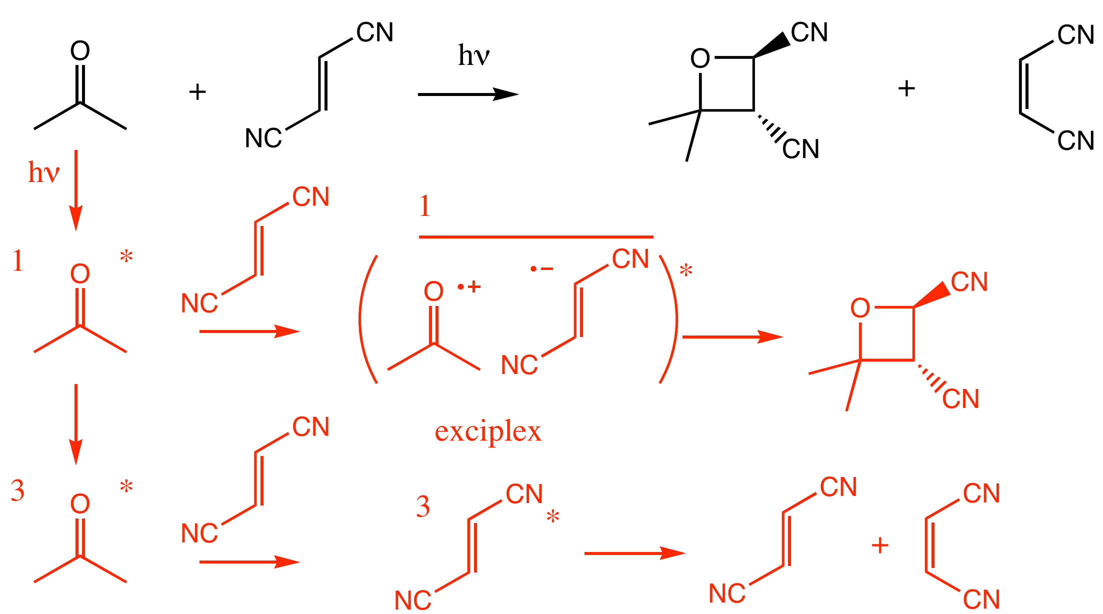
assume $k_d = k_{diff} \sim 1 \times 10^{10}\ M^{-1}\ s^{-1}$

therefore $tau = 19.99\ ./\ 10^{10}\ M^{-1}\ s^{-1}$

tau = 1.99 ns

**Question 3.**

At high concentrations, the alkene can intercept the short-lived excited singlet state. At lower concentrations, the singlet intersystem crosses to the longer-lived triplet, which is then intercepted by the alkene (check notes for detailed mechanisms).



**Question 4.**

This is a Type II reaction, X is the 1,4 triplet biradical. This is the reason it is not quenched by diene. It is, however, quenched by dimethylviologen. The product shown is one-electron reduction of the viologen. The other product must then be oxidized. The obvious electron to remove is that next to the oxygen, since the cation product is resonance stabilized.