RADICALS Fall 2016 **TWQ 3 (25points)** **Name**_____

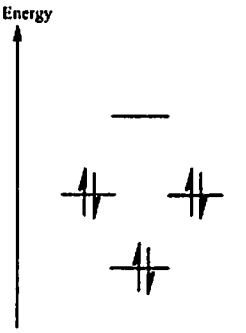
1-2) Photochemistry is dominated by two main rules. (One deals with the geometries of ground and excited states – the other deals with electron spin inversion upon excitation). State these two rules.

3) What is meant by the term CHROMOPHORE ?

4) What does the WAVELENGTH of absorption (in a UV Absorption spectrum) give you information about?

5) What does the ABSORPTION COEFFICIENT (ε) give you information about?

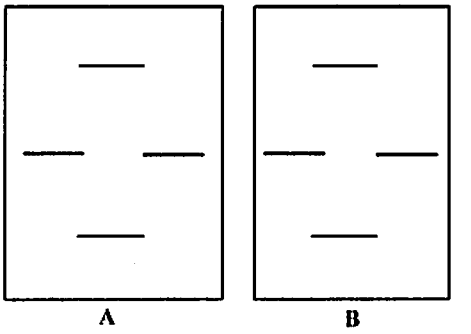
A section of the molecular orbital diagram for acetone is shown to the right:



6) Label the levels as **n**, π, and π^*

7) What does **n** stand for (or mean)?

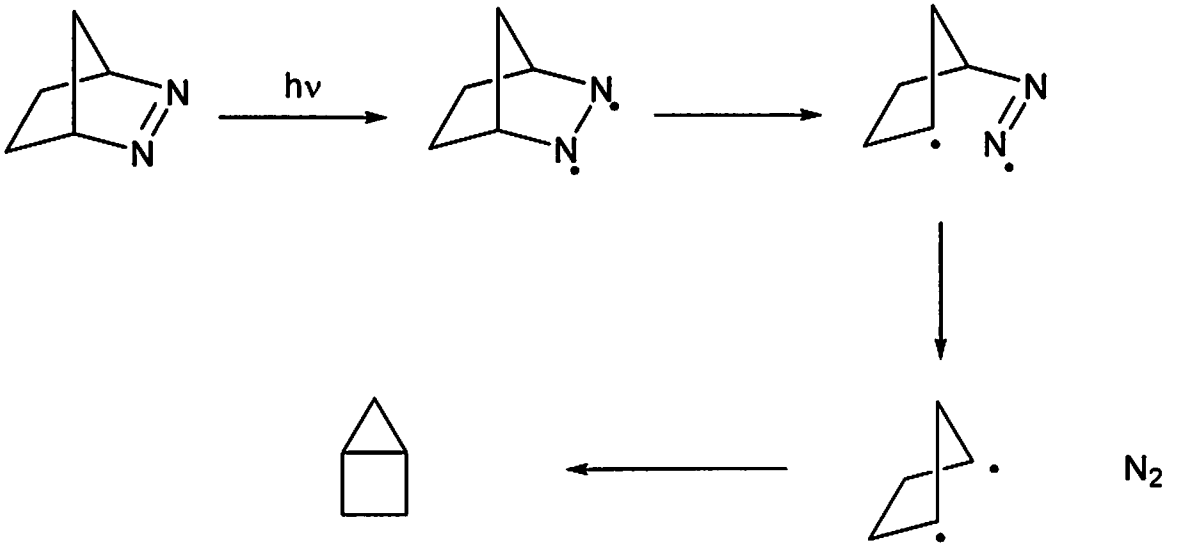
8) What is the meaning of the asterisk (*) ?



9) Draw in box A the electrons after an allowed n→π^* transition.

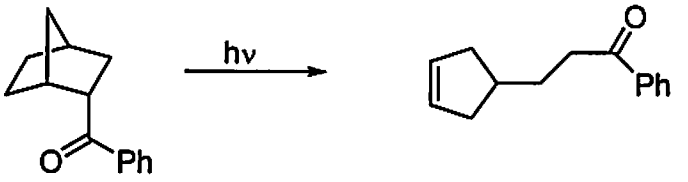
10) Draw in box B the electrons after an allowed π→π^* transition.

11-15) Provide the curly arrows that describe the following electron movement in this photochemical extrusion of Nitrogen.

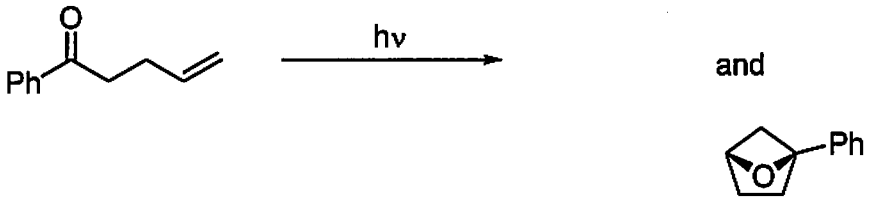


16-25) Write the mechanism for either problem A or problem B.

PROBLEM A

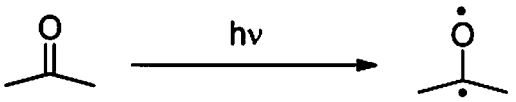


PROBLEM B



****Up to 2 bonus points****

Photochemical excitation of carbonyl compounds is typically via n→π* transition, and we often represent the photochemically excited state as the below diradical.



State two limitations (or drawbacks) of using a Lewis structure approach to represent the excited state.

RADICALS Fall 2016 **TWQ 3 (25points)** **Name** TWQ 3

1-2) Photochemistry is dominated by two main rules. (One deals with the geometries of ground and excited states – the other deals with electron spin inversion upon excitation). State these two rules.

(1) The initial excited state will have the same geometry as the ground state, (since excitation is faster than vibration).

(2) Electrons do not undergo spin inversion at the instant of excitation. (Conservation of agular momentum means singlet ground state → singlet excited state).

3) What is meant by the term CHROMOPHORE ?

A section of the molecule that absorbs the light energy leading to electronic excitation.

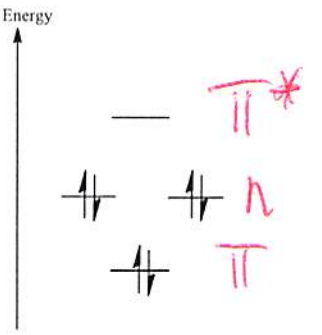
4) What does the WAVELENGTH of absorption (in a UV Absorption spectrum) give you information about?

λ is related to the energy of the radiation which is related to the energy levels' difference (which is related to the specific orbitals in the transition).

5) What does the ABSORPTION COEFFICIENT (ε) give you information about?

For electrons to move from one orbital to another, their wavefunctions must overlap. This amount of overlap is related to the "allowedness" of a particular transition, and is quantified by the Absorption Coefficient. (Large ε means 'more allowed').

A section of the molecular orbital diagram for acetone is shown to the right:



6) Label the levels as **n**, **π**, and **π***

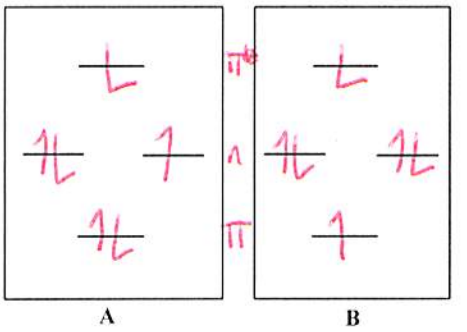
7) What does **n** stand for (or mean)? Non bonding electrons

8) What is the meaning of the asterisk (*) ?

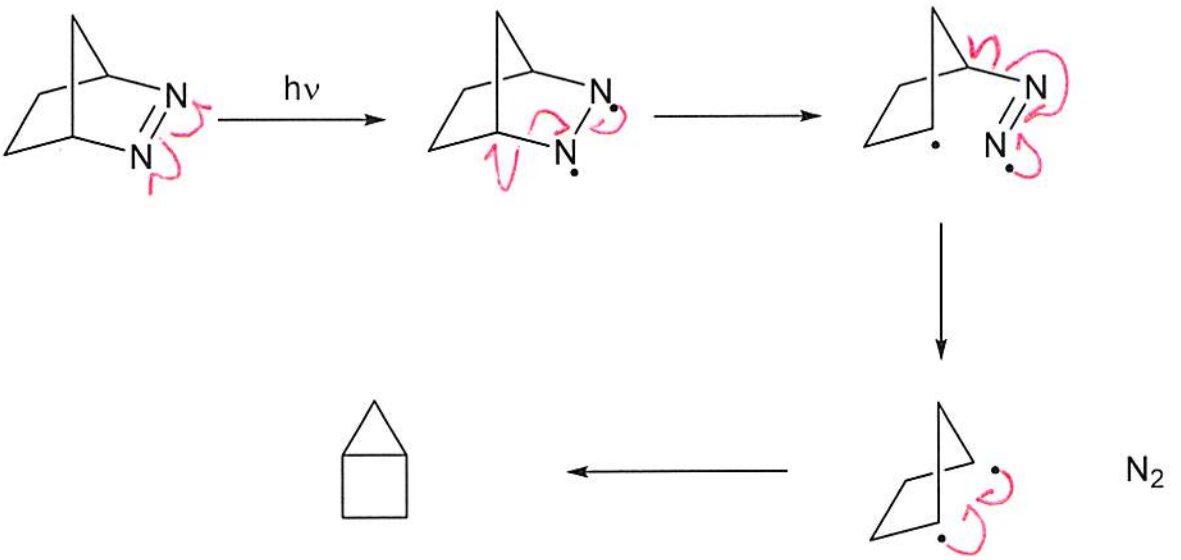
Anti-bonding (Molecular orbital)

9) Draw in box A the electrons after an allowed n→π* transition.

10) Draw in box B the electrons after an allowed π→π* transition.

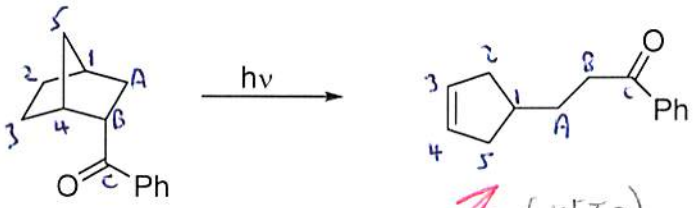


11-15) Provide the curly arrows that describe the following electron movement in this photochemical extrusion of Nitrogen.



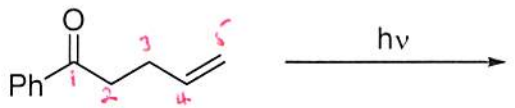
16-25) Write the mechanism for either problem A or problem B.

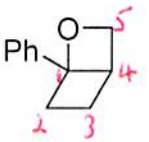
PROBLEM **A**



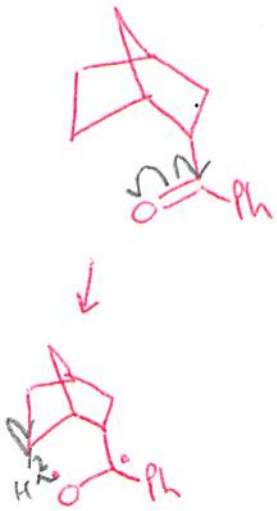
(KETO)

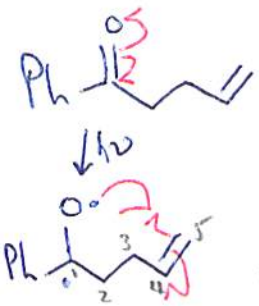
PROBLEM **B**



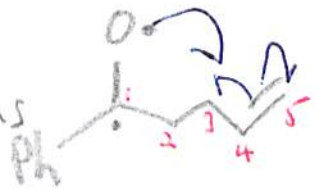


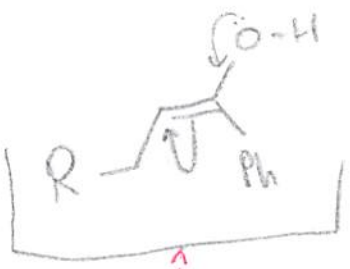
and

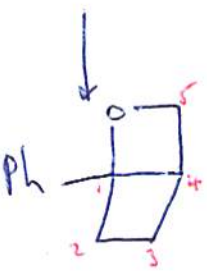


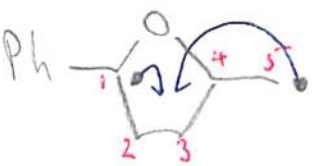


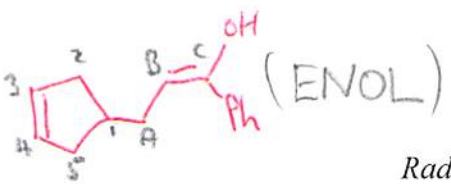
Same as











(ENOL)

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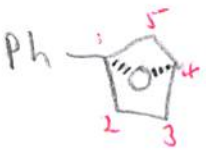

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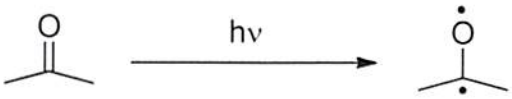

State two limitations (or drawbacks) of using a Lewis structure approach to represent the excited state.

(1) The lewis structure implies movement (excitation) of the π electrons, whereas it is the n (lone pair) electron that moves.

(2) It provides no information about the spin multiplicity of the excited state (meaning singlet or triplet state).