

No Crib for Analytical Cume

Written by Professor Kenttämäa

No Crib for Biochemistry

Cume

Written by Professor Hrycyna

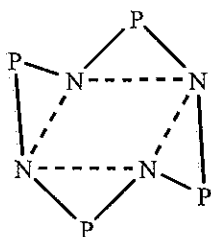
Inorganic Cumulative Exam *Crib*

January 14, 2006

1. (20 pt) Identify point symmetry group for each of the following molecules/ions.



(a)
cyclooctatetraene
 D_{2d}



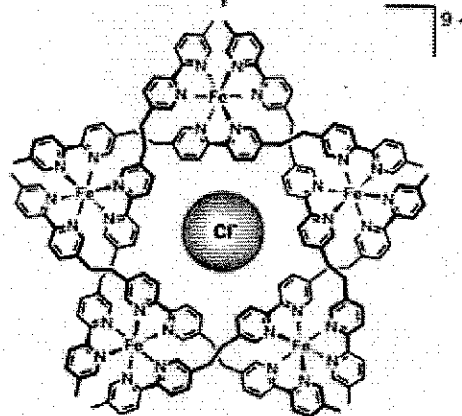
(b)
 C_{2h}

(c) cyclopropane D_{3h}



+ 5 FeCl₂

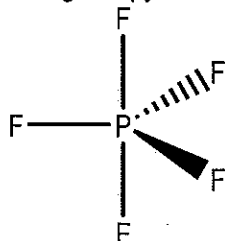
Ethylene Glycol,
170 °C



(d) Assign the complex ion at the bottom
 D_5

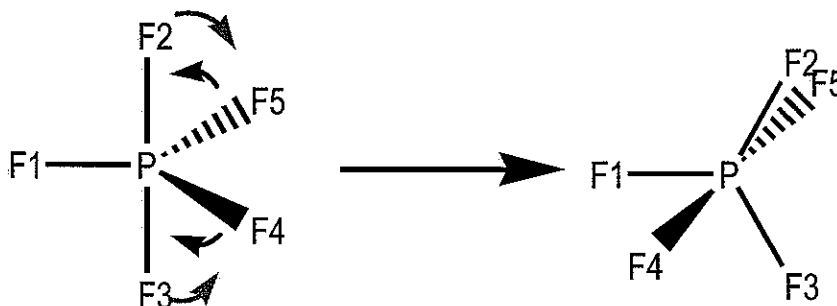
2. (15 pt) (A) Predict the shape of the PF₅ molecule based on the VSEPR model. (B) The ¹⁹F NMR spectrum of PF₅ recorded at the ambient temperature exhibits one doublet (each chemically distinct F nucleus gives rise to a doublet), but that recorded below -150 °C displays two doublets. Explain (including necessary structural sketches to support your argument).

(a) 5 pairs, trigonal bipyramidal



(b) PF₅ is highly fluxional, and the exchange rate of apical and equatorial F is much faster than NMR time scale, and hence cannot be distinguished. But, the exchange rate slows down significantly that two types of F can be resolved on NMR time scale;

The exchange proceeds via Berry pseudorotation, apical F2 and F3 rotate 30 deg to become equatorial (as red arrows indicate); Equatorial F4 and F5 rotate 30 deg to become apical (as blue arrows indicate)



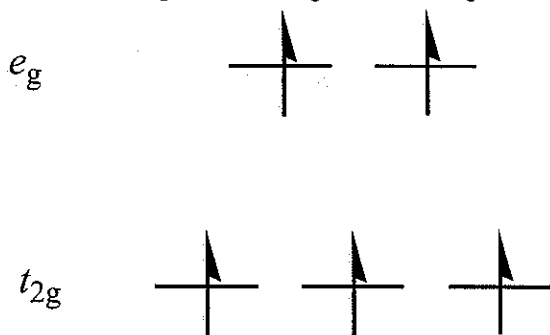
3. (20 pt) Aqueous solutions of MnSO_4 are almost colorless. Please provide a detailed explanation on the basis of what you have learned from CHM641.

Aqueous solutions contain $\text{Mn}(\text{H}_2\text{O})_6^{2+}$

H_2O is a weak field ligand

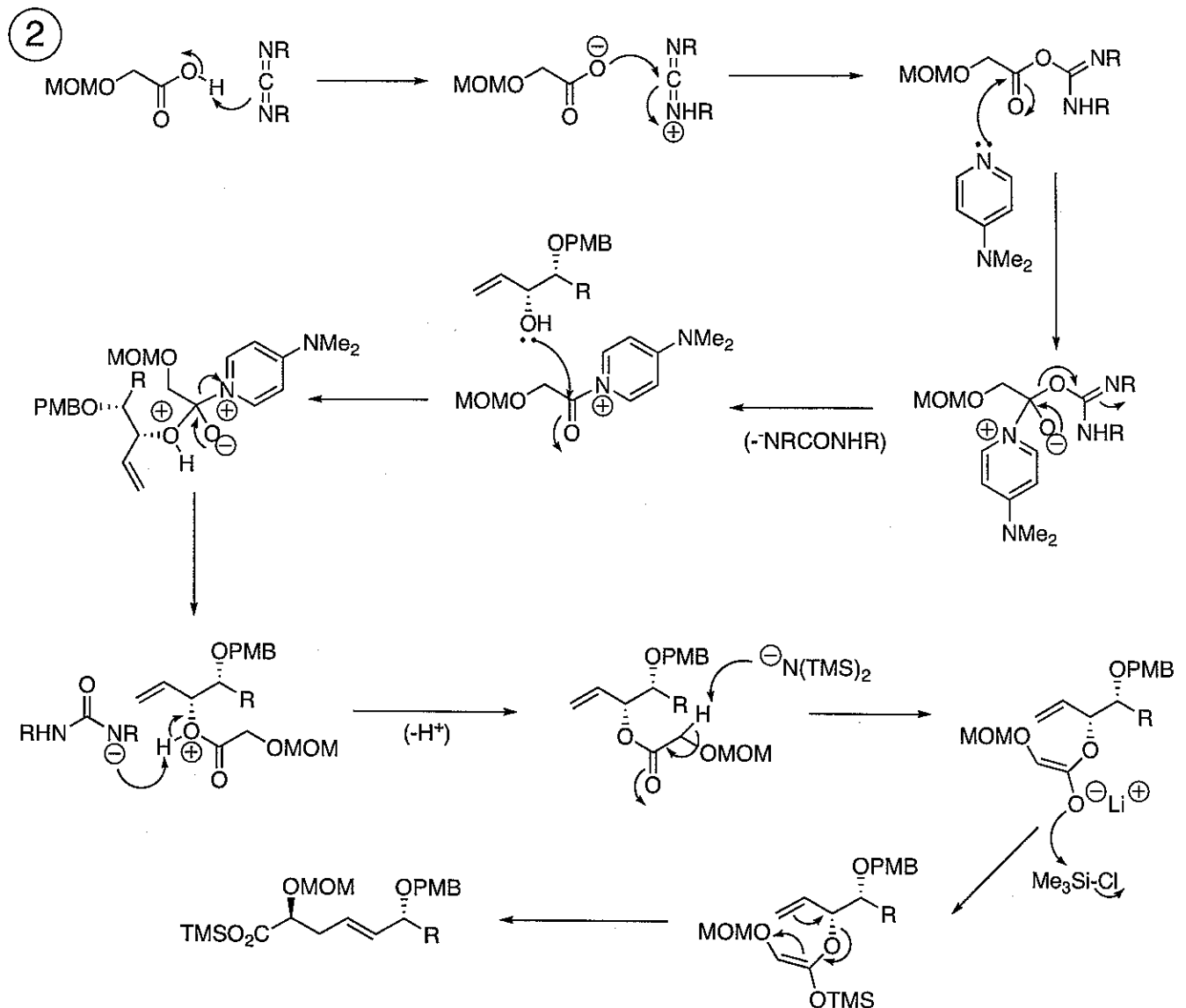
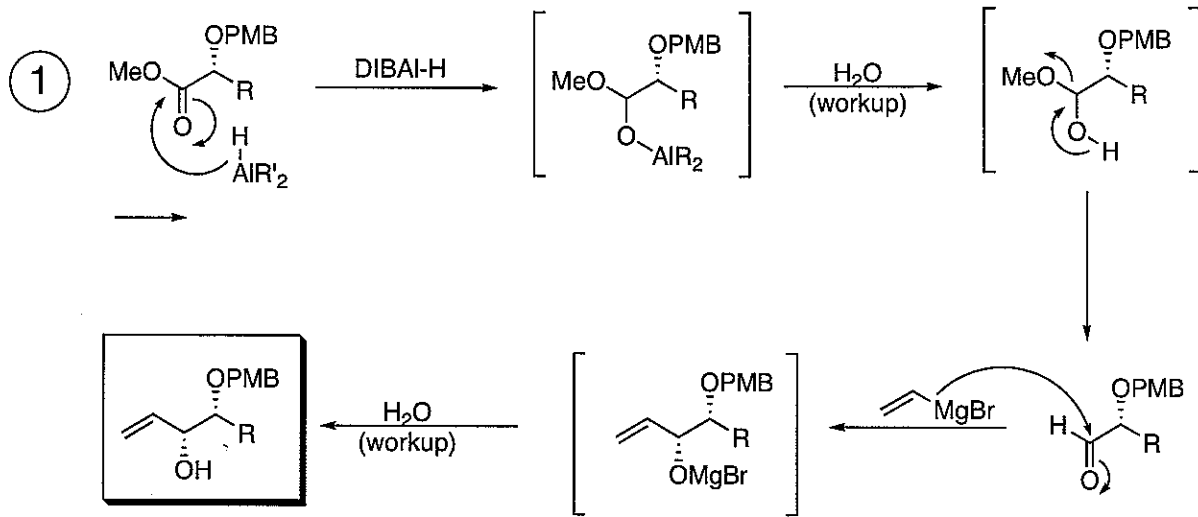
Mn^{2+} is d^5 , and high spin

Draw actual ligand field diagram and filling scheme

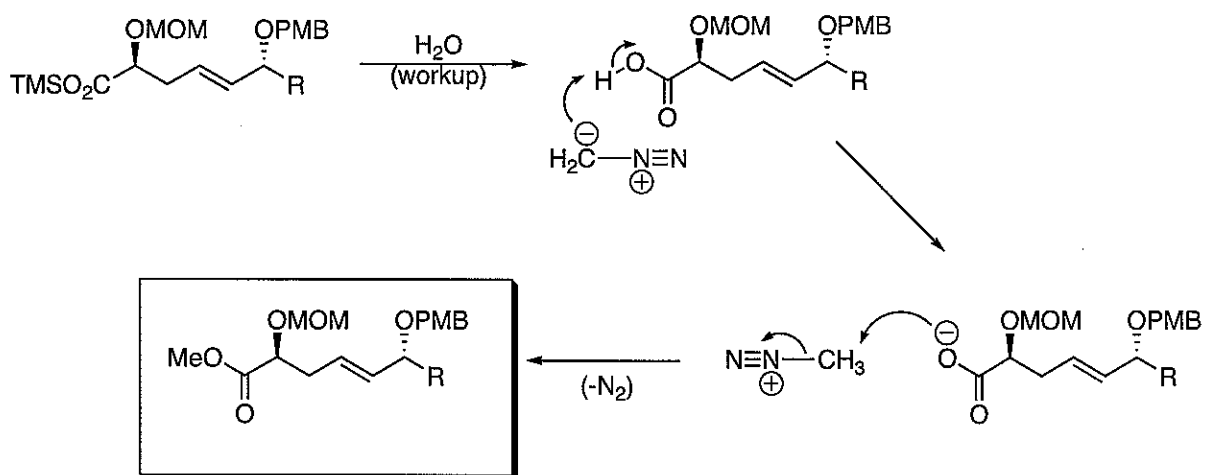


Based on the scheme above, a $d-d$ transition would require the "flip" of the spin of excited electron to conform to the Pauli principle. In doing so,

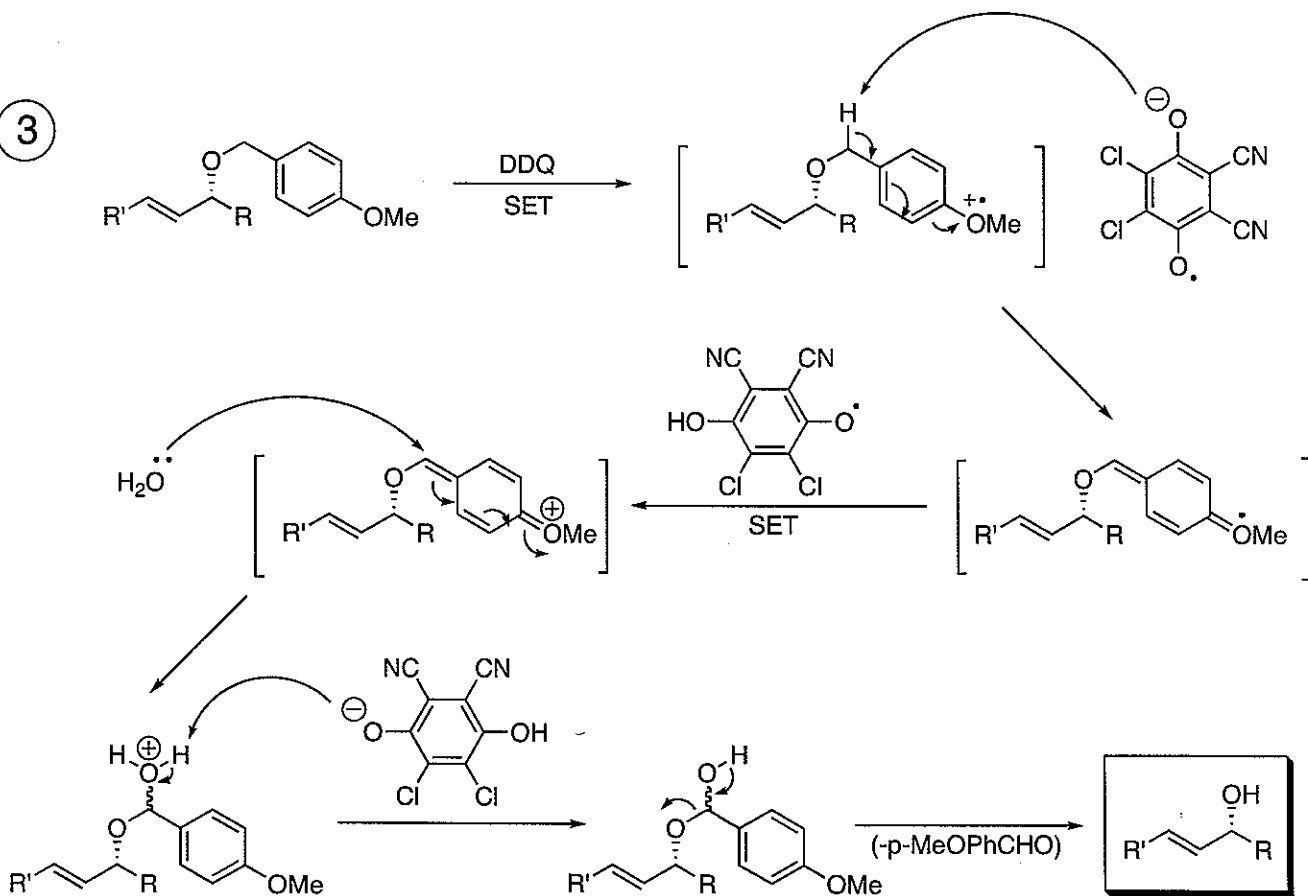
1. (60 points) Provide mechanisms for the reactions involved in steps 1-5. Use curved arrow formalism and show all likely intermediates. Assume an aqueous workup after each reaction. Your mechanism in step 5 should account for the formation of both products.

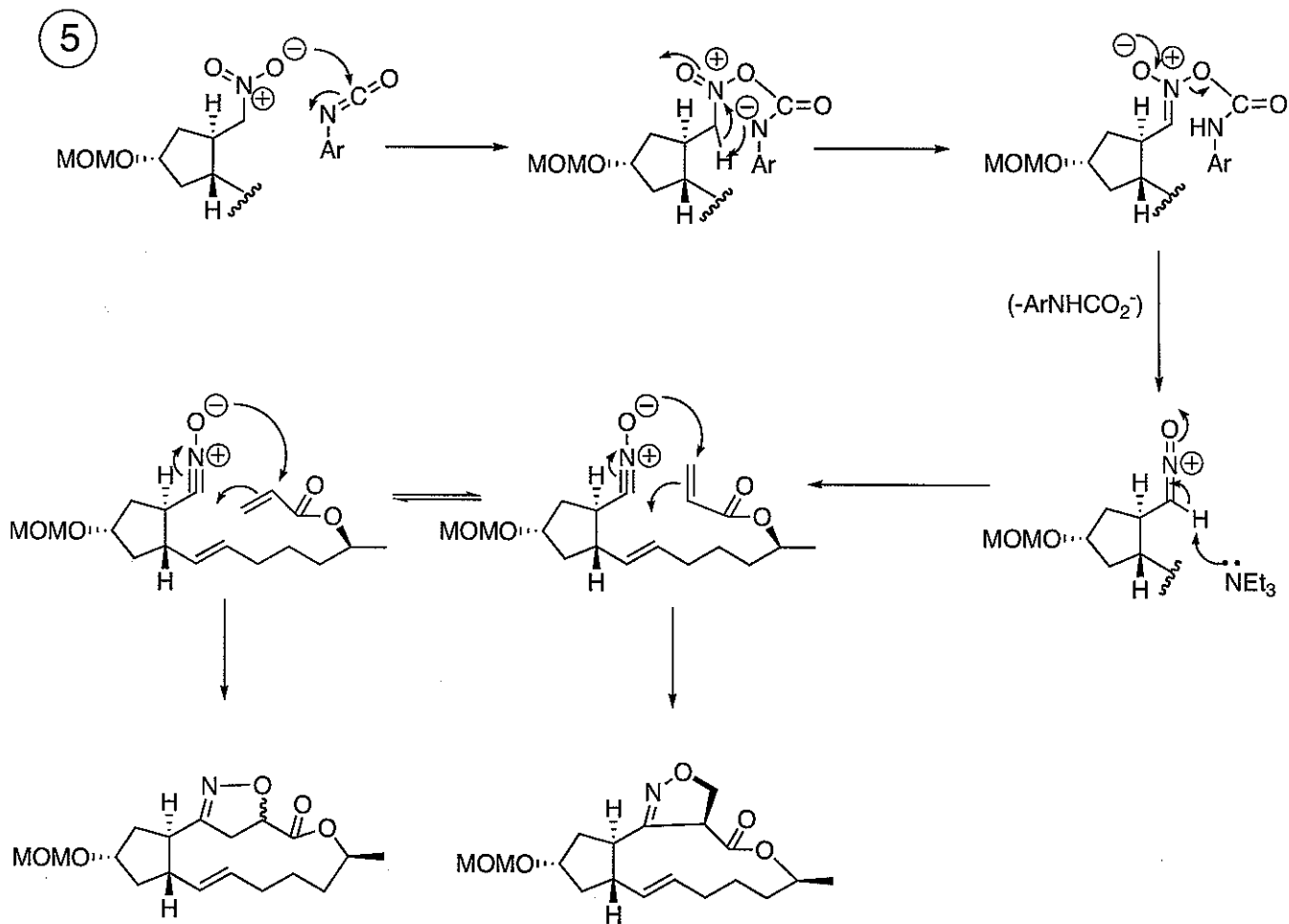
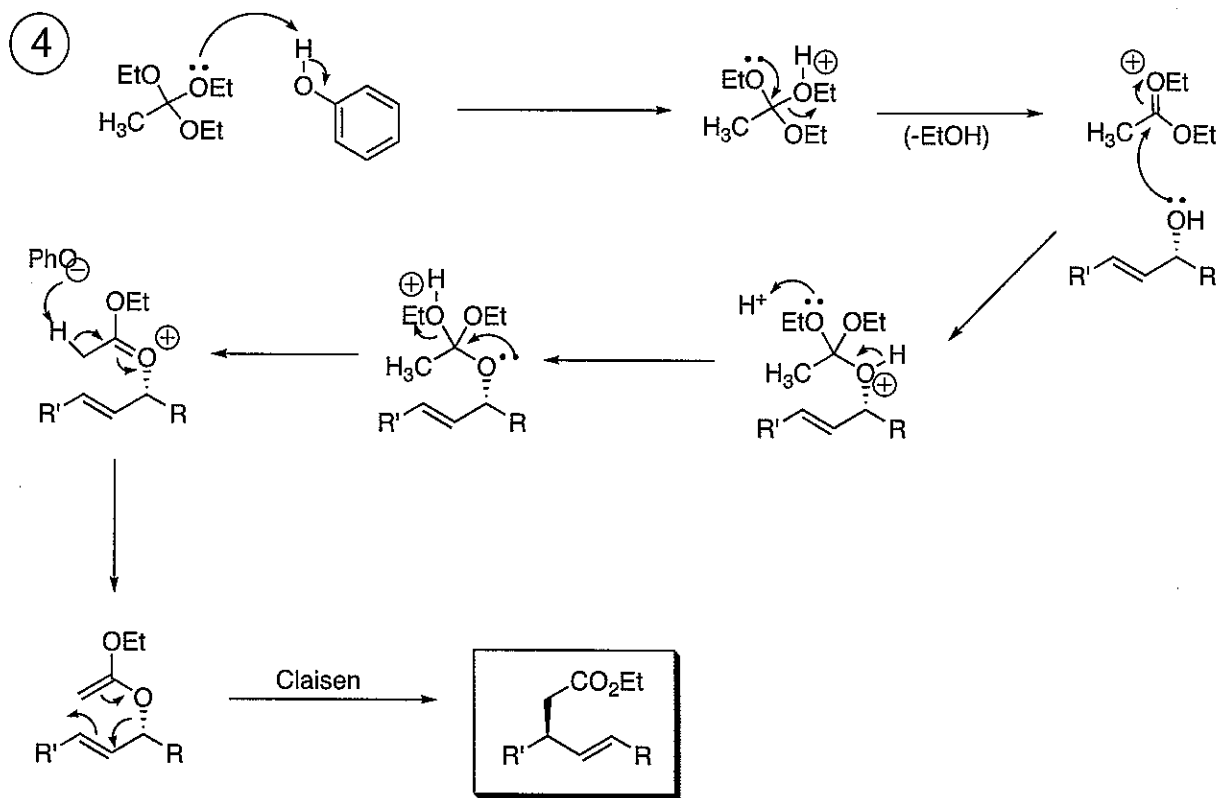


2 (Cont'd)



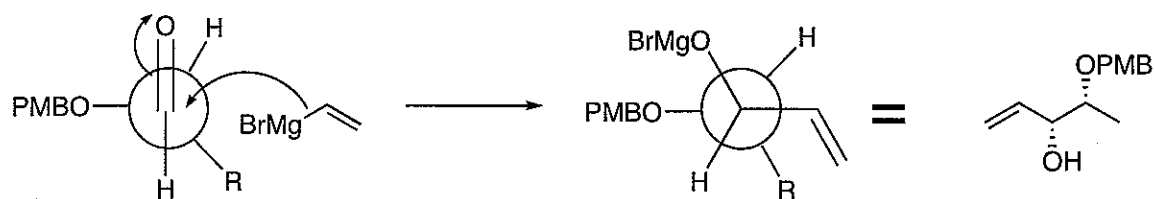
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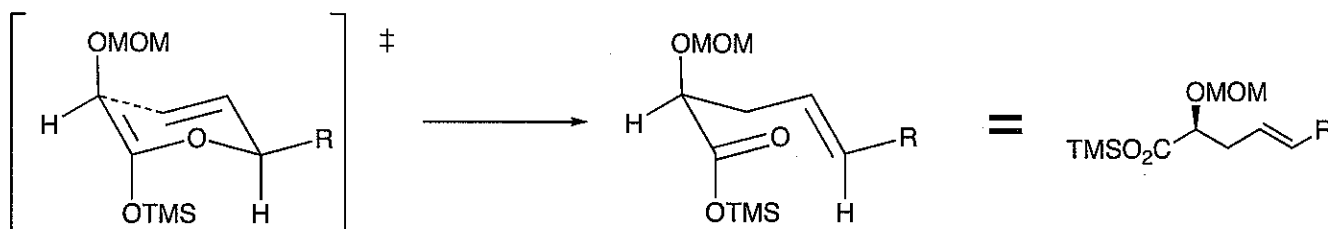


2. (40 points) Provide detailed explanations for the stereoselectivities observed in steps 1 and 2.

The first case is an example of Cram's Rule selectivity, which the Felkin-Ahn model explains:



The second case is an example of chirality transfer in a [3,3] sigmatropic reaction. This can be explained by the preference for a chair-like transition state where the substituent R occupies an equatorial position preferentially:



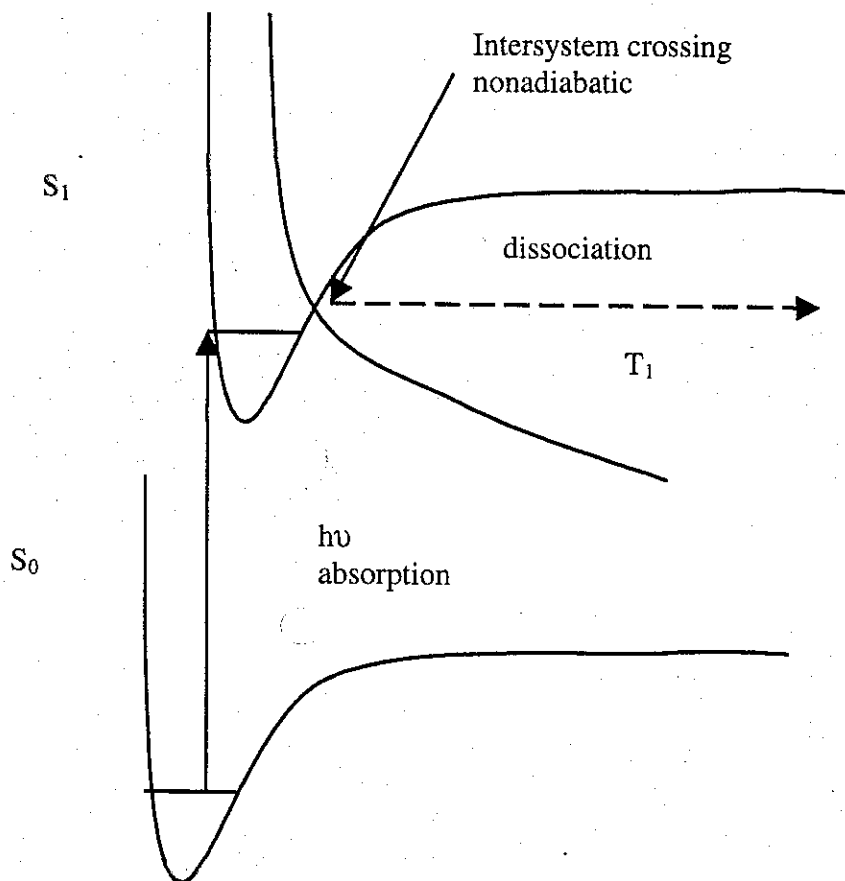
Solution

PCHEM

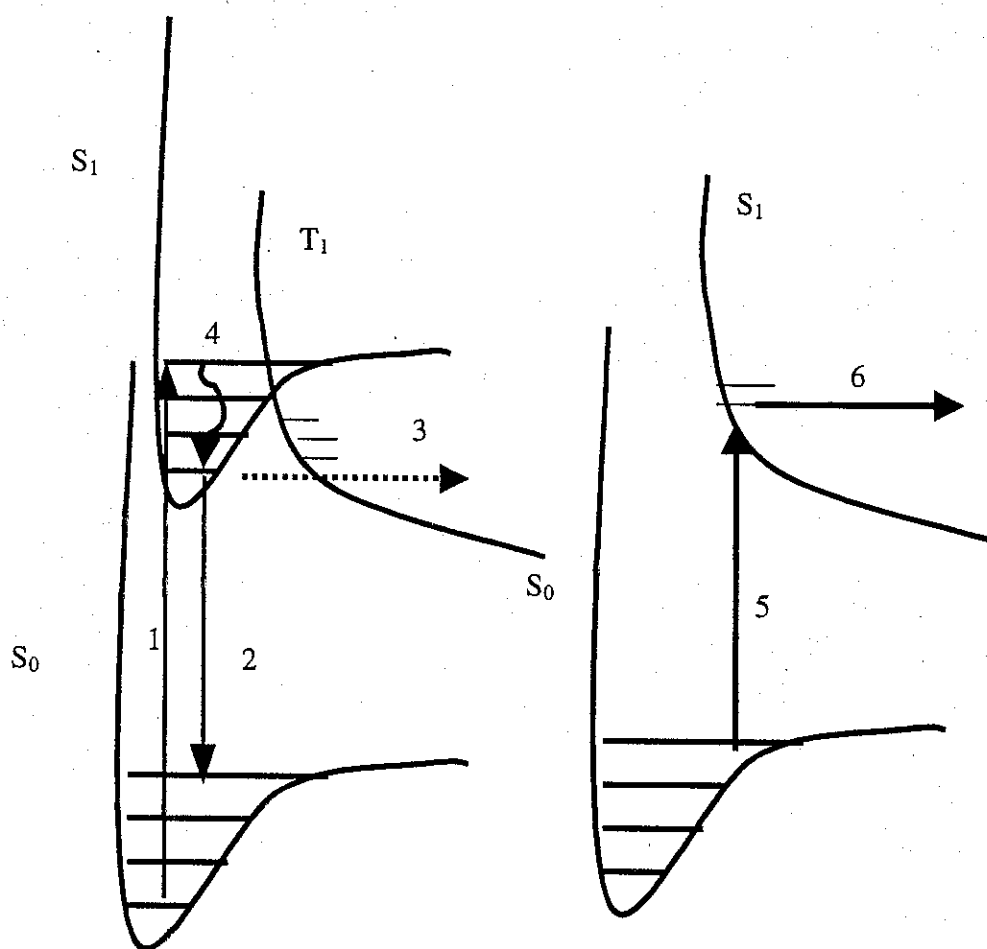
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A diatomic molecule A_2 in electronic state S_0 , with $n = 0$ and $J = 0$ strongly absorbs ultraviolet light. The resulting spectrum is structured (no continuous absorption) but it is observed that after a while (that is, not quickly) the molecule is dissociated. Sketch a set of potential energy curves and rotational, vibrational levels to describe this process. Explicitly describe all the processes that change the electronic state. Explicitly indicate any nonadiabatic processes.

Solution



For the two diagrams presented below identify and define the process corresponding to the numbered arrows. Be sure to state whether the process involves a photon or is a radiationless, whether it is adiabatic or non adiabatic. If the process involves a photon, state whether the spectrum will be structured (line spectrum) or continuous. Note S_0 = lowest singlet state, S_1 = first excited singlet state, and T_1 = first triplet state. The rotational Quantum numbers are ignored here.



Arrow 1: $S_0, n=0$ to $S_1, n=4$

Arrow 2: $S_1, n=0$, to $S_0, n=3$

Arrow 3: $S_1, n=0$ to an isoenergetic (same energy) T_1 state.

Arrow 4: $S_1, n=4$ to $S_1, n=0$. You need not consider whether or not this process involves a photon.

Arrow 5: $S_0, n = 3$ to S_1

Arrow 6: an S_1 process

Solution

Arrow 1: Absorption: molecule absorbs a photon. Line spectrum.

Arrow 2: Fluorescence: an excited molecule emits a photon and returns to ground state.

Line spectrum.

Arrow 3: Internal conversion: radiationless process where a molecule passes to another electronic state, and the total energy is conserved. Adiabatic.

Arrow 4: Vibrational relaxation (vibrational cascade): molecule loses vibrational energy. Non adiabatic process.

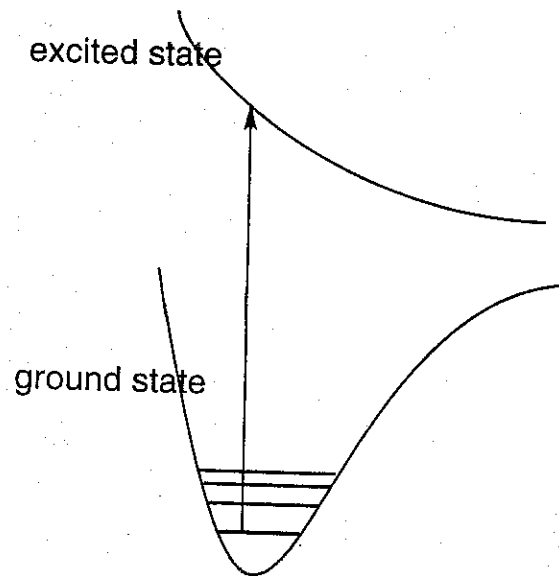
Arrow 5: Absorption: molecule absorbs a photon. Line spectrum.

Arrow 6: Direct dissociation, continuous absorption.

Solution

- O_2 and O_3 protect the earth from harmful radiation in a CONTINUOUS range, with wave lengths shorter than ~ 340 nanometers (the exact value of this limit is unimportant here). Absorption occurs into a dissociative electronic state. Even though the ground electronic states of O_2 and/or O_3 have discrete energy levels, they have dissociative excited electronic states. So, once an electron is excited, then it behaves like a free electron which has continuous energy.

(Wavefunction: $\Psi = Ae^{ikx}$, Energy eigenvalue: $k^2\hbar^2/2m$, where k can be any values)



- To determine force constants, you need the fundamental vibrational modes of CH_4 . The exact band positions of each fundamental mode is determined from its ro-vibronic spectrum, and not from its pure rotational spectrum.
- The earth is a low temperature blackbody; it gives low temperature radiation, most of which is in the IR region. In the atmosphere of the earth, there are lots of small molecules. If there is a dipole moment change in them, they can absorb IR radiation emitted by the earth, preventing it from escaping from the earth, then increase the earth's temperature. This is called the greenhouse effect. In the case of N_2 and O_2 , which are principal atmospheric gases, because there is no dipole moment change, there is no rotational or vibrational absorption spectrum. So, these gases do not contribute to the greenhouse effect.