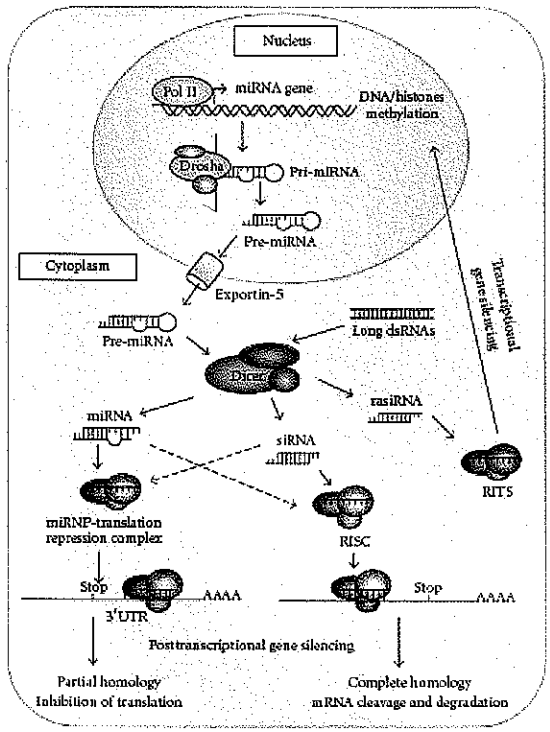
Answers: Biochemistry cume October 2006.

Question 1A (10 pts). For a review of RNA interference see Venturini et al., J Biomed Biotechnol. 2006;2006(4):87340. For a schematic diagram see the Figure shown below.

When introduced into cells, double-stranded RNA (dsRNA) may render genes nonfunctional in a sequence-specific manner. In cells, dsRNA can activate the mechanisms that lead to degradation of cognate mRNAs. This process, termed RNA interference, RNAi, is temporary and dosage dependent.

The current data suggest that long dsRNA molecules are cleaved into double-stranded small interfering RNAs (siRNAs). These are relatively short, about 21–25 base pairs and are produced from cleavage of the long dsRNA by an enzyme with RNaseIII-like activity (Dicer). Nonetheless, the siRNAs are long enough to associate with mRNA molecules that include sequences that are complementary with siRNAs.



The siRNA might form fully complementary base pairs with mRNAs. This association would guide the RNA-induced silencing complex (RISC) to degrade the mRNAs. Partial base pairing of siRNA with mRNA might cause inhibition of translation but not mRNA degradation.

Question 1B (15 pts). Gene silencing means stopping the production of proteins from a given gene. There are several mechanisms for gene silencing. For example: repression of transcription. In this mechanism repressor proteins bind to sequences that provide binding sites for proteins that activate transcription. This repression would prevent transcription of a gene. DNA methylation and chromatin remodeling provide another mechanism for repression of transcription. In the case of RNA interference, the mRNA is transcribed but it is degraded. Degraded mRNA cannot support protein synthesis and hence the term "gene silencing". This pathway is known as post-transcriptional silencing.

Question 1C (10 pts). Specific mRNAs can be target for degradation. This can be done by introducing into cells double-stranded RNA that includes sequences that are complementary to the mRNAs.

Question 2 (15 pts). Transcription is the mechanism through which the information in DNA is copied to produce RNA. Transcription of tRNA genes is important because tRNA molecules serve as adaptors of amino acids for the pathway of protein synthesis. Transcription of protein coding genes is important because this process produces the templates (mRNAs) that specify the amino sequence of proteins. Transcription of ribosomal RNA (rRNA) genes is important because rRNAs are the components of the machines (ribosomes) that translate the codes in mRNA into the polypeptide chains of proteins.

Question 3 (10 pts). Yes. Transcription of mRNA would lead to protein synthesis. Production of RNAi could cause degradation of mRNA and hence gene silencing.

Question 4 (30 pts). Primary structure defines the nucleotide sequence of RNA. Secondary structure results from formation of Watson-Crick type base pairs. Secondary structures include contiguous double-stranded regions, hairpins, and structures with bulges and internal loops. Tertiary structure results from folding of RNA molecules into complex three-dimensional structures that are stabilized by hydrogen bonds that are not of Watson-Crick type.

Question 5 (10 pts). In cells, DNA forms the double-helix, stabilized by Watson-Crick type base-pairing schemes. Viruses may contain single-stranded DNA. In that case, the types of secondary and tertiary structures observed in RNA might form. Under certain conditions, the cellular DNA might form unusual structures such as cruciform.

Total: 105 pts

INORGANIC CHEME

10/21/2006

Prof. M. Abu-Omar

KEY

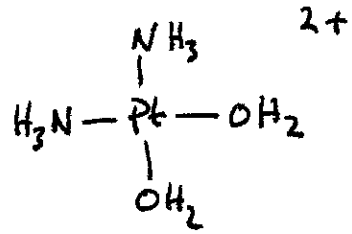
(a). Diamagnetic, d^8 square planar

— b_{1g}

↑↓ a_{1g}

↑↓ ↑↓ e_g

↑↓ b_{2g}

(b). $cis\text{-}Pt(NH_3)_2Cl_2 + H_2O \longrightarrow$ 

(c). $\frac{1\ mg}{1\ mL} \cdot \frac{1\ g}{1000\ mg} \cdot \frac{1\ mole}{300\ g} \cdot \frac{1000\ mL}{1\ L} = 3.33 \times 10^{-3}\ M$ or $3.33\ mM$

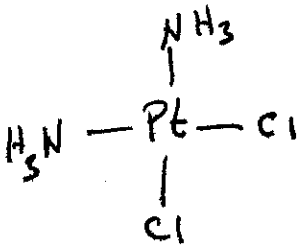
(d). N7 position on Purines.
Favors G.

(e). 1,2-intrastrand crosslinking.

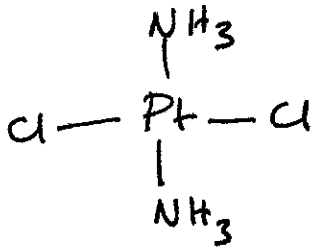
INORGANIC CLUME

Pg. 2

(f).

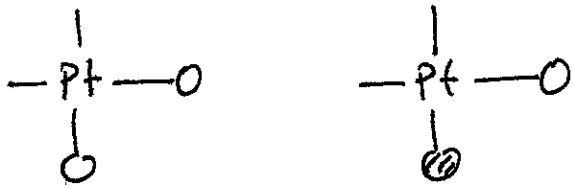


C_{2V}



D_{2h}

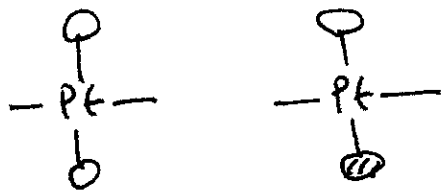
(g). cis



	E	C_2	σ_v	σ_v'
Γ	2	0	0	2

reduces to A_1 & B_2 ; both are IR active
(2 Pt–Cl stretching bands)

trans

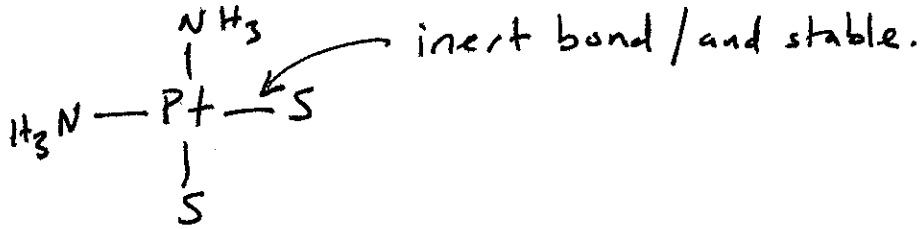


	E	C_2	C_2	C_2	i	σ	σ	σ
Γ	2	0	2	0	0	2	0	2

reduces to A_g & B_{2u} ; only B_{2u} is IR active
(1 stretch)

INORGANIC CURE
Pg. 3

(h). Blocks formation of DNA-cDDP adducts by coordinating to Pt.



Grading: Each 12 pts except (g), 16 pts.

$12 \times 7 + 16 = 100$.

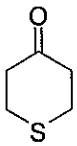
THE END!

CRIB ORGANIC CUME 10/06

①

Q 1. *JOC* **2006**, *71*, 8198

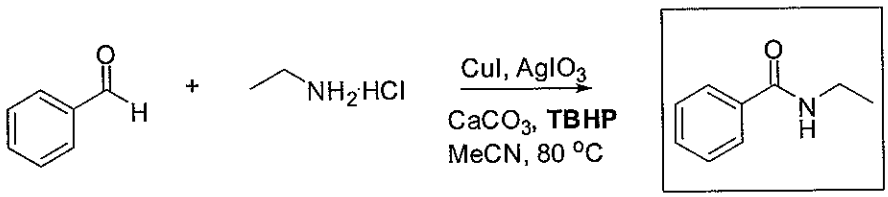
Reactant missing:



Aldol Reaction:

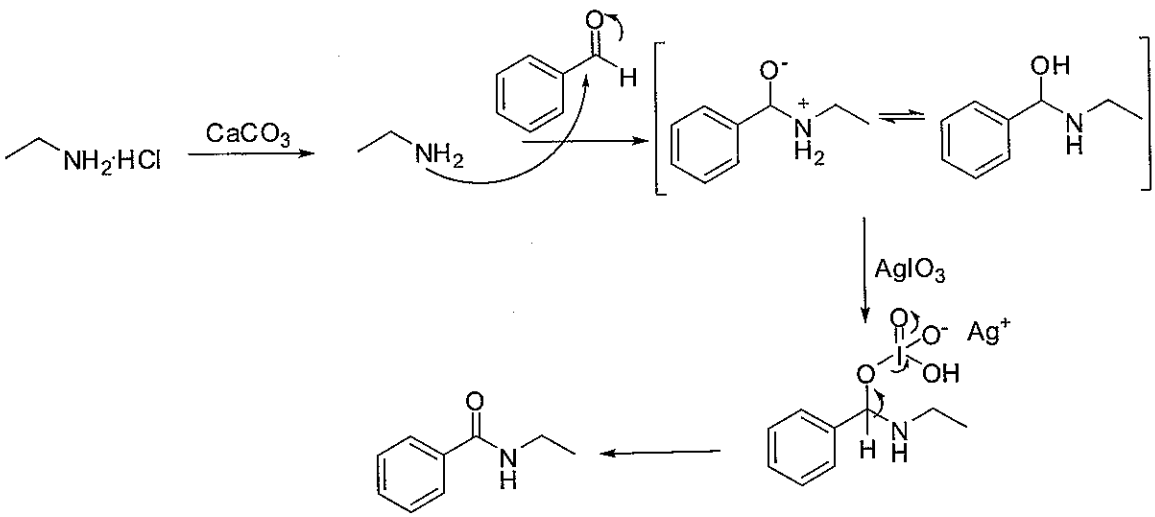
Please see any undergraduate text book.

Q 2. *JACS* **2006**, *128*, 13064

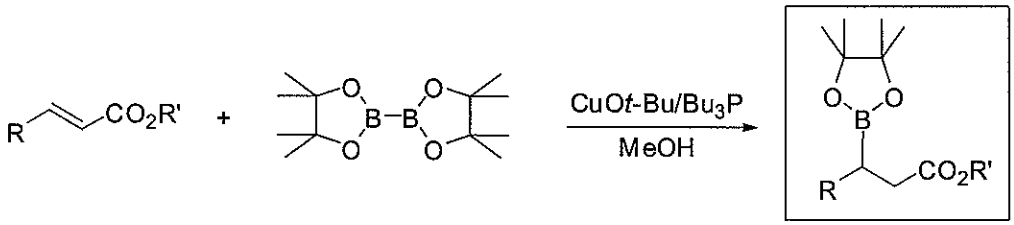


TBHP: *tert*-Butyl Hydroperoxide

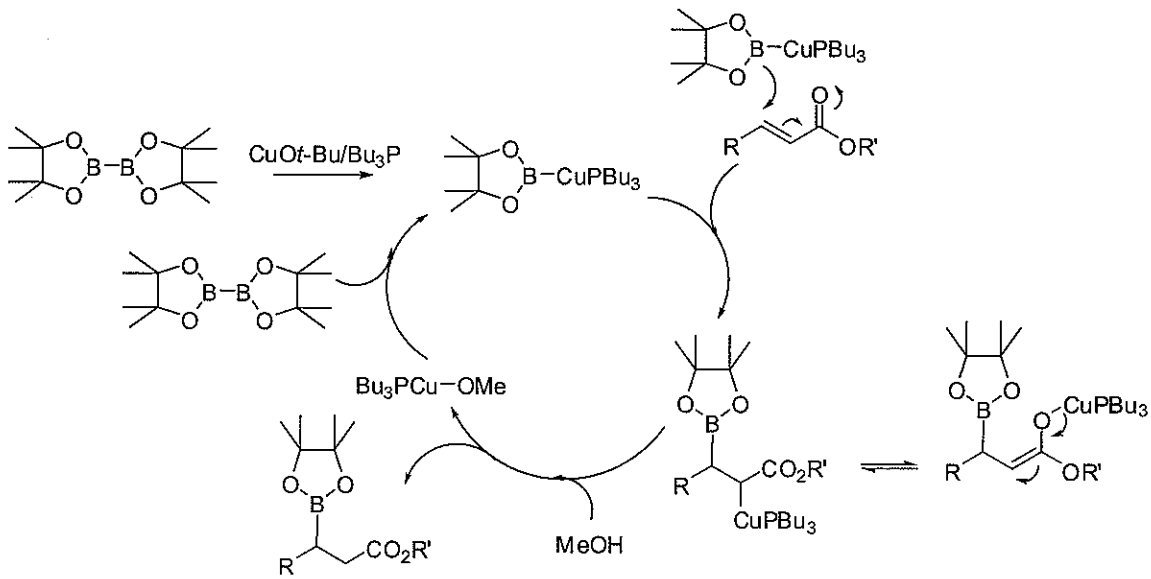
Mechanism:



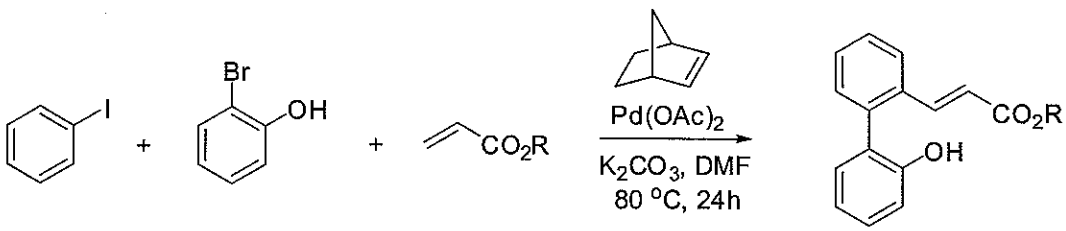
Q 3. *OL* **2006**, *8*, 4887



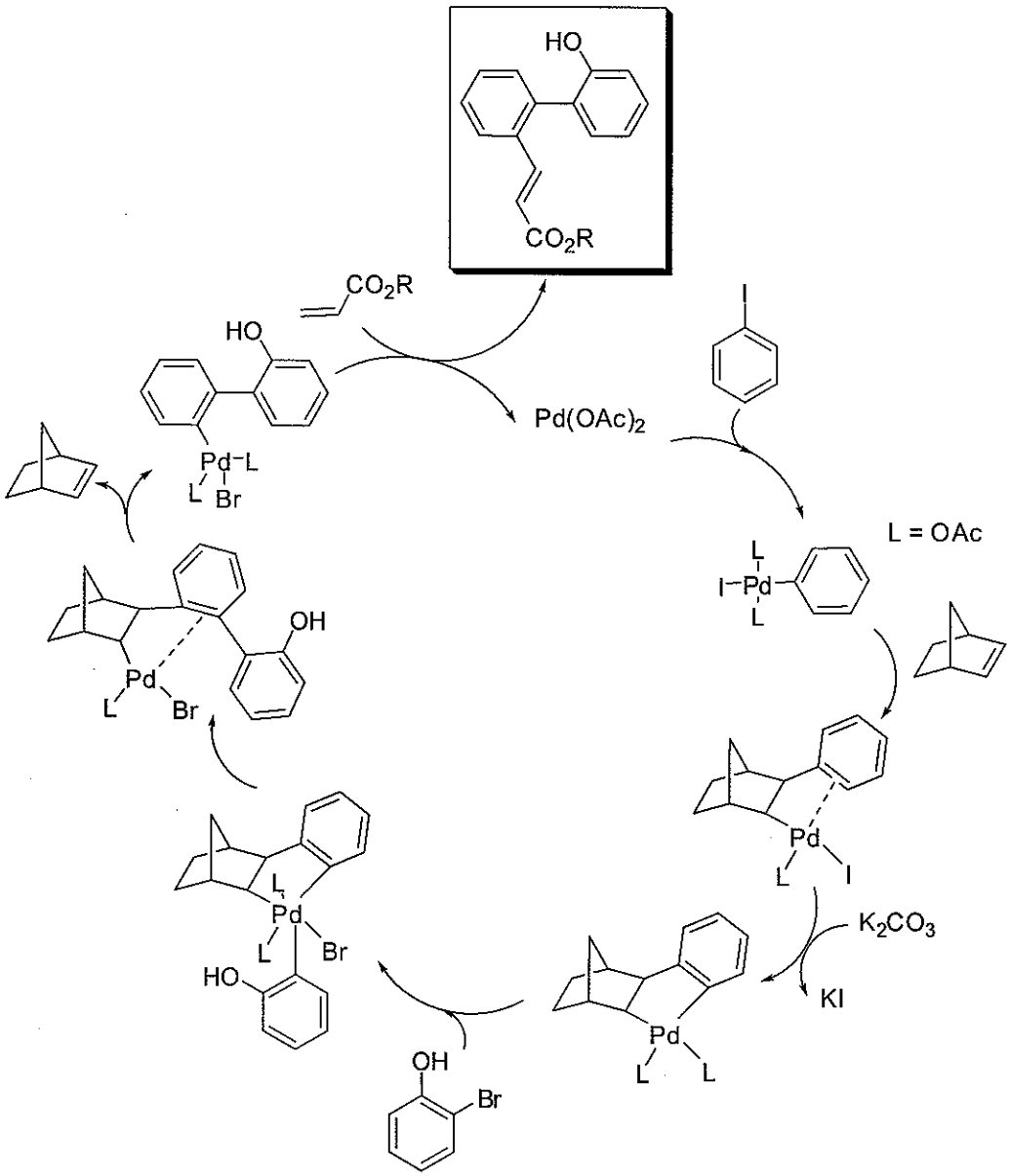
Mechanism



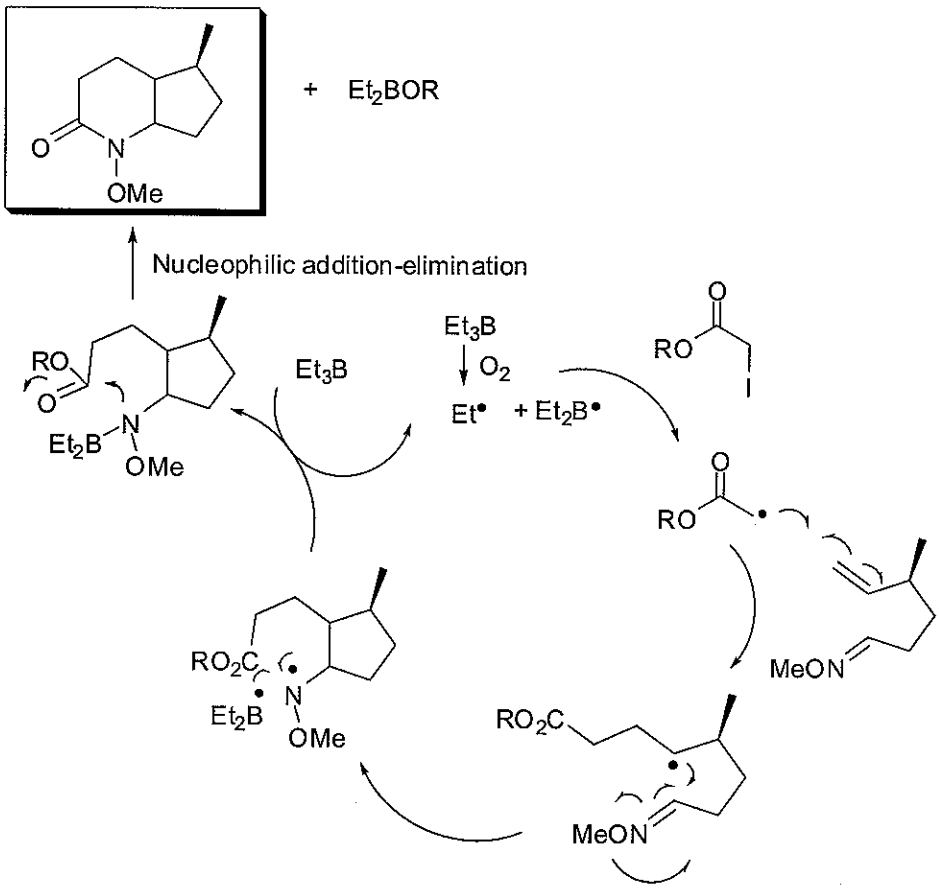
Q 4. OL **2006**, *8*, 3967



Mechanism


HO
CO2R
CO2R
HO
Pd(OAc)2
I
L = OAc
L
I–Pd
L
Pd–L
L Br
OH
Pd
L Br
Pd
L I
K2CO3
KI
Pd
L L
L
Pd
L Br
HO
OH
Br

Q 5. *OL* **2006**, *8*, 4871



P. Chem. Quiz Oct. 2006 (crib)

1) $C_V = \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$

2) 1st Law: $dU|_{N,V} = TdS - \cancel{PdV} = đQ_{rev} + \cancel{đW_{rev}}$

So, $\boxed{C_V = \left(\frac{đQ_{rev}}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_{V,N}}$

2nd Law: $dS \geq \frac{đQ}{T}$ and $dS = \frac{đQ_{rev}}{T}$ so, $\boxed{TdS = đQ_{rev}}$

So, $\boxed{C_V = \left(\frac{đQ_{rev}}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V}$

3) a. for argon C_V = const. so, $\left(\frac{\partial U}{\partial T}\right)_V = C_V$ implies that $\int dU = \int C_V dT \rightarrow U = C_V T + U_0$ } integration constant

$\boxed{U = \frac{3}{2}RT + U_0}$

b. $C_V = \frac{1}{2}R \times$ # of degrees of freedom

for argon x, y, z translational motion contributes 3 degrees of freedom so, $\boxed{C_V = \frac{3}{2}R}$

4) a. at low T the rotations and vibrations of H_2 are not active (because their quantum state spacing $\omega > RT$)

b. at 400K $\boxed{C_V \cong \frac{5}{2}R}$ for H_2 because translations (x, y, z) and rotations (θ, ϕ) are active — 5 degrees of freedom

c. at higher temperature expect the vibrations of H_2 to become active. Each vibrational normal mode contributes RT of average energy and so R to C_V

So, at high T, expect $\boxed{C_V \cong \frac{7}{2}R}$

5) a. Smaller rotational spacing of F_2 than H_2 means that rotations are already active in F_2 at 100K, as is the case for H_2 at 400K.

b. at 1000K $C_V \cong \frac{7}{2}R$ for F_2 because translations ($\frac{3}{2}R$), rotations ($\frac{2}{2}R$) and vibrations ($\frac{2}{2}R$) are all active, so, $\boxed{C_V \cong \frac{7}{2}R}$.

c. at much higher temperatures one would expect electronic degrees of freedom to contribute to C_V.