

# Chemistry 124 Sixth Examination Answers February 26, 2010

Average Score: 78.4/102 1/3 > 88 2/3 > 72  
(my mistake that there were 102 total points)

1. (6 min) Provide an approximate value in kcal/mole for the energy change of the following processes:

ethylene + H<sub>2</sub> → ethane -33 [difference between double + single and 3 singles]

benzene + H<sub>2</sub> → 1,3-cyclohexadiene +6 [endothermic because of aromaticity of benzene]

cis-2-butene → trans-2-butene (activation energy without catalysis) 66 [strength of π bond]

s-cis-1,3-butadiene → s-trans-1,3-butadiene (activation energy without catalysis) 4 [diene conjugation energy]

2. (3 min) The isomeric n-butyl and t-butyl cations differ in energy by 37 kcal/mole in the gas phase. Explain whether you would expect the difference to be larger or smaller in solution.

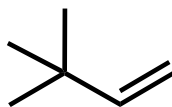
The difference should be smaller in solution because, while both ions should be stabilized by solvation (largely due to charge-induced dipole interaction, or charge-dipole interaction in a polar solvent), the primary cation should be **more** stabilized, because these interactions are short-ranged and the primary charged atom is more accessible to the solvent. In fact an important reason for greater stability of the tertiary cation in the gas phase is that its charged carbon is "intramolecularly solvated". This advantage is largely lost in solution.

[Of course the primary n-butyl cation can rearrange by a hydride shift to sec-butyl cation.]

3. (1 min) Why did Prof. Siegel recommend memorizing the pseudo-word "FONCLBRISCH"?

Because it can be handy to remember the order of decreasing electronegativity of the common elements F, O, N, Cl, Br, I, S, C, H.

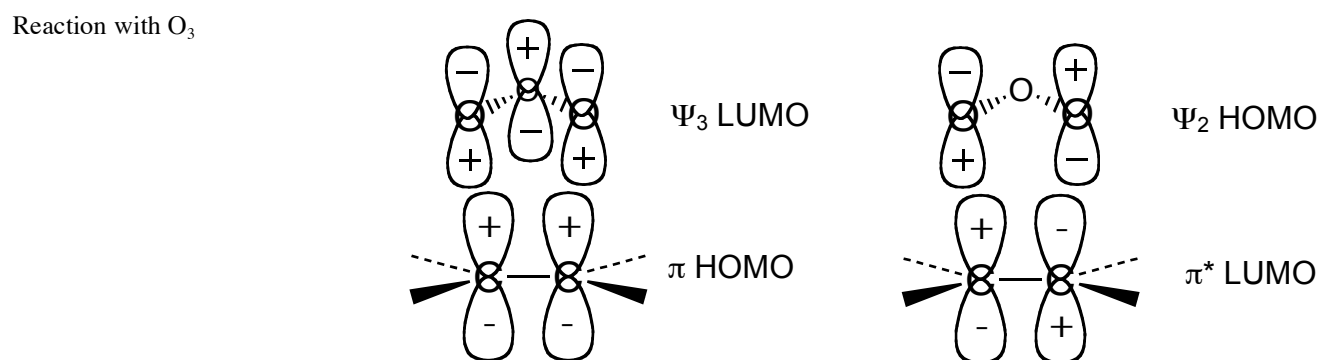
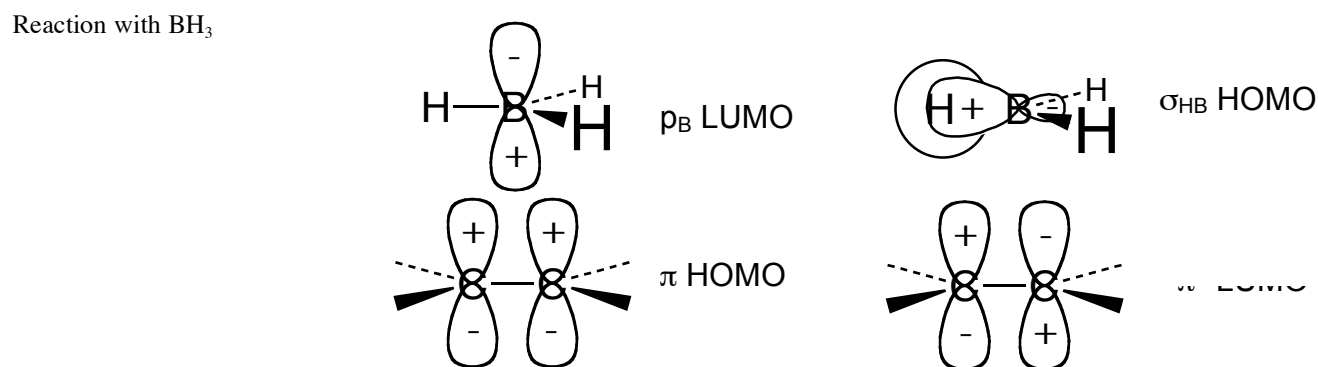
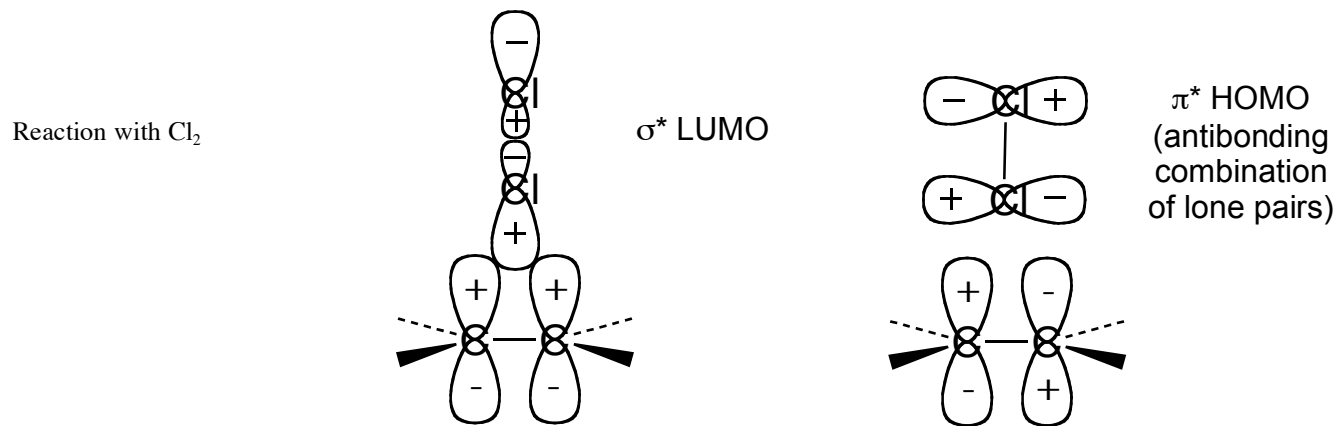
4. (3 min) If it is possible to add H<sub>2</sub>O to an alkene like 3,3-dimethyl-1-butene with simple acid catalysis, why might one choose to use the more complicated, indirect sequence of reaction with Hg(OAc)<sub>2</sub> and water followed by reduction with NaBH<sub>4</sub> to achieve H<sub>2</sub>O addition to the alkene?



To obtain the secondary alcohol with an unrearranged carbon skeleton.

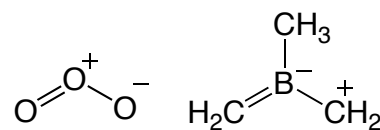
The HgOAc cation can bridge between the two carbons of the alkene, where the proton bonds to only one carbon. Without bridging, the secondary cation is prone to rearrangement to a tertiary cation by methide shift, giving an unanticipated product.

5. (9 min) Two new bonds to carbons (involving two electron pairs) are formed simultaneously in reaction of  $\text{Cl}_2$  with ethylene, in reaction of  $\text{BH}_3$  with ethylene, and in reaction of  $\text{O}_3$  with ethylene. Position each reagent properly with respect to the ethylenes below (two frames for each reagent; one for each electron pair), draw their relevant LCAO-MOs (with signs and HOMO/LUMO labels) to show how these three reactions are analogous



6. (2 min) Explain why the hypothetical reagent  $\text{CH}_3\text{B}(\text{CH}_2)_2$  should not react like  $\text{O}_3$  in the reaction of Question 4, even though their dipolar formulae look similar

$\text{CH}_3\text{B}(\text{CH}_2)_2$  has only one pair of pi electrons, while ozone has two pairs. Thus the HOMO of the boron-containing compound would be  $\Psi_1$  instead of  $\Psi_2$ . Having identical signs on the terminal atoms, this HOMO would not overlap with the LUMO of ethylene. Rather it would mix with the HOMO of ethylene, resulting in repulsion rather than bonding.



7. (8 min) By choosing different reagents 2-butyne can be converted selectively to either isomer of 2-butene.

A. Give the reagent(s) for forming cis-2-butene : the Lindlar\* catalyst, Pd / CaCO<sub>3</sub> / Pb (poisoned by Pb and quinoline to prevent subsequent hydrogenation of the product alkene)

B. Give the reagent(s) for forming trans-2-butene : Na / NH<sub>3</sub>  
(N.B. use Na metal, not Na<sup>+</sup> ion, as source of e<sup>-</sup>.)

C. Draw a mechanistic sequence (curved arrows and all) to explain how **ONE** of these processes occurs (*either A or B*).

For A same as frame 17 of Lecture 51, except that an extra C-C bond is required for starting with a triple bond.

For B see pp. 453-454 of the text (frames 22-23 of Lecture 42), though I would prefer that the points of curved arrows that generate bonds terminate between the atoms to be bonded.

8. (5 min) Explain how cross-linking natural rubber (by vulcanization) can both keep it from becoming brittle in the cold and from becoming runny when hot.

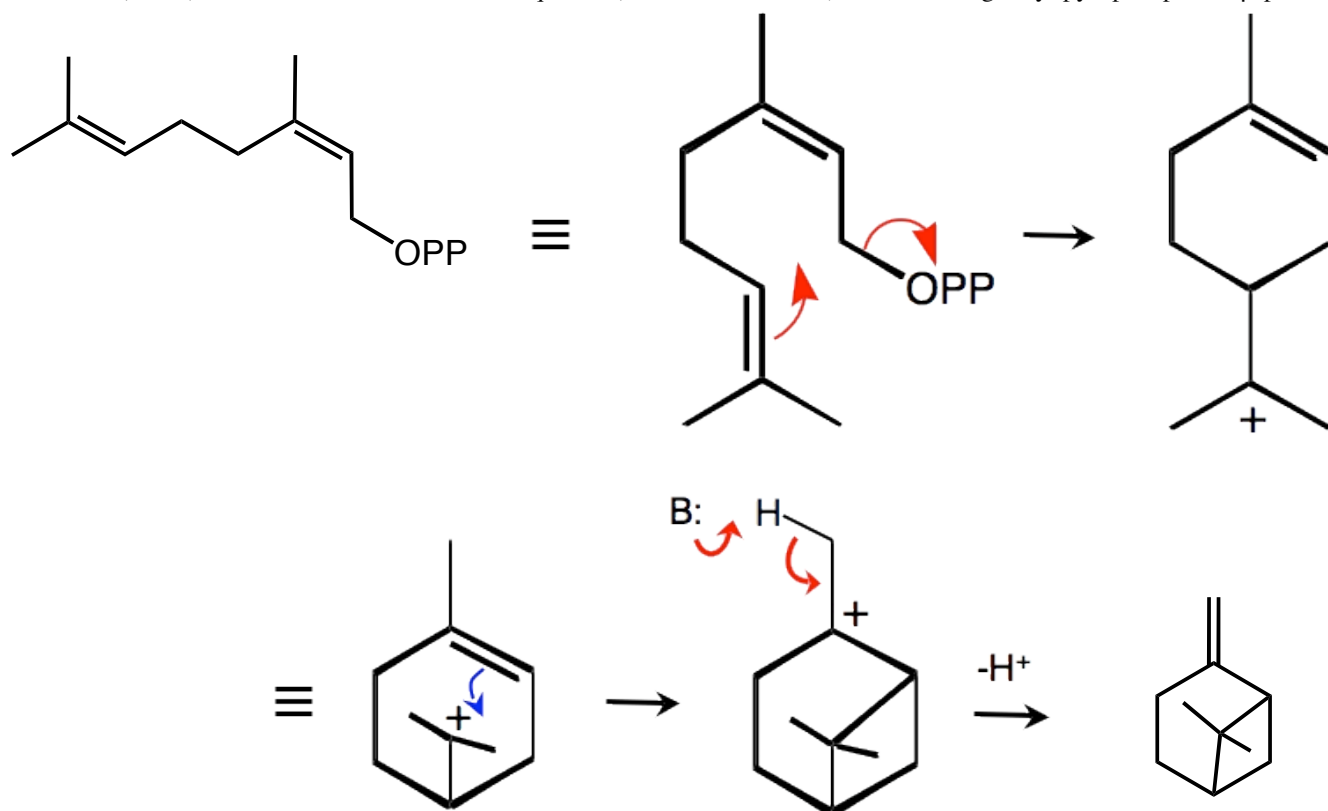
Cross-links prevent chains from sliding past one another for long distances and thus stops the reptation that allows long-chain polymers to flow, as they must do to become runny.

Cross-links also prevent prevent long runs of polymer from lining up tightly side-by-side and thus "crystallizing" so as to become brittle in the cold.

\*) Not surprisingly there is a lot of subtlety associated with preparing a reagent that will hydrogenate a CC triple bond in good yield but will not hydrogenate a CC double bond. This is all the more complex when the reagent is an insoluble solid, the microscopic physical form of which is important. To help others repeat such useful procedures, a group of synthetic organic chemists founded an annual publication called *Organic Syntheses* in 1921. The inventors of selected procedures are invited to submit detailed recipes which are thoroughly checked in the lab by referees before publication. 86 volumes have been published. Lindlar, of the Swiss pharmaceutical company Hoffmann-Laroche, developed the Lindlar catalyst for use in vitamin syntheses during the early 1950s. It was published in the *Organic Syntheses* volume for 1966. You can see exactly how the catalyst is prepared and used by looking at the on-line version of this procedure at

<http://www.orgsyn.org/orgsyn/orgsyn/prepContent.asp?prep=CV5P0880>

9. (9 min) Draw a reasonable reaction sequence (with curved arrows) for converting neryl pyrophosphate to  $\beta$ -pinene.



10. (5 min) What is the mechanistic significance of the fact that addition of DCl to 1,3-pentadiene at  $-78^\circ\text{C}$  gives three times as much of the 1,2- as of the 1,4-addition product? [It might help to draw the reaction intermediate.]

Considered in isolation the 1,3-dimethylallyl cation intermediate is symmetrical (but for D vs. H), suggesting that it should be equally likely for the chloride anion to attack adjacent to the carbon bearing D (1,2-addition) or three carbons away (1,4-addition). That 1,2-addition is strongly favored suggests that the allyl cation Cl anion pair never becomes truly symmetrical before collapse to the addition product, and the bias results from chloride's preferentially attacking end of the allylic system that is nearer the site of its generation (by loss of  $\text{D}^+$  to the diene).

[Incidentally, this runs counter to the intuition of most organic chemists.]